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boiler water treatment

Principles and Practice

Colin Frayne

Vol. I: Boiler Basics and Steam Water Chemistry

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Boiler Water Treatment
Principles and Practice

Volume I

Boiler Basics and Steam-Water Chemistry

Volume II

Treatments, Program Design, and Management

Colin Frayne



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PREFACE

This is my second book. It follows a similar style and with similar objectives and outlook to *Cooling Water Treatment: Principles and Practice*, which was published in early 2000. In the preface to that book, I stated that "the vital key to successfully providing water treatment programs today is something it has always been—excellent customer service!" In this particular aspect, some things just do not change, and for the vast majority of industrial, institutional, and commercial boiler plant owners around the world, this message is hopefully welcome. I say this because in order to attain and maintain optimum day-to-day boiler waterside operating conditions, owners and operators will continue to need the very best technical advice and other services possible to manage proactively the water treatment programs they employ.

There are some differences, however, between cooling water customers and boiler water customers in their overall requirements for water treatment program management (in **Sandler® Sales Institute** sales training "speak," the level of customers' "pain"). And it is these differences that, in part, gave rise to my decision to write this particular book.

It is a certainty (at least in my mind) that there is no *cooling system* anywhere in the world, from the smallest to the very largest, whose owner or operator cannot benefit from working with an appropriately qualified water treatment service company to some degree or other. The complexities of interrelated waterside problems, the variability of today's water supplies, and the sheer range of modern chemical treatments (now globally available), equipment options, and application techniques are simply overwhelming. This means that owners and operators of cooling water systems cannot remain conversant with all the causes and effects of waterside problems or keep abreast of marketplace technologies and developments in support services.

However, it is not always the case with certain types of modern boiler plant that the respective owners, operators, and technical committees can significantly benefit from working with a water treatment company.

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For example, in some very specialized areas of boiler water treatment (such as nuclear power units and especially utility power generation), there is probably little or nothing of any practical value that service companies can teach the current practitioners.

For a second group, however, comprising the owners and operators of just about every other type of commonly available boiler plant, this is not always the case. The engineers responsible for the great majority of "ordinary" boiler plants found in commercial buildings, hospitals, hotels, and general industry around the world typically do not have the same level of resources as the power generation industry. Consequently, they need to be in a position to reliably obtain specialty waterside treatment programs and technical support services.

It is these differences in in-house boiler plant facility resources and the perceived need to obtain technical support from an external source that led me to consider grouping boiler plant systems in a slightly different way than is typically perceived, which in turn provided a focus for this book. Thus, although commercial, industrial, and utility steam generators can be classified in several different ways (such as by pressure, output, fundamental design type, etc.), their owners and operators can be classified as members of one or other of only two groups.

The first group consists almost exclusively of these large utility organizations that operate electrical power generators and employ high-pressure, fossil fuel or nuclear power fired boiler plant for steam generation. This international power generation group understands their own particular waterside problems very well and the chemicals, mechanisms, and protocols needed for proper control. Their field of water treatment is fairly narrow, but they possess an incredibly deep knowledge of high-pressure boiler waterside technology and consequently need no assistance from me. (Nevertheless, for the sake of completeness, and hopefully for the interest of many operators, some information on higher pressure boiler water treatment practice has been included in this book).

The second group consists of every other type of boiler plant owner or operator. This group includes not only all the engineers operating steam generators in countless small factories, commercial premises, and institutional buildings, but also the various larger process industries and some facilities that may, in fact, generate electricity (albeit at only moderately high pressures) such as the cogeneration/combined cycle plants.

Within this second group, the various types and designs of boiler operated are very broad and the classifications and applications of boiler water treatments are equally wide.

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At first glance, and despite there having been little in the way of ground-breaking advances in treatment chemicals, equipment, or program applications for many a year, the fundamentals of the science and business of boiler water management appear to be, on the whole, still imperfectly understood by this group.

It also appears that most commonly available technical books and other sources of literature tend to concentrate on the higher pressure "glamour" end of the boiler plant range, and there is little that is sufficiently practical or comprehensive concerning the lower pressure market. And, of course, it is this lower pressure market (when measured by physical number) that globally constitutes the vast majority of boilers and where the user skills and experience in applied water treatment are most often limited.

In mitigation, a deep knowledge of such a specialist area generally is not required for most lower pressure boiler owners and operators, as they need to focus their attention on primary profit-making activities and other core business competencies.

It is, thus, to the second group that this book on boiler water treatment is primarily addressed. My key objective was to provide the reader with useful and practical boiler plant information that will help improve waterside cleanliness and add value to their facilities' operational efficiencies.

Additionally, a personal objective was to provide the information contained within this book in such a way that it could be used regularly in the field rather than be relegated to a bookshelf with other works of occasional reference. As such, although this book is essentially concerned with applied chemistry, I found it necessary to devote several of the initial chapters to a discussion on some basic but practical engineering aspects. Subjects covered include fluid dynamics, thermodynamics, the various types and designs of boilers to be found, and the function of all the critical system auxiliaries and components. The subject of boiler water chemistry is so inextricably bound up with the mechanical operation of boiler plants and all their various systems and subsystems that it is impossible to discuss one topic without the other.

As with my first book, which covered cooling water treatment, this book also started life after rereading the (still largely relevant) books written by the late James W. McCoy, who was a supervisor of refinery services at Standard Oil Company of California. This time my primary source of inspiration was *The Chemical Treatment of Boiler Water*, which was first published by Chemical Publishing Company of New York in 1981.

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In this preface I also wish to highlight the contributions to the subject from some other publications, such as the more modern book *Procedures of Industrial Water Treatment* by J.N. Tanis and the *NALCO Guide to Boiler Water Systems Failure*, as well as the massive, but superb tome, *Steam, Its Generation and Uses* from Babcock & Wilcox, which is now in its 40th edition. These are all excellent works.

Other notaries are the *Consensus on Operating Practices for the Control of Feedwater and Boiler Water Chemistry in Modern Industrial Boilers* (1994 edition), published by the American Society of Mechanical Engineers, and *BS 2486:1997 Recommendations for Treatment of Water for Steam Boilers and Water Heaters* from the British Standards Institution. The 1994 Consensus (with its engineering background) and the 1997 version of BS 2486 (with its strength in operational chemistry) complement each other well. I consider that the tables and propositions contained in these two booklets jointly represent a true standard for boiler water treatment operational control. Consequently, I am pleased to be able to reproduce in this book all the tables from both publications, having received permission from the respective organizations to do so.

An acknowledgment of the more than 160 technical references that supported my efforts is provided in the bibliography at the back of this book.

As before, I give due recognition to my wife, Carol, for her unstinting loyalty and support in this project. Her support was especially important, as during the course of writing this book we relocated from Georgia to New York City and most of the problems associated with moving and then remodeling an old Tudor style house were left to her. During much of this period I was busy working in an office during the day, writing at night, and generally insulated from much of the everyday drama.

I also thank Dr. Bennett P. Boffadi for taking time away from his consulting work to pore through this book and correct my technical mistakes.

Finally, I thank Silvia Soto-Galicia and her staff at Chemical Publishing Co. for their perseverance and confidence in publishing my work for a second time.

Colin Frayne
New York City, 2002

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INTRODUCTION: THE FUNCTION OF BOILER WATER TREATMENT AND ITS MARKETING

Boilers are heat-transfer devices, wherein water, in the form of either *liquid water* or *gaseous steam*, is commonly employed as a medium for the transport of heat to some distant point of use. Although other heat-transfer mediums are sometimes utilized, water is particularly suitable because of its relative abundance, low cost, and high heat capacity. It is generally the medium of choice in most boiler applications, whether for domestic, commercial, institutional, or industrial purposes.

However, a boiler can only carry out its primary functions of transferring heat to water and (in steam generators) separating steam under pressure from water most efficiently if the quality of the various types of water used (such as *makeup water*, *feedwater*, and *boiler water*) are effectively and continuously controlled. The difficulty in this quality control process is that water is a "universal solvent," and as a result, all sources of water contain various natural concentrations of dissolved minerals and gases in addition to suspended solids and biological matter. The relative amounts of each of these impurities tend to vary considerably with geographic location and season. This phenomenon results in countless permutations of water type and quality around the world, each potentially available as a source of makeup supply to boiler plant systems, evaporators, and other forms of water heating and steam generating devices. In many industrial applications, the negative impact of these natural impurities may be further compounded by the presence of small concentrations of process contaminants.

The effect of these various impurities or contaminants is to hinder the heat-transfer and steam generation processes, to adversely affect the

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quality and purity of steam, and to act as primary instigators in the corrosion and wastage of boiler plant system materials of construction. A wide variety of chemical reactions and physical mechanisms can and will take place, including the deposition of various crystalline and noncrystalline scales on the waterside of heat-transfer surfaces, the formation of sludges, metal corrosion, and carryover of contaminants into the steam.

The function of boiler water treatment, therefore, is to control the waterside chemistry of boiler plant systems within certain agreed and relevant parameters and specifications. As these adverse processes are by no means limited to the boiler itself, in practice, *boiler water treatment* also includes *pre-boiler* and *post-boiler* functions and further requires that all the various types of water utilized are controlled through a comprehensive treatment and proactive management program.

Clearly, the lack of or the use of an inappropriate boiler water treatment program creates significant operational difficulties and impacts the economics of the entire process, from start to finish.

With regard to the marketing of boiler water treatment programs and services, in the preface to this book I suggested that, although boiler plant can be classified in several different ways, there are from my perspective, only two groups of boiler plant owner/operator to be addressed.

1. The first group consists almost exclusively of the large utility organizations that operate electrical power generation facilities.
2. The second group consists of all the other types of boiler facilities and is clearly a very large and extremely diverse group, utilizing boiler plant ranging from very small steam producers to very large ones and including many that also produce some electricity together with process steam.

From a water treatment technical and marketing viewpoint, there is, in fact, a fundamental distinction between these two groups, as discussed below.

Utility power generation group: This group of boiler operators typically possess boiler plant installations of complex water-tube configuration, often producing steam in excess of 1,500 to 2,000 psig and increasingly, up to double this pressure. They tolerate only very high-purity makeup (MU) water, use very little chemical treatments, and what they do use is generally of a commodity nature.

Internationally, this group has within its ranks an army of experienced chemists and engineers plus a seemingly almost unlimited source of research and development information. Much of this information is

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tightly held within the international utility power generation community and if available in book or other hard-copy form is generally prohibitively expensive for outsiders to purchase.

The fundamental reason for the commitment of this group to attaining the highest purity of feedwater (FW) and the most exactingly controlled internal boiler waterside conditions is the nature of the primary product made available for sale. This group generates electricity, on which all developed and developing nations critically depend for their economic and social well-being. The production of steam is merely an intermediate, but the quality and quantities of steam produced has a direct bearing on total electricity output, generation efficiency, operational and maintenance costs, and ultimately the price paid by the consumer.

Heating, process steam, and cogeneration group: As a contrast to the utility power generation group, operators of all the other types of boiler plant typically have installations producing steam (or hot water) at very much lower pressures. In fact, most facilities operate boilers somewhere within the range of only 5 to 125 psig, although larger process plants and cogenerators may reach pressures of up to 1,500 psig.

Because of the diversity of this group, there is no global standardization with regard to makeup (MU) water, FW quality, or boiler water (BW) chemistry control, irrespective of boiler design, pressure rating, or ultimate steam purpose. True, there are various national standards and boiler manufacturer association recommendations, and while these guides are extremely useful, they seldom universally agree on any given parameter or protocol. In mitigation, they cannot hope to provide answers to the myriad of problems and specific circumstances that develop. Rather, they should be viewed as a starting point for control purposes.

What is clear is that it is seldom that MU water or FW quality (i.e., the lack of contaminants) used by this second group ever reaches the incredible standards demanded and produced by the first group. Indeed, it is not at all uncommon to find lower-pressure boiler installations with MU water and FW both inadequately treated and simply inappropriate to the facilities needs.

Low standards of water treatment and waterside chemistry are generally caused by a combination of bad advice and lack of operator motivation or resources, and provide an initiator for the onset of downstream waterside operational problems. However, despite these apparent water treatment imperfections, most operators somehow still manage to function and produce steam of an acceptable quality and quantity, year after year!

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This second group also, in fact, contains many electricity producers, the so-called *cogenerators* or *combined-cycle plant operators*. While there is no apparent clear-cut distinction between these facilities and the large utilities, in practice, the cogenerators tend not to operate at such high pressures (although the generation of power economically usually requires at least 650 psig). Also, although the demands for good quality FW treatment and steam purity in this group is high, it tends not to reach such extremes of sophistication as demanded by the utility group.

It can be seen that the first group demands the highest possible quality of steam purity and steam generation operating control and water-side chemistry is "knife-edge" technology. Consequently, from a water treatment products and services marketing viewpoint, this group offers the minimum of opportunities as a potential source of revenue. Even where an opportunity exists, perhaps for the supply of a special *polymeric dispersant* or an esoteric *oxygen scavenger*, the service company may often discover that because of the bureaucratic and accreditation systems to be worked through, the gain may not be worth the effort.

Looking further at the second group, although many of the larger, non-utility operators around the world retain a resident water services chemist or trained technician, there is a marked tendency for *all* owners or operators, whether large or small, to work in conjunction with a water treatment service company. There is also a common purpose to use branded BW treatment chemical products rather than commodities.

Thus, a good source of potential revenue for products and services exists in the multitude of smaller boiler-houses to be found operating around the globe. It is here that practical advice is most often needed concerning the suitability and correct application of chemical treatments, the regular interpretation of analytical results obtained, and the strategies to be employed to maximize efficiency and reduce costs.

Marketing to this second group is typically based on selling some form of services-based annual contract, using the customers boiler plant operating capacity or potential for steam production as a guide for determining base requirements and for pricing purposes.

Hot water heating and LP steam systems are relatively easy to treat, given:

- Customer acceptance of the need for treatment (which is not always forthcoming).
- An appropriate water treatment program (which is not always provided, often due to cost issues).

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- Some customer/vendor cooperation (which, thankfully, is usually the case).

In contrast, the treatment of *industrial steam generation plants* is usually more difficult. There is a need to conform to a good working standard and to produce quality waterside conditions for a long period of time without serious upsets, as the systems are always very dynamic and operating conditions can continually vary. This is especially the case with those facilities whose manufacturing operations may employ some form of on-off cycle or up-down batching process, rather than a steady-state, continuous production stream.

With the smallest *heating boilers* or *low volume/low pressure steam producers*, water treatment service companies tend to promote easy-to-understand programs, typically based on only one or two multiple-component, blended chemical products (*multiblends* or *one-drum treatments*), or increasingly, the novel crystalline solid concentrates (*solid water treatment*). These customers often have only very limited, water-related, in-house technical skills, and multiblend product programs will seem attractive because they are relatively easy to apply. However, the blending process makes it notoriously difficult to control individual component reserves in the boiler and generally adds considerably to the overall program costs.

Thus, programs based on multiblends are relatively expensive to use compared with programs based on the use of separate products that are matched to the potential for particular problems identified in a boiler plant. Nevertheless, they remain commonplace for the smallest boiler houses, but as the organizational size of the customer and its volume of daily steam production increases, so the trend for individual chemical treatments on the site tends to predominate. Often, more sophisticated chemical feed and control arrangements are also employed.

Traditionally, customers employ water treatment service companies simply as *external contractors* to assist in the maintenance of clean and efficient waterside surfaces in their various heating, steam generating, cooling, and certain industrial process systems. The customers benefit from genuine improvements in operating efficiency, reductions in maintenance time, and replacement component costs. In addition, where industrial processes are involved they often profit from an "added-value," due to an improved product quality or reduction in manufacturing cost.

In this external contractor role, water treatment companies providing technical application and problem solving services are required to possess some general design component and process operating knowledge

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of all the very many different types of industrial water systems to be found. In addition, they must possess specific and relevant water treatment technical knowledge, together with the practical experience of anticipating and solving water-related problems. Thus, the service companies that can best utilize their "storehouses" of knowledge and provide the necessary customer technical support and practical field skills also tend to gain a good reputation. Ultimately, they generate profit from their solid asset-base of people and knowledge.

It is a fact of life that the cost of providing water treatment services increases with the size and complexity of boiler plant. This cost may be recovered with larger boiler plants by the higher volumes of chemical treatments sold, as often the chemical selling prices will include an allowance for all the anticipated (and expensive) technical service time requirements.

For smaller chemical volume consumers, especially those with little in the way of in-house BW treatment technical skills, the overall program costs can be relatively high. This typically is due to the disproportionately high requirement for on-site technical service time (including the travel time to and from a customer's site) compared to the volumes of chemical treatment sold. Travel and on-site time is expensive. Typically, the cost of labor and technical service is two to three times the cost of the chemical raw materials used to provide treatments.

As a result of the high costs of technical services, most water treatment vendors employ a variety of methods that allows them to charge an economic rate for the programs they sell. They will negotiate a price with the customer based on providing the most suitable balance of on-site service time and chemical/equipment requirements, that anticipates and resolves problems, meets the customers needs, and relieves his or her "pain."

Traditionally, a common solution to the problem of matching relatively higher levels of technical support with lower chemical volumes for these smaller customers has been via a one- to three-year, fully inclusive product and services contract. Such a contract will specify the frequency of service visits to be made to the customer's site and the type of work to be carried out. It will also, perhaps, limit the maximum volumes of chemical treatments to be supplied during the contract lifetime, or perhaps designate the amount of chemicals required based on treating a certain annual volume of boiler FW. Contracts may include for the provision of chemical feed and control equipment and for the supply of labor for boiler cleaning, chemical addition, and drum removal services (drumless delivery). Product and services contract prices may some-

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times be specified as a cost-per-unit of steam produced (i.e., so many cents per 1,000 lb. of steam) or a cost-per-unit of production.

Under these conditions, the customer will receive a demonstrable benefit and, provided the on-site time and the volume of chemicals shipped are adequately controlled, the Service Company will derive a satisfactory profit.

Nevertheless, and irrespective of the particular mechanisms of payment for program services rendered, profit and a win-win situation will only arise for both parties if the work performed is managed competently and in a spirit of mutual cooperation.

Thus, if a field representative believes that the task is completed when the testing of water samples is performed and a service report is issued, or if the representative's interpretation of results is poor, problems will undoubtedly develop. Also, if he or she fails to adequately review the "bigger picture" rather than merely individual results, the problems will magnify and the contract will ultimately be lost.

Similarly, if the customer refuses to be involved, at least to some degree, in the ongoing water treatment program or fails to take the advice and undertake necessary actions designed to control the program and the boiler system efficiency, the program will again ultimately fail and the contract will be lost.

Today, the traditional view of boiler water treatment (and water treatment in general) is changing. The marketplace is indicating that water treatment is merely part of a more comprehensive technical support and management services industry for various water, wastewater, and manufacturing process systems. Increasingly, water treatment is widening in scope to support global market demands. It is becoming an outsourcing services business for managing all forms of water, energy, utility, and environmental needs.

Even without the current outsourcing trends, it has always been difficult for service companies to find sufficient numbers of well-trained, experienced, and motivated field representatives. This is because the range of water treatment problems and potential solutions are very wide and the business involves the marketing of many different types of chemicals and equipment, coupled with consulting work and innovative trouble shooting.

In the water treatment industry, the first line of service providers has always been the vendor's technical sales representatives, who, for the most part, are chemists, engineers, microbiologists, or similarly trained people. The field representatives typically rely on a combination of their primary disciplines and a depth of water treatment problem-solving

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experience to overcome technical and operational problems and also add value to their customers operations. But in today's global economy, the sheer permutation of available niche services, the growing demands for both outsourcing of non-core utility functions, and economic fine-tuning, requires that water treaters now commonly have to additionally act as managers and administrators of their customers entire water system facilities.

Today, water treatment companies sell environmental reassurance and technology-based utility support services, not chemicals or equipment.

Boiler water treatment is now an energy management function. And while the business and practice of this industry may be well over 100 years old, it remains a vitally important function and is a cornerstone of the global industrial services market.

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SYMBOLS AND ABBREVIATIONS

Å	angstrom unit
AA/AMPS	acrylic acid/2-acrylamido-2-methyl propane sulfonic acid copolymer
AA/COPS	acrylic acid/sodium 3-allyloxy-2-hydroxy-propane sulfonate (polymer)
AA/NI-AS-LS	acrylic acid/nonionic aromatic and linear sulfonate (polymer)
AA/SA	acrylic acid/sulfonic acid
AA/SA/NI	acrylic acid/sulfonic acid/ nonionic (polymer)
AA/SA/SSS	acrylic acid/sulfonic acid/sodium styrene sulfonate acrylic acid/sulfonic acid/substituted acrylamide (polymer)
ABMA	American Boiler Manufacturers Association
ACH	aluminum chlorhydrate
AGR	advanced gas-cooled reactor
AMP	aminotri-(methylenephosphonic acid)
AMP	2-amino-2-methyl-1-propanol, AKA isobutanolamine
AO	All-Organic
AP	5-aminopentanol
AP/AO	All-Polymer/All-Organic
ASB	Shell Boiler Makers Association (UK)
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
1-AP	1-aminopyrrolidine
ATMP	aminotri-(methylenephosphonic acid)
AVAT	All-Volatile alkaline treatment
AVP	All-Volatile programs

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AVT	All-Volatile treatment
Barg	bar (pressure), gravity
BD	blowdown
BDHR	blowdown and heat recovery system
BF	blast furnace
BOF	basic oxygen furnace boiler
BOOM	build, own, operate, maintain
BOP	balance of plant
BS&W	basic sediment and water
BSI	British Standards Institution
BTA	benzotriazole
Btu/lb	British thermal unit(s) per pound
BW	boiler water
BWR	boiling water reactor
BX	base-exchange water softener
CA	cellulose acetate
CANDUR	Canadian deuterium reactor
CDI	continuous deionization
CFH	critical heat flux
CFR	Code of Federal Regulations
CHA	cyclohexylamine
CHF	critical heat-flux
CHZ	carbohydrazide
CI	cast iron boiler
CIP	clean-in-place
CMC	carboxymethylcellulose
CMC	(sodium) carboxy-methylcellulose
CMC	critical miscelle concentration
COC	cycle of concentration
cogen	cogeneration boiler
CR	condensate return
CTTD	condenser temperature terminal difference
CW	cooling water

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d	distance
DA	deaerator
DA	dealkalization
DADMAC	polydiallyl-dimethylammonium chloride
DAE	1,2-diaminoethane
DBNPA	2,2,-dibromo-3-nitriloproprionamide
DC	direct current
DCA	deposit control agent
DCHA	dicyclohexylamine
DEA	diethanolamine
DEAE	diethylaminoethanol, AKA diethylethanolamine
Dealk	dealkalization
DEEA	diethylethanolamine, AKA diethylaminoethanol
DEG	diethanolglycine
DEHA	diethylhydroxylamine
DEHA	N,N-diethylhydroxylamine
DEHA	diethylhydroxylamine
DETPMP	diethylenetriaminepenta (methylene phosphonic acid)
DT	differential temperature
DHA	dihydroxyacetone
DI	deionization
DMAE	2-dimethylaminoethanol, AKA N-N-dimethylethanolamine
DMAEP	dimethylaminoethylpropanol
DMAP	dimethylamino-2-propanol
DMEA	N,N-dimethylethanolamine, AKA 2-dimethy-laminoethanol
DMIPA	dimethylisopropanolamine
DNB	departure from nucleate boiling
DO	dissolved oxygen
DOT	Department of Transportation
DR	distribution ratio
DSP	(anhydrous) disodium hydrogen phosphate

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DTPA	diethylenetriaminepentacetic acid
DVB	divinylbenzene
DVGW	Deutsche Vereinigung des Gas-und Wasserfaches e.V
EC	erosion-corrosion
ED	electrodialysis
EDG	ethanoldiglycine
EDI	electrodeionization
EDR	equivalent square feet of steam radiation surface
EDR	electrodialysis reversal
EDTA	ethylenediaminetetraacetic acid
EMF	electromagnetic filtration
EMS	electromagnetic separation
EPIDMA	epichlorohydrin-dimethylamine
ESA	ethoxylated soya amine
ETA	ethanolamine
f	force
FB	firebox boiler
FBC	fluidized bed combustion boiler
FBR	fast breeder reactor
FCC	fluid catalytic cracking
FD	forced draft
FFCPP	full-flow condensate polishing plant
FGD	flue gas discharge
FSHR	flash steam and heat recovery
FT	fire tube boiler
FTA	Federal Technology Alert
FW	feedwater
GAC	granular activated carbon
g_c	proportionality constant
GCV	gross calorific value
gph	gallon per hour
GRAS	generally regarded as safe

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GRP	glass reinforced plastic
GTM	gas transfer membrane
HAD	hexadecylamine
HAN	heavy aromatic naphtha, AKA solvent naphtha
HE	hydrogen embrittlement
HEDP	1-hydroxyethylidene-1,1-diphosphonic acid
HEDTA	N-hydroxyethylenediaminetriacetic acid
HEIDA	hydroxyethyliminodiacetic acid
HLB	hydrophile-lipophile balance
HMDTMP	hexamethylenediaminetetra (methylene phosphonic acid)
hp	horsepower (boiler)
HP	high pressure
hph	horsepower per hour
HQ	hydroquinone
HQC	3-hydroquinuclidine
HR	heat recovery
HRT	horizontal return tubular boiler
HV	high voltage
HVAC	heating, ventilation, air conditioning
HW	hot water
HWR	heavy water reactor
Hyfor	hydroxyacetic acid (glycollic acid)/formic acid
I & I	industrial and institutional
IBA	isobutanolamine, AKA 2-Amino-2-methyl, 1-propanol
ID	induced draft
IDA	iminodiacetic acid
IP	intermediate pressure
IPA	isopropyl alcohol
IX	ion exchange
K_a	acidity dissociation constant
K_b	basicity dissociation constant
kcal/min	kilocalorie per minute

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kg	kilogram
kPa	kiloPascal
kW	kiloWatt
kW/hr	kiloWatt per hour
lb	pound
LP	low pressure
LPHW	low pressure hot water
LSI	Langelier saturation index
LTHW	low temperature hot water
LV	low voltage
LWR	light water reactor
m	mass
m	meter
M	mega
3-MPA	3-methoxy-N-propylamine
MAWP	maximum allowable working pressure
MB	mixed bed ion exchange
MBT	(sodium) mercaptobenzothiazole
MCR	maximum continuous rating
MEA	monoethanolamine
MEKO	methylethylketoxime
MIC	microbiologically induced corrosion
μS/cm	microSeimen per centimeter
mm	millimeter
MM	multimedia filtration
MN	mega Newton
MOPA	3-methoxy,n-propylamine
MPHW	medium pressure hot water
MSP	anhydrous sodium dihydrogen phosphate
MT	mixed treatment
MTHW	medium temperature hot water
MU	makeup water
NaMBT	sodium mercaptobenzothiazole

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NC	neutralizing capacity
ND	not detectable
NDT	nondestructive testing
NF	nanofiltration
ng	nanogram
NOWL	normal operating water level
NO_x	nitrogen oxides
NPSH	net positive static head
NRV	non-return valve
NTA	nitrilotriacetic acid
NTU	nephelometric turbidity unit
NVAT	Non-Volatile alkaline treatment
°C	degrees Celcius
ODA	octadecylamine
°F	degrees Fahrenheit
OH	hydroxyl radical
°K	degrees Kelvin
OS&Y	outside steam and yoke (valve)
OSHA	Occupational Safety and Health Administration
OT	oxygenation treatment
OVGW	Österreich Vereinigung des Gas-und Wasserfaches e.V
P	pressure of gas
PAA	(sodium) polyacrylate
PAA/PAM	acrylate/acrylamide copolymer
PAA/VS	acrylic acid/vinyl sulfonate copolymer
PAC	polyaluminum chloride
PAG	polyalkyleneglycol, AKA polyetherglycol
PAGMBE	polyalkyleneglycol-monobutylether
PAM	polyacrylamides
PBTC	2-phosphonobutane-1-2-4-tricarboxylic acid
PCA	phosphinocarboxylic acid
PCA type 16	phosphinopolycarboxylic acid

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PCC	precommission cleaning
PEG	polyethylene glycol
PEL	permissible exposure limit
PF	pulverized fuel
PHWR	pressurized heavy water reactor
PLC	programmable logic controller
PLWR	pressurized light water reactor
PMA	polymaleic acid
PMAA	polymethacrylic acid
POC	preoperational cleaning
POE	polyoxyethylene
POP	polyoxypropylene
PS	precipitation softening
psi atm	pounds per square inch, atmospheric
psia	pounds per square inch, absolute
psig	pounds per square inch, gravity
PV	pressure vessel
PVA	polyvinyl alcohol
R	universal gas constant
RDF	refuse derived fuel
RNC	relative neutralizing capacity
RO	reverse osmosis
RW	raw water
SAC	strong acid cation
SBA	strong base anion
SCC	stress corrosion cracking
SCR	selective catalytic reduction
SG	steam generator
SHMP	sodium hexametaphosphate
SHR	sodium heated reactor
SM	Scotch marine boiler
SNCR	selective noncatalytic reduction processes
SS	stainless steel

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SS/MA	sulfonated styrene maleic anhydride
SSU	Saybolt seconds universal
STMP	sodium trimetaphosphate.
STPP	(anhydrous) sodium tripolyphosphate
SV	safety valve
T	temperature
t	time
TDS	total dissolved solids
TFC	thin film composite
TH	total hardness
THM	trihalomethane
TOC	total organic carbon
TQM	total quality management
TSP	(anhydrous) trisodium phosphate
TSPP	(anhydrous) tetrasodiumpyrophosphate
TTA	tolyltriazole
UF	ultrafiltration
USDA	United States Department of Agriculture
UT	ultrasonic testing
v	volume of gas
v	volt
VB	vinylbenzene
VCI	volatile corrosion inhibitor
VOC	volatile organic compound
VOS	volatile oxygen scavenger
VPI	vapor phase inhibitors
W	work
WAC	weak acid cation
WBA	weak base anion
WH/HR	waste heat/heat recovery boiler
WT	watertube boiler
ZST	zero solids treatment

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1

STEAM GENERATION

A boiler is a device for heating water or other liquids and is most commonly constructed as a closed pressure vessel, containing a furnace area, purpose-designed heat transfer surface areas, and other functional components.

Boilers are commonly used for space heating and domestic hot-water heating purposes, in residential, commercial, and institutional markets. Here they are often categorized based on temperature or pressure ratings, and thus may be designated as **low temperature/low pressure hot water** (LTHW/LPHW), **medium temperature/medium pressure hot water** (MTHW/ MPHW), or **high temperature/high pressure hot water** (HTHW/ HPHW) types. Sometimes *thermal fluids* other than water are used.

However, for all power generation and most industrial process purposes, boilers are employed to generate **steam**, which is achieved by transforming liquid feedwater (FW) into gaseous steam; hence the term *boiler* is commonly interchangeable with the term *steam generator*. (Steam boilers are also employed in the residential, commercial, and institutional markets for space heating and domestic hot-water heating applications, but typically at a steam pressure below 15–30 psig).

The objective of generating steam from boiling water is to provide a convenient and (relatively) efficient means of transporting **heat energy** for subsequent consumption in a particular process, or for conversion to useful work. As a result, the boiler vessel is in fact merely one part of a more comprehensive steam generating, separating, and distribution system containing auxiliary equipment such as fuel burners, FW pumps, fans, FW tanks, and so forth. This system is variously known as a **steam-raising plant** or a **boiler plant**, or by a similar name, and is usually contained within a **boiler house** (although in suitable climates many field-erected power boiler plants are framed in steel but are nevertheless open to the elements).

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*NOTE: Water (H_2O) is **dipolar**, wherein the two hydrogen atoms are positively charged and the oxygen atom is negatively charged. The dipolar nature of water causes molecules to mutually attract each other by virtue of the linking of opposite charges (**hydrogen bonding**). Thus, water only changes to a vapor state with an exceptionally high input of heat energy, sufficient to break the hydrogen bond and permit the release of water molecules (as occurs in a boiler). It is this high thermal capacity (specific heat), as well as wide availability and high critical temperature that makes water an ideal medium for most industrial process and power generation heat delivery purposes.*

Steam generators were first demonstrated over 2,000 years ago, although continuously focused improvements in design only began to be developed from the late eighteenth and early nineteenth century to meet practical applications such as factory steam engines, locomotives, and the like. As a result of the Industrial Revolution, the growth in production of boiler plants was phenomenal, and by the mid-nineteenth century many hundreds of thousands of small boilers of **fire tube** (FT) and early **water tube** (WT) design were in daily operation, especially in Europe and the United States. Marine boilers were also widely in use by this same time. Although continuous *steam generator* development took place, their early safety record was abysmal and their operational life often was short. These problems led, among other things, to the implementation of statutory regulations, insurance codes, and the beginnings of a *boiler water treatment industry*.

Safety is, of course, paramount with modern boilers, and, as with other types of pressure vessels, they are subject to construction codes and operational regulations in almost all countries of the world. These requirements have been developed over many years and are designed to ensure the continuously safe operation of the overall boiler system.

Today boiler plants are manufactured in an almost infinite number of permutations with regard to their materials of construction, operational design, fuel requirements, and steam-raising capacity. For example, small factory-assembled, gas-fired fire tube boilers may be designed for perhaps only 500 to 1,000 lb/hr (approximately 14.5–29 hp) at 10 to 100 psig, while the largest, pulverized-fuel, water tube or nuclear power boilers may produce several million lb/hr at pressures exceeding 2,900 psig.

NOTE: The commonly assumed zero enthalpy (internal energy) for air is approximately 14.7 pounds per square inch pressure absolute (psia), equivalent to 1.01 bar at 80 °F (27 °C). However, boiler pressure is commonly

*measured in **gauge pressure** (psig), or **bar gauge** (barg), where 0.0 psig = 14.7 psia.*

Today boiler vessels are usually fabricated from special boiler plate and firebox steels of varying thickness, while their **auxiliaries** (*supplementary equipment*) and **appurtenances** (*boiler accessories and instruments, especially those employed for safety reasons*) may be produced from any of several different constructional metals, alloys, and other materials, including cast iron, copper alloys, stainless steels, and so forth. Tubes and tube plates may be variously constructed of carbon steel, low-alloy steels, or special alloy steels, with each design providing for particular required levels of thermal and mechanical stress and corrosion resistance. The overall boiler plant system may have a life expectancy in excess of 50 to 60 years, although individual components may need to be replaced periodically during this period.

Boilers perform two primary functions:

1. They generate steam by heat transfer.
2. They separate this steam from circulating boiler water.

They can only carry out these functions consistently and efficiently if the feedwater (FW) and boiler water (BW) chemistry and the overall boiler operation are properly controlled. Thus, over the years, in addition to improvements in engineering design and practice, many different forms of **external water treatment processes** and **internal water treatment programs** have been developed.

Today a wide range of modern water treatment processes and programs are available that have been developed and perfected to suit the many different types and applications of boilers now operating. These include the many high-pressure (HP) units around the world, which tend to be operated within extremely strict (often *"knife edge"*) control parameters.

Although many of the FW pretreatment processes and individual chemical inhibitors have changed little over the last 20 to 30 years, many significant improvements in the areas of program design, application, results evaluation, corrective strategies, and customer education have been made. These program improvements have led to further gains in boiler operational efficiency and reduced maintenance bills. However, the successful application of these programs continues to require very careful feed, monitoring, and control arrangements.

Furthermore, to obtain the maximum benefit, BW treatment programs demand an innovative and proactive mindset from owners, oper-

ators, and field service representatives. Benefits include optimum operational efficiency, control over maintenance time and costs, and freedom from worry.

1.1 BASICS OF STEAM GENERATION

Boilers are designed to boil water by **heat transfer**. Although the contained water may sometimes be electrically heated, most boiler designs provide for the heat transfer process to take place primarily across banks of tubes located within the boiler. The water may either be contained within the tubes (WT design) or on the outside of the tubes (FT design) according to boiler type. Only a percentage of the available heat energy can be converted to useful operational energy via the heat transfer process; the remainder of the available energy is lost to the combined boiler house and atmospheric **heat sink**.

The boiling of water results in the continuous absorption of heat energy until a point is reached, for any particular pressure, at which the liquid (water) changes into a gas (steam). This **boiling point** or **(heat) saturation temperature** occurs when the water vapor pressure is equal to the local pressure.

The **boiling point** of water is 100 °C (212 °F) at atmospheric pressure, and at this same point the **enthalpy of evaporation (latent heat of vaporization)** is 970 Btu/lb.

NOTE: The boiling point of water decreases with increase in height above sea level.

In other words, at its boiling point water requires the further addition of 970 Btu of energy to convert one pound of water to steam, which is 5.39 times as much energy as required to raise the water temperature from 0 °C (32 °F) to 100 °C. The temperature of the hot water remains constant until it has been entirely vaporized, at which point the steam is fully saturated with heat and the **enthalpy** of the steam (*heat content as calculated from a starting point of 0 °C*) is 1,150 Btu/lb.

If additional heat is applied within the confines of a pressure vessel, the pressure of the steam increases and the boiling point is raised, requiring yet more heat energy to reach the new saturation point.

The application of heat beyond the saturation point results in **superheated steam** and a further increase in steam temperature. Superheated steam is particularly useful in power generation boilers because the heat-

ing process removes water droplets that can seriously erode and pit turbine blades and also improves general turbine efficiency by maintaining the steam above its saturation temperature (at which point condensation begins, heat losses occur, and **water hammer** may take place).

NOTE: In most large HP boiler-turbine designs it is necessary to ***reheat*** *the steam part way during its passage through the turbine to maintain the steam above its saturation temperature. This is achieved by sending the HP turbine exhaust steam back to the boiler, where it enters the reheat section. From there the steam returns to the intermediate pressure (IP) stage of the turbine.*

Higher pressure steam has a correspondingly higher temperature, has a reduced volume, and contains more energy than lower pressure steam, thus providing the potential for greater efficiency in energy utilization.

In a boiler, with the continued application of heat, steam under pressure is produced via a combination of *steam bubble formation* (**nucleate boiling**) and *direct evaporation at the steam–water interface* (**convective boiling**), as shown in the sketch of different generated steam flow forms in Figure 1.1.

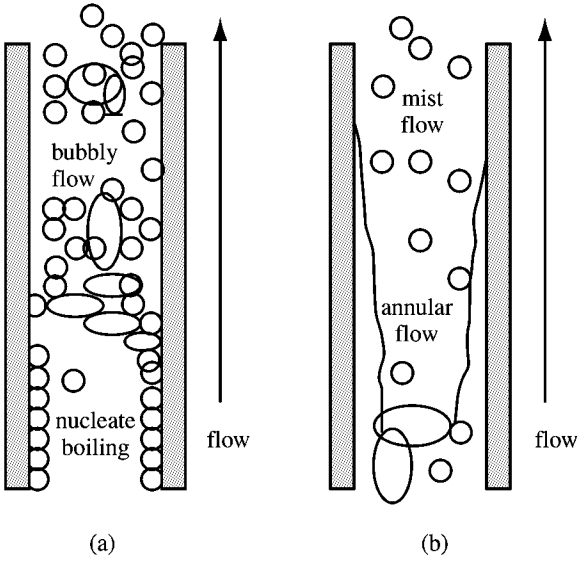


Figure 1.1 Steam generation from a heated surface, showing nucleate boiling, leading to bubbly, intermediate, annular and mist flow forms of convective boiling. Steam bubbles in water (a) leading to water droplets in steam (b).

Heat transfer rates in modern boilers are relatively high, and when the first stage of boiling (**incipient boiling point**) is quickly reached, small bubbles of steam begin to form on the heated, waterside metal surface (**steam bubble nucleation**) but initially collapse when cooled by contact with the bulk water.

With continued heating, the local saturation temperature is reached and the steam bubbles move into the larger, bulk-water **nucleate boiling region**. Because the resulting steam bubble–water mixture close to the heated metal surface has a lower density than cooler water farther away from the heated surface, the steam bubble–water mixture rises.

Gravity, acting on higher density, unheated water, provides a driving force, and the *natural circulation* (**free convection**) of water begins within the boiler. The heat is carried elsewhere within the boiler. Good boiler design is obviously critical to ensure adequate convection, especially with larger and more complex boilers.

NOTE: Due to reduced water/steam density differences, some very high pressure boiler designs employ forced convection (by use of pumps) as well as, or in place of, free convection.

In high **heat flux** (*heat transfer rate per unit area*) boilers, such as power water tube (WT) boilers, the continued and more rapid convection of a steam bubble–water mixture away from the source of heat (**bubbly flow**), results in a gradual thinning of the water film at the heat-transfer surface. A point is eventually reached at which most of the flow is principally steam (but still contains entrained water droplets) and surface evaporation occurs. Flow patterns include **intermediate flow** (*churn flow*), **annular flow**, and **mist flow** (*droplet flow*). These various steam flow patterns are forms of **convective boiling**.

Some *nucleate boiling* still takes place in high heat-flux designs. It is critical that this process continues in order to remove heat, thus cooling the heated metal and consequently reducing the risk of tube failure through overheating.

Typically, FT boilers tend to have lower rates of overall heat-flux and lower steam/water quality, and *nucleate boiling* predominates. Water tube (WT) boilers tend to have higher heat fluxes and higher steam/water quality; under these conditions, *annular flow convective boiling* tends to dominate.

In a dirty boiler the presence of unwanted deposits on the waterside heated-metal surface may lead to uneven heat transfer; the development

of large, irregularly shaped steam bubbles (rather then nucleate bubbles); and inadequate metal surface cooling. The *drag* caused by this deposit can reduce the convective forces in the boiler and lead to lower flow rates, the deposition of more BW contaminants, and possible premature steam separation. Cause and effect leads to the surging of these bubbles through the BW (**surge boiling**) and higher localized metal temperatures—with the inevitable result of a reduction in boiler design safety margins and, most probably, eventual tube failure.

Most steam generating plants operate below the critical pressure of water, and the boiling process therefore involves **two-phase, nucleate boiling** within the boiler water. At its critical pressure of 3,208.2 pounds per square inch *absolute* (psia), however, the boiling point of water is 374.15 C (705.47 °F), the *latent heat of vaporization* declines to zero, and steam bubble formation stops (despite the continued application of heat), to be replaced by a smooth transition of water directly to *single-phase* gaseous steam.

1.1.1 Steam Tables

For any given pressure up to the **critical pressure** (*the pressure at which water and steam have the same specific weight and there is no separation in phase*), there is a corresponding boiling point, and these correlations are given in commonly available **steam tables**.

A simple saturated steam table is given in Table 1.1, while a more comprehensive table is provided in the appendix.

Steam tables indicate an arbitrary zero internal energy and entropy for water in its liquid state, at the **triple point** of water.

> *NOTE: The triple point is the point at which water coexists as a solid (ice), liquid, and vapor (steam). This point corresponds to 32.02 °F (0.01 °C) at a vapor pressure of 0.089 psia (0.611 kPa).*

Steam is the working fluid in most boiler operations and usually can be treated as an ideal gas; that is, a gas that obeys the **ideal gas law**. This law states that the pressure (P) of a volume of gas (v) is equal to the product of the universal gas constant (R) and temperature (T).

$$Pv = RT$$

1.1.2 The Separation of Steam and Water

Fire tube boiler designs employ the upper internal portion of the boiler vessel as a compartment to hold the generated steam, while WT boilers

Table 1.1 Saturated steam temperatures at various boiler pressures

Saturated steam pressure psig	*Absolute pressure psia*	*Bar absolute*	*Approximate temperature °F*	*Approximate temperature °C*
0	14.7	1.10	212	100
50	64.7	4.46	298	148
100	114.7	7.91	338	170
150	164.7	11.36	366	186
200	214.7	14.80	388	198
300	314.7	21.70	422	217
600	614.7	42.38	489	254
900	914.7	63.07	534	279
1200	1214.7	83.75	569	298
1500	1514.7	104.4	598	314

incorporate one or more separate pressure vessels, primarily the **steam drum** (*top drum*), to provide the same function.

In modern boilers, both FT steam spaces and WT steam drums incorporate various devices to promote the effective separation of steam from water and the production of **"dry steam."** These devices include *horizontal separators* and *baffle plates* in the steam/water space, and *chevron driers, cyclone separators*, and *secondary steam scrubbers* in the steam space. Older or simpler boiler designs with steam release velocities of below 3 ft/s (0.9 m/s) may rely solely on the *natural separation* of steam from water.

The effective separation of steam from water is vital for several reasons, including:

1. To prevent the **carryover** of water droplets, which can mar many industrial process activities or cause damage to *superheaters* and *turbine blades*.
2. To remove dissolved solids contained within the water droplets, which contaminate the steam.
3. To discourage the generated steam from remaining in the boiler (**carryunder**) because this limits output and steam pressure.

There are various factors that affect the quality of steam/ water separation, such as:

- **Overall boiler design**, including steam and water space dimensions, boiler rating, pressure, and separation equipment arrangements.
- **Boiler operating factors**, including boiler and steam load, pressure, water level, boiler water contaminants (as determined by analysis), and chemical treatments.
- Steam containing water droplets is termed **"wet steam"** and has a reduced enthalpy.
- Steam produced from a **packaged boiler** (fire tube or water tube) should *always* contain less than 5% entrained water.
- Steam containing between 1 to 5% water may be considered **"moist steam."**
- Good design and operation may bring the level of moisture down to between 0.1 and 0.5% (**dry steam**).

Steam from a **field-erected boiler** almost always contains significantly less entrained water than the preceding figures because of the greater sophistication of steam separation devices. However, some caution is required because even dry steam from an efficient HP boiler may contain volatilized salts (such as chlorides and silica) through the process of **steam stripping**.

NOTE: The moisture content of steam can be measured by means of a ***throttling calorimeter*** *or by analysis of the sodium content in a sample of condensed steam, using perhaps a* ***specific ion electrode*** *or* ***flame photometer****.*

The dimensions of the steam space in horizontal FT boilers varies according to design and the boiler steam-generation rating. As a general rule, high-capacity FT boilers have a larger pressure vessel/steam storage space than smaller boilers, but this steam space is not necessarily of greater vertical height. Thus, FT boilers with relatively small steam space volumes tend to raise steam at the desired pressure more quickly than those with larger steam space volumes. But they also are more prone to problems of carryover of boiler water droplets (which contain potentially troublesome *dissolved solids* and especially *sodium salts*). Good boiler design and good operational control, aided by an appropriate water treatment program, typically including an *antifoam* chemical, is therefore vital under these circumstances.

In WT boiler steam drums, the normal water level is at or slightly below the horizontal centerline to maximize the steam-to-water surface area.

Although the primary purpose of the steam drum is to facilitate effective steam and water separation, most designs incorporate several other design functions. These design functions include:

- Provide an access point for FW and facilitate thorough mixing of this water with BW.
- Provide an access point for the injection and intimate mixing of water treatment chemicals into the BW.
- Provide a water storage buffer to accommodate changes in load.

1.2 ENERGY, WORK, AND POWER

Energy and **work** are interchangeable, and various terms and conversion factors are in common usage throughout the world today. These conversion factors are equivalencies unrelated to operational efficiencies because practical energy and work conversions are never 100% efficient.

Energy is the capacity for doing work and overcoming inertia, either by heat, light, radiation or mechanical and chemical forces.

Potential energy is the energy that is due to the position of one body relative to another, whereas **kinetic energy** is manifested by bodies in motion.

Work (W) is the transference of energy from one body to another and is expressed as the product of the force (f) and the displacement or distance (d); it can be expressed as:

$$W = f \times d$$

Force is anything that changes or can change the state of rest or motion of a body; it is expressed as the product of mass (m) and acceleration, divided by a proportionality constant (gc):

$$f = m \times \text{acceleration}/gc$$

- In the English system, when one pound force (1 lbf) is exerted on a one pound mass (1 lbm) the mass accelerates at the rate of 32.17 ft/s^2. Thus, in this system, gc is equal to 32.17 lbm ft/lbf s^2.
- In the SI (metric) system, when one kilogram (1 kg) of mass accelerates at 1 m/s^2, one Newton (1N) of force is exerted. Thus, gc is equal to 1 kg m/N s^2.

Power is the time rate at which energy is converted to work. It is expressed:

$$\text{Power} = W \times t$$

A boiler does no *work*; it is merely a machine or an agent that provides the facility for work to be achieved. A boiler is said to develop *one horsepower* when it provides the potential for 33,000 ft lb per minute (equivalent to 2,545 Btu/hr) of work.

NOTE: Btu/lb always means Btu/lb ***mass*** *and ft lb/lb always means ft lb* ***force/lb mass****.*

Designers, manufacturers, and operators of boilers continue to use many of these terms, without undue deference to unit standardization, to define, measure, and report on plant steam-raising capacities (*power output*) and operating parameters. (In continuance of this common practice therefore, many of these various terms are freely used in discussions throughout this book.) However, to familiarize the reader and minimize confusion, some energy terms and notes are provided here. A more complete list of units and conversion factors is provided in the appendix.

- 1 Btu (British thermal unit) is the energy required to raise the temperature of 1 lb of water by 1 °F.
- 180 Btu are required to heat 1 lb of water from 32 °F (freezing point) to 212 °F (boiling point).
- 1 calorie is the energy required to raise the temperature of 1 g of water by 1 °C.
- 1 joule (J) is the energy expended in 1 second by 1 ampere flowing through a resistance of 1 ohm.

1.2.1 Boiler Energy and Power Units

Boilers can be classified, rated, sized, and compared by means of several energy and power terms. All boilers have a **nameplate** indicating net and gross output, which may be variously indicated in **Btu/hr**, **horsepower** (hp), **pounds of steam per hour** (lb/hr), or **square feet of heating surface** for any given pressure and temperature listing.

- 1 British thermal unit (Btu) = 778.16 ft lb

- 1 kiloWatt per hour (kW/h) = 3,413 Btu
- 1 horsepower per hour (hph) = 2,545 Btu
- 1 calorie = 4.18 Joules (J)
- 1 horsepower (hp) = 550 ft lb/s
- 1 kW = 1.34 hp
- 1 kilo calorie per minute (kcal/min) = 4,186 J/min
- 1 therm = 100,000 Btu
- 1 kiloJoule (kJ) = 0.948 Btu

In addition, manufacturers' boiler operational manuals provide hard-copy data ratings for **heat transfer coefficients, local heat flux, fuel utilization, furnace heat release rates, maximum continuous rating** (MCR), and other parameters.

Boiler horsepower is an old method of rating boiler output and is still commonly used in the United States despite its validity being extremely questionable under present-day conditions.

Another old term that is still common is **equivalent square feet of steam radiation surface** (EDR).

- 1 boiler hp is the energy required to evaporate 34.5 lb of water per hour into dry saturated steam *from and at* 212 °F (100 °C).
- EDR is the surface area required to emit 240 Btu/hr with a steam temperature of 215 °F at a room temperature of 70 °F.

NOTE: With HW heating, the EDR value of 150 Btu/hr, with a 20 °F drop between inlet and outlet water, is commonly used to determine space heating requirements.

- 1 boiler hp = 33,472 Btu/hr
- 1 boiler hp = 139.5 sq ft EDR
- 1 boiler hp = 10 sq ft boiler heating surface (fireside) *[old value—see below]*
- 1 lb steam = 970 Btu/hr (from and at 212 °F)

From the above it can be seen that 10 sq ft of boiler heating surface was commonly considered to provide 34.5 lb of saturated steam, from and at 212 °F. Whereas, because of the much higher heat transfer rates today, modern boilers often generate anywhere from 100 to 500 lb/hr of steam from the same heated surface area (3.5–0.7 sq ft per boiler hp).

Typically, a modern three-pass, dry-back, FT boiler requires only 5 sq ft of heating surface per boiler hp, which is 200% of the old style rating. Thus, the MCR of generated steam (lb/hr or kg/hr) is a more sensible term to use.

An example of energy consumption and power output ratings, typical of the kind of information provided by boiler manufacturers for an older (but still widely used) design, four-pass FT boiler, is shown in Table 1.2.

1.2.2 Heat Release Coefficients

Boiler designers must be in a position to accurately predict the various heat release rates from furnace and burner designs and to match them to limitation standards for both heat input and boiler constructional steels. Some considerations are:

- **Furnace heat release coefficients:** For packaged FT boilers, designs vary from 60,000 to 125,000 Btu/hr/ft^2/°F (340.7–709.8 kW/m^2/°K) across the radiant surfaces (*essentially the furnace tube*).
- **Heat transfer coefficients:** In modern, natural circulation, fossil fuel WT boilers, overall heat transfer coefficients vary between 5,000 and 20,000 Btu/hr/ft^2/°F (28.4–113.6 kW/m^2/°K).
- **Highly rated boilers:** Various authorities [e.g., the British Standards Institute (BSI) and the American Society of Mechanical Engineers (ASME)] have differing views on what level of *heat flux* constitutes a **"highly rated" boiler**. However, from an operational

Table 1.2 Typical energy consumption and output ratings for a fire tube boiler

Energy/power parameter	*Rating*
Boiler horsepower:	500
Pounds of steam *from and at* 212°F:	17,250
Output: 1,000 Btu/hr	16,735
EDR steam, sq. ft.: (gross rating)	69,500
EDR steam, sq. ft.: (hp and ACC net)	57,250
Approximate oil consumption rate: gph @ 80% efficiency	150
Approximate gas consumption rate: therms per hour @ 80% efficiency	210

viewpoint, boilers with a high, local maximum heat-flux (primarily power generation boilers) unfortunately have an in-built design potential for attracting debris and forming concentrations of caustic and other materials at the site. Localized increased boiling-point temperatures (**wick boiling**) and **dryout** at the site may also develop and cause permanent damage to the heat transfer surface. Thus, highly rated boilers need exceptionally fine control if these types of problems are to be avoided.

Authoritative guidelines on operating practices indicate that boilers having a maximum local heat-flux of between 44,000 and 82,780 Btu/hr/ft^2/°F (79,250–149,000 Btu/hr/ft^2/°K, 250–470 kW/m^2/°K) should be considered *highly rated.*

- **Volumetric heat release rates:** The rates of volumetric heat release from shell boiler furnaces fired by oil and gas are typically 175,000 to 235,000 Btu/ft^3/hr. (Heat releases from the various tube passes are significantly lower than from the furnace, thus reducing the overall heat-flux rating.)
- **Steam release velocities:** Older or simpler boiler designs with steam release velocities below 3 ft/s (0.9 m/s) may rely solely on the *natural separation* of steam from water by gravity. Many modern boilers with higher generation rates may be designed for steam release velocities of double this value and consequently require complex separation devices if steam quality is to be maintained.
- **Boiler water (and two-phase mixtures) circulation rates:** Natural circulation rates vary according to design but are typically 1 to 2 m/sec (3.3–6.6 ft/sec).

1.3. BOILER PLANT EFFICIENCY

Comparing energy in to energy out, modern boilers are typically 78 to 85% efficient in producing steam, dependent on design. Earlier designs were often less than 50 to 60% efficient, although the use of **economizers** and similar heat-recovery equipment could boost efficiencies to 65 to 70% or greater.

Very large, modern WT boilers with sophisticated heat-recovery auxiliaries may attain efficiencies approaching 88 to 90%. However, the overall efficiency of a fossil fuel utility power generation plant system falls to only 32 to 38% when the efficiency of electricity generation and condenser cooling is included. Nevertheless, it only requires 10% more in fuel costs to operate a boiler at 1,250 psig than

at 450 psig, and there are significant gains in turbine efficiencies to be obtained at higher pressures.

Also, by use of **combined cycle** (*cogeneration*) systems, industrial power generation efficiencies can be raised to almost 50%. In designing modern, high heat-flux fossil fuel boilers and nuclear reactor fuel bundles, high heat-input rates are matched by high heat-transfer rates, which improves operating efficiency and provides the means to adequately cool all exposed heating surfaces.

High heat-transfer rates and sufficient cooling via internal, two-phase flow and circulation are consequently necessary to ensure that modern boilers operate below their particular **critical heat-flux** (CHF) conditions. This minimizes poor thermal efficiency performance, risks of thermal metal fatigue, and probable tube failures from excessive temperatures.

At *constant* heat flux, CHF occurs at *lower* steam qualities as pressure rises, thus reinforcing the need to provide the very highest quality of waterside conditions in HP industrial and power boilers.

There are various ways in which both designers and experienced operators can influence and maximize boiler system efficiencies. Of course, the continuous provision of an effective treatment program for all water/ steamside surfaces is perhaps the single most important area in maintaining efficiency and keeping costs down (without it, the boiler may simply fail in service—a condition to avoid at all costs). However, correct combustion, the judicious use of heat recovery equipment, good housekeeping, effective maintenance, and various individualized "fine-tuning" techniques are also necessary. Some areas relating to operational efficiency are discussed in the next sections.

1.3.1 Combustion Efficiency

The realization of the potential heating values of various fuels is a function of boiler design and combustion efficiency. Boiler efficiency decreases if some of the heating value of the fuel is lost either as **sensible heat** or by incomplete combustion. The largest loss is always the loss of sensible heat in dry stack gases. However, an oversupply of **excess air**, beyond that required for optimum combustion of the fuel, also may result in a significant loss of energy and also serves to cool the boiler, further decreasing efficiency.

A drop in steam pressure necessitates an increase in the fuel supplied to the burner and vice versa. However, any change in the quantity of fuel supplied requires a corresponding change in the volume of air supplied to the boiler, and if the **fuel-to-air ratio** is not balanced within the

full range of **low to high fire rates**, the overall boiler efficiency decreases.

The percentage of excess air required for complete combustion varies according to fuel types and burner design.

- Coal firing may require 20 to 50% excess air.
- Gas or oil firing typically requires 5 to 20% excess air.
- Excess air above the theoretical minimum is necessary to ensure adequate mixing and rapid combustion within the furnace area. However, the air must be heated, so the volume must be controlled to limit the amount of heat it transports out of the boiler with the exit-stack gases.
- Gas fuel contains more hydrogen than coal, thus giving rise to more water vapor in the boiler-stack gases and a relative reduction in thermal efficiency (**enthalpy loss**), due to the cooling effect of the water.
- Each 10% of excess air typically results in a 1% loss of boiler efficiency.
- Annual fuel costs may be four to six times as high as the initial boiler plant capital cost. Thus, a small efficiency improvement of only, say, 1% can produce significant savings in fuel costs.
- Power plant boilers with full heat recovery and utilizing high-grade coal in the form of **pulverized fuel** (PF) tend to provide the highest full load efficiencies, at 85 to 90%.
- Modern burner design typically provides for high **turndown ratios** (8–10:1) to reduce **purge cycle** losses under low and variable load conditions.
- Modern FT boiler combustion designs can provide very low **nitrogen oxide** (NO_x) emission levels (generally $<$ 20–60 ppm NO_x), typically by using combustion air to draw fourth-pass flue gas along with clean air. Modern standard package WT boiler designs typically control NO_x emissions to below 50 to 200 ppm (approx. 0.1 lb/MBtu).

Fuels, especially coals, are ranked according to limits on *fixed carbon, volatile matter*, and *calorific value*. Typical *gross* heating values of some common fuels (based on approximately 80% fuel to steam efficiency) are listed here:

- **Petroleum coke** = 11,500 to 15,000 Btu/lb (6,400–8,350 kcal/kg, 26,750–34,900 kJ/kg)
- **Anthracite coal** = $\cong$14,000 Btu/lb (7,800 kcal/kg)

- **Bituminous coal** = 11,500 to 14,000 Btu/lb
- **Subbituminous coal** (*black lignite*) = 8,500 to 11,500 Btu/lb
- **Lignite** = 7,000 to 9,000 Btu/lb
- **Peat** = 5,000 to 7,000 Btu/lb
- **Bagasse** = 3,500 to 4,500 Btu/lb
- **Wood** = 2,500 to 3,000 Btu/lb when wet, rising to 8,000 to 9,000 Btu/lb when dry
- **No. 1 fuel oil** (*distillate or kerosene*) = ≅19,850 Btu/lb (137,000–138,000 Btu/US gal)
- **No. 2 fuel oil** = ≅ 19,500 Btu/lb (141,000–142,000 Btu/US gal, or 0.295 US gal per boiler hp/hr)
- **No. 5 fuel oil** (*light residual*) = 18,500 to 19,000 Btu/lb (148,000–149,000 Btu/US gal, or 0.280 US gal per boiler hp/hr)
- **No. 6 fuel oil** (*residual oil*) = 18,000 to 19,000 Btu/lb (10,000–10,500 kcal/kg), or about 150,000 to 152,000 Btu/US gal (10×10^6 kcal/kg), or approximately 0.275 US gal per boiler hp/hr
- **Natural gas** = 1,024 to 1,032 Btu/ cu ft, or 40.9 cu ft per boiler hp/hr
- **500 Btu/cu ft gas** = 84 cu ft gas consumed per boiler hp/hr

1.3.2 Steam Pressure Efficiency

For optimum efficiency of usage, steam should be employed at its highest energy level, consistent with each particular application need. And, as noted above, additional fuel costs to supply steam at *higher* rather than lower pressures are small compared with the delivered energy benefits. Ultimately, therefore, higher pressures produce overall financial savings and maximize efficiencies.

All larger boiler installations have a **deaerating heater** (*deaerator*), and this can provide a steam pressure efficiency example. Thus, supplying sufficient energy to a deaerating heater in order to permit the steam to condense at, say, 10 psig, rather than the more usual 2.5 or 3 psig, produces a higher operating temperature (240 °F compared to 220 °F). This action improves the efficiency and rate of O_2 removal and ultimately provides for savings of approximately 2% in the fuel consumed.

1.3.3 Feedwater and Air Temperature Efficiency

It is standard practice in many boiler plant designs to incorporate an **economizer** (to heat FW) and an **air heater** (to heat combustion air) in the flue-gas exit system.

Looking at the overall heat transfer surfaces available in a large boiler plant, the economizer and air heater may typically provide 50% of the total heating surfaces yet extract only 15% of the available heat energy.

The *law of diminishing returns* ensures that heat exchangers near the end of the heat path require increasingly larger heating surfaces to extract heat from the lower temperature gases than those at the beginning of the heat path.

Some notes on FW and air temperature efficiency are given in the following list. A very simple guideline to the relationship between relative heat transfer surfaces compared with heat absorbed is shown in Table 1.3).

- With the incorporation of an *economizer* into a boiler system, typically a 1% gain in boiler efficiency can be achieved for every 40 to 50 °F reduction in stack temperature.
- *Air heaters* should not extract so much heat that the flue-gas temperature is reduced below its **dewpoint** because moisture will condense out of the flue gas and corrosion may occur.
- *Feedwater tank* water temperatures on package boiler systems not fitted with *deaerator heaters* should be as high as practically possible, while consistent with the avoidance of FW pump cavitation.

  Typically, a FW tank temperature of 180 to 190 °F (82–88 °C) is preferred and can be achieved by the direct application of "*live steam*" (from a LP steam supply or from a **flash steam recovery system**) through a perforated **sparge pipe** or by indirect heating via steam, gases of combustion, or electrical-resistance heaters. Each temperature rise of 10 °F (5.6 °C) results in at least a 0.3 to 0.4% fuel saving. Tanks should, of course, be properly designed and lagged.

Table 1.3 Relationship between heat transfer surfaces in a boiler and the relative heat absorbed

Boiler plant heat-exchange units	*% total heat-transfer surfaces*	*% of total heat absorbed in boiler*
Furnance water walls	10	50
Boiler bank	30	20
Superheater	10	15
Economizer	10	7
Air heater	40	8

- Where excess turbine exhaust steam or gases of combustion are used for FW heating, each 10 °F (5.6 °C) rise typically results in a 1% fuel saving.

1.3.4 Boiler Loading Efficiency

Boilers are designed to operate within a range of firing levels; the greater this range (**turndown ratio**), the more flexible they are in operation. However, boiler efficiency changes with variation in steam output, and most boilers produce their maximum efficiency at about 80 to 85% of MCR.

Where multiple boiler facilities exist, operators can meet the necessary steam demand and maximize overall boiler-house efficiency by providing a prudent loading to each boiler.

1.3.5 Steam Trap Efficiency

Steam traps are installed in *condensate, mechanical return systems* and are a frequently overlooked item for reducing operating costs. Large industrial process plants typically have many hundreds of steam traps installed to recover low-energy condensate and remove (potentially corrosive) air and carbon dioxide.

Defunct or poorly operating traps allow heat-containing condensate, insulating air, and corrosive gases to accumulate within the condensate return system, thus reducing efficiency and greatly increasing the risks of system deterioration.

- Traps that stick open may allow considerable volumes of steam to blow through, thus resulting in a reduction in overall boiler system efficiency.
- Traps that stick shut lead to waterlogged lines and water hammer.
- Traps that are corroded and leak steam and water waste heat energy. This wastage can add up to a significant extra requirement for primary fuel.
- Traps should be fitted to **steam heated tracing lines**, rather than allowing them to blow to the atmosphere (as is common), to avoid a direct steam loss.

1.3.6 Blowdown Efficiency

All steam-generating boilers operating at over 15 psig require at least daily **blow down** (*blow off*) to deconcentrate *total dissolved solids*

(TDS) in the boiler water, to remove *sludges*, and for safety reasons.

Nevertheless, prudently decreasing the total amount of blowdown per unit time (e.g., by consistently running boiler TDS levels closer to the maximum suitable for the boiler design and operation) saves money from reduced waste heat and generates a subsequent lower demand for *chemical treatments* and *makeup* (MU) *water*.

Further savings can be made by the use of a suitable *blowdown* (BD) *water* **flash steam and heat recovery (FSHR) system**. Such systems are standard equipment on large power boilers but are less common on smaller plant. However, the FS component (and often the HR component as well) can usually be justified for smaller systems because the *capital cost payback* of such equipment generally is less than 12 months and such systems continue to save fuel and high-quality water year after year.

In most larger systems, the recovered flash steam is used in a **deaerator**, while the HR heat exchangers serve as **FW preheaters** for both HP and LP boiler plants.

In smaller boiler plants with HR systems, steam from the SR flash vessel is fed to the FW tank, while the HR heat exchanger transfers useful **residual heat** to the cold MU water.

- Typically, a 1% saving in blowdown results in an approximate 0.2% savings in fuel.
- An FSHR system typically recovers about 80% of the waste heat in the BD. Slightly more than half the savings accrue from the FS flash vessel, with the balance derived from the HR heat exchanger.

1.3.7 Turbine and Condenser Operation Efficiency

Electricity is produced by the conversion of **heat energy** (produced in a boiler and transmitted as steam) into **mechanical work** by use of a turbine, which is connected to an **electrical generator** (*turbine generator*).

The conversion of energy is a difficult and inefficient transformation because 100% efficiency is only possible if the exhaust gas is received at absolute zero (approximately –273 °C or –459 °F).

As a practical reality, world ambient temperatures are typically on the order of ≅15 °C (+59 °F), and as a result most turbines are less than 80% efficient. Therefore, to maximize turbine generator efficiency, it is necessary to provide as great a temperature differential as possible between the incoming steam and the exiting steam. Thus, power

system designers continue to seek ways to refine and provide the most cost-effective systems for the delivery of HP (high temperature) steam to the turbine hall.

NOTE: The electrical generation process is somewhat more efficient than the steam turbine section (up to perhaps 97% efficient).

Efficiency is related to turbine loading and the response to changes in operation. Key factors in part-load turbine performance are the operational methods employed to control steam flow to the turbine and the actions taken to reduce **boiler cycling, low-load conditions**, and **boiler water carryover**.

The efficiency of power generation is significantly reduced by any deposits formed on the turbine blades by BW carryover and severe turbine damage may also result. Turbine efficiency also is reduced by demands for output that exceed the rated maximum and by extended operation beyond the maintenance period or design life. Additionally, errors in steam flow meters, thermometers, and pressure gauges, and so forth cause the control system to regulate the generation of electricity at some further reduced level.

Utility plants primarily employ **reheat condensing turbines**, whereas cogeneration plants and larger process industries that produce their own electrical power tend to employ **extraction turbines**. Both types of turbine rely on a **surface condenser** to receive exhaust steam from the LP turbine stage and condense it to liquid for reuse.

- Utility plants operate at the *highest* level of condensing possible.
- Where extraction turbines are employed, it is most efficient to operate at the *lowest* level of condensing possible (the highest level of extraction). This occurs when steam from the turbine is extracted and directed by various **takeoffs**, either to air or water heaters or to industrial processes requiring steam. This practice occurs because no heat is lost from the steam flowing from the throttle to the extraction takeoff (whence it can be delivered for beneficial use by the industrial process), whereas over two-thirds of the heat flowing from the throttle to the surface condenser is ultimately rejected, so efficiency suffers.

Noncondensing turbines (back-pressure turbines) are widely used by industry to fulfill any number of process requirements. As a general rule, turbine generator design efficiency is *reduced* by the absence of a

condenser. The primary function of a *surface condenser* is to minimize turbine back-pressure by condensing steam and creating an adequate vacuum. The vacuum produced by the reduction in steam-to-water volume is typically on the order of 26 to 29 inches of mercury and is maintained by air ejectors or mechanical pumps.

NOTE: A loss of 1 inch of mercury (25.4 mm Hg) in condenser vacuum typically results in a 1% loss of efficiency in electricity generation.

The efficiency of the condenser is reduced by poor removal of air and other noncondensable gases because these gases will blanket the tubes, reducing heat transfer and perhaps eventually destroying the vacuum.

Efficiency also is reduced significantly by operating a dirty or plugged unit, such as can be caused by fouling on the cooling-water side of the condenser. Mussels and other forms of marine life, leaves, scale, corrosion, algae, biofilms, and other microbiological growths all contribute to condenser fouling. (An effective cooling water program is therefore required.)

The effects of condenser efficiency reduction is limited by providing up to 15% overcapacity at the design stage, by preventative measures (both physical and chemical), and by periodic cleaning during operation.

2

BOILER TYPES AND APPLICATIONS

There are four fundamental types of boiler available today—**electric boilers, fire tube (shell or FT) boilers, water tube (WT) boilers**, and **nuclear reactor boilers**. Electric boilers apart, all other types are essentially developments from shell and tube heat-exchanger designs.

Each boiler type may be further classified according to design, output, pressure rating, and application, although not every type is available in all permutations.

- Boilers may be either *hot water generators* or *steam generators*, designed for *land*, *locomotive*, or *marine duty*, either *portable* (trailer mounted) or *stationary*.
- They may be supplied as *package (preengineered) boilers*, *job-built boilers* (fully factory constructed and then cut into pieces for difficult access sites), or *field-erected boilers*. All very large WT boilers are field-erected but often arrive on-site in modular form.
- Boilers can operate at *subcritical*, *critical*, or *supercritical* pressures, either in *once-through* or *recirculating* designs.
- Boilers may be *direct fired* or *indirect fired*. Energy supply designs account for various combustion methods using *fossil fuels*, *municipal waste*, *process residues*, *waste heat*, and *by-products*. Special boiler combustion systems to reduce pollution or improve efficiency include *fluidized-bed* and *combined cycle*.
- Boilers may be used for *domestic hot water heating*, *space heating*, *waste heat*, or *chemical recovery*. They also may be used for *mechanical work*, *electrical power generation*, *cogeneration*, and *innumerable industrial process applications* using *direct (live) steam* or *indirect steam* (e.g., coil heated) processes. Both FT and WT designs are commonly employed for *heat-recovery* applications.

- The first three boiler types may be variously used for *commercial*, *institutional*, or *industrial* applications. Fire tube boilers also may be used for *steam turbine generator* duty at lower electrical outputs, whereas only WT and nuclear reactor boilers are employed for *utility power generation*.

For most larger industrial applications around the world, either FT or WT boilers are generally employed. Design permutations are considerable, and many factories have both types installed, feeding into separate steam distribution systems (typically at different pressures) or a common **steam header**. A discussion on the various types of boilers follows:

2.1 ELECTRIC BOILERS

Electric storage hot water heaters and *instantaneous water heaters* are used for simple domestic applications and are not considered in this text. For many smaller HW and lower pressure steam generation applications (including bakery ovens and proofers, jacketed kettles, fish pots and other cooking equipment, wineries, breweries, textiles, laundries, phosphatizing processes, humidification, steam baths, clean rooms, and pharmaceuticals), *electric boilers* offer significant advantages over *fossil-fuel boilers* and are often the product of choice.

Typically, electric boiler designs are limited to under 600 kWh (2,000 lb/hr) output. However, in some countries where electricity is of particularly low cost (say, where where supplied by hydroelectric generation) electric boiler designs of up to 12,000 to 24,000 kWh (40,000–80,000 lb/hr) or more are commonly used in large-process industry. The maximum continuous rated (MCR) output is about 175,000 lb/hr.

Electric boilers are generally inherently simpler to own and operate because there is no combustion system required (fuel tanks, pumps, burners, regulators, flame safeguards, etc.). Also space requirements are smaller and capital and maintenance costs often are lower. In addition, electric boilers typically do not require full-time operators.

The efficiency of electric boilers is high, often 95 to 98%, with perhaps a 5 to10% efficiency decrease from high fire to low fire (compared with an oil-fired boiler, which may only ever reach 82% efficiency and may have a 10 to 15% spread).

There are two principal types of electric boiler, the **electrical resistance boiler** and the **electrode boiler**.

2.1.1 Electrical Resistance Boilers

Electrical resistance boilers use banks of fixed, immersion-type, resistance heating elements (typically sheathed in seamless *copper*, *Incoloy 800*, or *316SS*) to provide an energy source that is contained within a carbon-steel pressure vessel. The vessel is provided with a sight glass and all normal boiler controls, valves, and regulators necessary for automatic operation. The vessel is generally well insulated and housed within an enameled metal cabinet. Various electrical supply options are available.

Very small boilers only provide LP steam at 15 or 30 psig. However, larger units may operate at 125 to 150 psig or higher. Equipment options also may include a system for accepting condensate return to the boiler.

Electrical resistance boilers for industrial applications are typically available in sizes up to 3,500 kWh (350 developed boiler hp, 12,000 lb/hr *from and at* 212 °F, or 11.6M gross Btu/hr output) with startup amperages of up to perhaps 4,600 amps (440 v/3 phase) or 9,740 amps (220 v/3 phase).

Some manufacturers of this type of boiler claim that water treatment of any kind is not necessary and that no chemicals are required, especially with smaller units below, say, 240 kWh (800 lb/hr). Instead they rely on the on–off expansion–contraction cycles within the vessel to drop scale from the heating elements, or on a daily manual flush of the boiler vessel together with frequent replacement of elements and periodic acid cleaning. (Some improved design models thankfully have an automatic flush system that is actuated upon boiler shutdown.)

Most of these claims are spurious. In the presence of hard water and the absence of adequate condensate return, no matter how small the boiler, the elements quickly scale up, reducing efficiency and life-span. These boilers may fail in service well before a scheduled acid clean or element replacement service occurs. In addition, regular acid cleaning on small boilers can be risky and is not recommended.

> *NOTE: Almost all types of commercial or industrial boilers, of whatever type, size, and application, must be provided with fully softened FW as an absolute minimum form of external water treatment. This requirement includes electrical resistance boilers. Probable exceptions to this rule are HW heating boilers and steam boilers operating at below 15 psig and receiving in excess of 95% returned condensate.*

Although electrical resistance boilers are more tolerant of variations in water quality than electrode boilers they still require some measure

of control to limit the TDS and to minimize the risk of *priming* and *carryover*. In addition, the fact is that, apart from softening and TDS control, some form of *oxygen scavenging* and *sludge control* is generally needed and provides additional benefit to even the smallest electrical resistance boiler.

Operators who balk at the cost of providing water treatment for resistance boilers are perhaps the very same people who fail to provide adequate maintenance from the beginning of their employment and end up complaining because of unplanned production shutdowns and considerable (and unnecessary) high-cost repairs. Water treatment does not have to be sophisticated or expensive for such relatively small and simple items of boiler equipment, but some form of treatment and control *is* required.

Take, for example, a very small 75 kWh steam boiler, operating for, say, 12 hours per day with no returning condensate. This boiler has a gross output of only 250 lb/hr, requiring 360 gallons per day of FW to be supplied. If a day tank is supplied to hold this volume of FW (filled each night via a water softener), the simple, daily, manual addition of perhaps half a pint of a suitable *multiblend, nonprecipitating, chemical treatment inhibitor* before boiler start-up will prove to be a much better course of action than doing nothing until the boiler fails.

Of course, improvements could be made to this simple program. The day tank could be heated to drive out most of the oxygen, or the chemical treatment could be added proportionally to the FW via a dosing/feed pump. As a result of the extremely low consumption, this last action most probably would require the "added burden" of using suitable quantities of dilution water to provide an acceptable degree of pump discharge accuracy.

To size an electrical resistance hot water boiler use the following formula:

$$kW = gph \times T\ °F / 410$$

Where: kW = boiler output rating
gph = hot water flow rate
T = temperature rise of the water

To size an electrical resistance steam boiler:

$$10\ kW = 34.5 lb/hr\ steam = 1\ boiler\ hp$$

NOTE: Sizing allowances must be made for cold FW and radiant losses from the boiler and steam distribution system.

2.1.2 Electrode Boilers

As a general principle, in *electrical resistance boilers*, the higher the output, the larger and more complex they become, with an increasing number of circuits, fuses, contactors, and other electrical equipment, until a point is reached at which electrode boilers become more practical and cost-effective. (Although in the marketplace there are *low voltage* electrode boilers available that are designed to directly compete with small, low-cost electrical resistance boilers.)

Electrode boilers produce hot water or steam (generally saturated steam) by conducting current through the BW. The water provides resistance, which causes heat to be generated when electrical current flows from one electrode to another. As a consequence, the electrical conductivity of the water is a primary factor in the satisfactory operation of these boilers. Other aspects of water treatment control (such as alkalinity levels, oxygen content, and foam control) and maintenance also must be considered if optimum efficiency is to be obtained.

There are several designs of electrode boiler for hot water and steam generation, each with specifically designed mechanisms for producing and controlling the output of HW or steam, and each with its own specific requirements for water treatment. A failure to meet these requirements quickly results in boiler shutdown and perhaps blown fuses. However, under these circumstances, neither the boiler nor the electrodes typically suffer permanent damage and the condition usually can be quickly rectified.

The various designs may conveniently be classified as either **submerged electrode boilers** or **sprayed electrode boilers (water-jet electrode boilers)**.

Electrode boilers are manufactured as factory-ready and are therefore examples of "packaged" boilers. Smaller units are normally housed in square, sheet metal cabinets, but larger units are normally round pressure vessels with the insulation following the shape of the vessel.

The largest electrode boilers can have a diameter of 8 to 10 ft (2.4–3.0 m) and may be supplied with electricity at 16,000 v.

2.1.2.1 Submerged Electrode Boilers

Submerged electrode boilers operate with three-phase (four-wire) alternating current, flowing from phase to phase within an aqueous electrolyte.

Steam or HW is generated according to design as current flows from each of the three electrodes to the neutral walls of the shields or cylindrical balance compartments that contain and control the electrodes.

Submerged electrode hot water boilers operate in a totally flooded condition, and electrode insulating shields are mechanically adjusted by an automatic control system to provide the required HW temperature. As the insulating shields are adjusted between the electrodes and the neutral walls, so the current path is lengthened and heat generation (and thus output) is decreased.

2.1.2.1.1 Fixed Water Level, Submerged Electrode Boilers These boilers operate on a similar principle to the HW boilers, except that the vessel is not flooded but held to a fixed water level. Steam is produced in the space between the electrodes and neutral and escapes at the waterline.

2.1.2.1.2 Variable Water Level, Submerged Electrode Boilers These boilers include both low- and high-voltage types and regulate steam by varying the amount of water in contact with the electrodes. As the water quantity increases, more current flows and more heat (and steam) is generated. When the water level drops below the bottom of the electrodes, no current flows and no steam is produced.

The electrical conductivity of the water is critical to the correct operation of this type of boiler, and the precise level varies with design and power requirements. However, the conductivity is always relatively low (often specifications require a level of below 15–50 μS/cm), so demineralized or reverse-osmosis (RO) quality FW is usually specified.

2.1.2.2 Sprayed Electrode Boilers (Water-Jet Electrode Boilers)

The sprayed electrode boiler boiler is provided with a pump that draws BW from close to the bottom of the pressure vessel and circulates it back to the top of the vessel into an injection cylinder. From there the water is sprayed through multiple jets directly onto the electrodes, a current path is established, and steam is produced. However, the water flow is considerably greater than the steam evaporation rate, and the excess water is recirculated once more around the boiler

Different designs are available that limit the volume of water reaching the electrodes, which has the effect of changing the rate of steam produced while still maintaining pressure. This is achieved by either raising or lowering a control sleeve to deflect the jets of water, or by directly controlling the volume of water flowing through the jets.

Electrical conductivity must be strictly controlled, as with the submerged electrode boiler, but the limits are higher (normally around ≅3,500 μS/cm maximum).

Various chemical inhibitor treatments are also required, especially for corrosion control.

2.2 FIRE TUBE (SHELL) BOILERS

Fire tube boilers (shell boilers or shell and tube boilers) convert heat from burning fuel within a furnace (*combustion chamber*, *firebox*, or *furnace tube*) to generate either HW or steam. Fire tube boilers are designed to direct the combustion gases through *tubes* (held within *tube sheets*) that are surrounded by BW, thus providing for a greater heat-transfer surface area and improved efficiency.

The fire tubes in a shell boiler are held in place by rolling and flaring the ends of the tubes against the flat, circular tube sheets at the front and rear of the steam–BW compartment. This process effectively seals the tubes against leakage from the BW that surrounds the tubes and provides structural reinforcement (along with *stay bars*) against the pressures generated within the boiler.

Stay bolts are also used in many FT boiler designs. Typically, these bolts are provided with a drilled weep hole that leaks if deterioration of the stay bolt occurs due to waterside corrosion, thus providing an early warning to the operator.

Because of the stresses involved in operating large-diameter pressure vessels incorporating flat tube sheets at each end, a number of design limitations and controls are necessary. These involve restrictions on shell size, pressure, firing rate, and other paramaters. Typically, the various national codes and regulations restrict FT designs to approximately 12 to14 ft (3.7–4.3 m) maximum shell diameter and 300 to 350 psig (20.7–24.2 Barg, 2.07–2.42 Mpa) maximum pressure. (Some codes restrict HP FT boilers to only 250 psig.)

These pressure rating restrictions relegate FT boilers to *water heating* and less complex commercial and industrial steam generation processes, but because this category includes perhaps 70 to 80% of *all* commercial and industrial applications, it is not a particular hardship! In fact, FT boilers are globally very popular because of their relatively low capital cost, compact size, and flexibility. Also, because of the relatively high volume of water within FT boilers (and thus the limited risk of overheating), they are suitable for use when minimum operator attendance is required.

Apart from general industrial applications, FT boilers also are sometimes used for special process purposes such as waste heat recovery.

2.2.1 The Development of FT Boiler Designs

2.2.1.1 Horizontal Return Tubular Boilers

Early twentieth century designs of FT boilers were often **horizontal return tubular** (HRT) designs. These boilers were classified as **externally fired FT boilers** and had an external, refractory brick furnace located under a near-horizontal shell and tube heat exchanger. The exchanger was supported on brick piers and tilted 1 to 2 inches down toward the blowdown pipe at the rear of the boiler to reduce the risk of burning the bottom shell plates because of sludge buildup.

The hot combustion gases were directed through the heat exchanger tubes, and to this day FT boiler *combustion gas tubes* continue to be variously called *fire tubes*, *smoke tubes*, *flue gas tubes* (or simply *tubes*).

Later HRT versions employed a fusion-welded shell rather than a riveted shell, plus baffle plates or dry pipes to improve steam dryness. They were manufactured and shipped from the factory as complete preengineered units (*packaged boilers*).

Further boiler design developments produced various other types of compact, self-supporting, externally fired FT boilers, with the shell mounted over a steel-encased furnace. These designs were loosely called **economic boilers** and were typically coal- or oil-fired, three-pass boilers with an arched top (the crown sheet) and stayed side-sheets and other flat steel surfaces.

NOTE: The top part of a boiler shell (or drum) is still called a crown sheet, even though there is no physical, individual steel sheet involved.

This type of boiler remained in regular use in many countries until the late 1970s. Occasionally, HRT boilers designed for HW heating duty and dating from the mid-1920s, still may be found in daily operation (especially in some metropolitan New York City apartment buildings).

2.2.1.2 Internally Fired FT Boilers

Other boiler designs in regular use since before or around the turn of the twentieth century included **vertical boilers**, **locomotive boilers**, **firebox boilers**, and **Scotch marine boilers (Scotch boilers)**. All these designs were classified as **internally fired FT boilers**.

Early *vertical boilers* were constructed in several different designs, including FT and *tubeless*, *dry-top*, and *wet-top* versions. Typically, however, they were single-pass FT units containing an inner, combined BW and steam shell—through which a number of small fire tubes passed—and an outer combustion chamber.

The early vertical boilers of dry-top design (*steam on one side and hot combustion gases on the other side*) were subject to the risk of overheating in any fire tubes located above the waterline, but these boilers could provide relatively dry steam with some degree of superheat.

Modern versions of vertical boilers (both FT and tubeless) are widely available and similar to older designs; they continue to have fairly limited steam outputs (< 5–10,000 lb/hr), but they are compact and require very little floor space. These boilers were (and still are) gas-fired, employing either *top-down* or *bottom-up* firing.

Locomotive boilers are one-pass, horizontal, internally fired boilers (although the rectangular firebox is not contained within the shell) and were once very widely employed for both stationary and steam engine railway duty around the world. However, a primary reason for the general demise of steam locomotives on the railways was the absence of a condenser in their design, so efficiency was relatively low and water consumption was high. (Nevertheless, even in the year 2000 some coal-fired steam locomotives continue to be used in Africa and elsewhere for both hauling coal and goods yard duties.)

Other internally fired, horizontal FT boiler designs that incorporated the furnace as a pressure part within the shell included **Lancashire** and **Cornish** designs. The Lancashire was a twin furnace tube design (often corrugated) but without any fire tubes (*single-pass*), while the Cornish was a similar but smaller boiler with only one furnace tube. These boilers were generally fired by hand-stoked coal or waste wood and contained a large volume of water relative to their heating surface areas. Steam output was modest, and they were quite inefficient, being at best only 60 to 65% efficient based on gross calorific value (GCV). This position was made worse by the fact that most operators used hard-water MU and poor chemical treatment programs, thus resulting in thick deposits of scale that required periodic acid cleaning. (Treatment programs were typically hand-dosed, powdered blends, based on combinations of **phosphate**, **soda ash or caustic soda**, **wattle tannin**, or **lignin**, and sometimes **starch**.)

Many Lancashire boilers were still in use in the 1970s, but the industry saw their demise at this time as a result of increasing fuel prices

worldwide. A few boilers that had been fitted with economizers (which improved their efficiency to perhaps 70–75% GCV at best) remained in use for some time longer, but most had long been replaced with economic boilers, Scotch boilers, or other packaged FT boiler designs.

At the end of their useful life, Lancashire and Cornish boilers were sometimes converted for further duty as *accumulators* (steam storage vessels providing a buffer against variable demands).

2.2.1.3 Scotch Marine Boilers

Scotch marine boilers (SM boilers) derive their name from the Scottish shipyards that built marine vessels for the British Navy. They were the first design of FT boiler to incorporate both furnace tubes and fire tubes inside the shell and replaced the brick-set boilers that used to burn through the bottoms of ships. The SM boiler was a particularly versatile design and quickly became the boiler of choice for many stationary (land) applications as well as for marine duty. Land-based SM boilers (now commonly called Scotch boilers) were not simply marine boilers adapted for stationary duty but incorporated specific design modifications to meet the requirements of land-based industry.

Early SM boilers were manufactured with between two and four corrugated furnace tubes in **wet-back** and **dry-back** versions and generally incorporated heat recovery equipment such as economizers and air heaters. Some designs also provided for superheaters and for coal, oil, or gas fuel firing. Many of the best features are incorporated in the SM boilers commonly available today.

Modern SM boilers are widely used for **hydronic heating**, LP steam applications, and some HP processes. They are available in forced-draft gas, oil, and combination fuel modes, typically producing up to 1,200 hp (41,400 lb/hr). U.S. manufacturers today build to a 5 sq ft of heating surface per hp standard (6,700 Btu/hr/sq ft).

NOTE: ***Corrugation*** *of self-supporting furnaces (as found in some SM boiler designs) is one method of resisting the compressive forces in FT boilers. Rings, flanges, and stays are also used.*

In ***wet-back boiler designs*** *the rear wall of the furnace and the point at which the first-pass exit gases reverse direction is surrounded by water; thus, no combustion chamber refractory is required and maintenance costs are reduced.*

In ***dry-back boiler designs*** *the tubes pass through the rear tube sheet before returning to the steam and BW compartment, which provides for a relatively larger horizontal heating surface and thus quicker steaming.*

Also, there is an unrestricted access to the rear of the tubes for cleaning. However, valuable heat is lost to the refractory rather than the water.

2.2.1.4 Firebox Boilers

Firebox boilers (FB boilers), like SM boilers, have a long history, and many old, riveted, and unlagged shell boilers dating from the 1920s can still be found in large apartment complexes and commercial buildings, where concern over optimum operating efficiency is not critical. Typically, they have been employed for seasonal HW heating (**hydronic heating**) and LP steam heating applications. However, they remain very popular today for a wide range of applications, including various manufacturing processes.

The modern FB boiler is a compact economical design (typically more compact than SM boilers) and provides minimum combustion efficiencies of 80% for gas-fired and 83% for oil-fired models. They usually are small units, seldom exceeding 150 hp, and operate on a variety of fuels at typically 4 to 5 sq ft of surface area per hp.

FB boilers are similar to SM boiler designs except that, instead of a fully immersed furnace tube, they have a bottom furnace (with a crowned combustion chamber) that sits on a refractory floor. *Two-pass fire tubes* (smoke tubes) connect the combustion chambers to the gas exit vent (smoke stack).

Because of the furnace design, which incorporates a relatively large and unrestricted combustion zone, FB boilers are entirely suitable for coal and other solid fuel firing.

2.2.1.5 Cast Iron Sectional Boilers

Cast iron (CI) boilers are manufactured in sections and assembled at the job site, which makes them suitable for applications where access is limited. Like SM and FB boilers, CI boilers are also widely used in hydronic heating systems.

Low-pressure steam-generating CI models are particularly sensitive to changes in water chemistry, and their rough waterside surfaces makes them susceptible to deposition, and thus to the risk of overheating and subsequent cracking. Typically, they are quite small boilers, most being less than 200 hp.

Despite the need for good water treatment, CI boilers generally have a long life expectancy. However, they can be extremely prone to **priming** or **surging** and **carryover** problems. Any deviation in water chemistry

from tight control limits induces priming and carryover. This is not to say that CI boilers, as a class, are more prone to carryover than other classes; they are not. Rather, it is that the designers of these smallest residential and commercial boiler plant systems tend to employ CI boilers because of their flexibility in sizing and rating at the lower end, and these smaller systems are especially susceptible to carryover because of the limited water volumes and steam space available, and the relatively poor steam–water separation devices generally incorporated.

2.2.2 Modern, Packaged Horizontal and Vertical Boilers

All modern, **packaged horizontal FT boilers** are basically descended from the SM internally fired, FT boiler design. They became immensely popular during the early 1960s because of their versatility, cost-effectiveness, and relative efficiency (this last factor became very important following the fuel price crises of the early to mid-1970s).

A schematic, cross-sectional drawing of a four-pass, packaged horizontal FT boiler (looking from the front) is shown in Figure 2.1.

Modern, **packaged vertical boiler designs** are also very popular and are widely used for smaller or specialist applications. Today's vertical boilers are the product of over 50 years of continuous development.

Both horizontal and vertical packaged boilers are very compact, prewired, preengineered units. All are supplied and shipped ready for

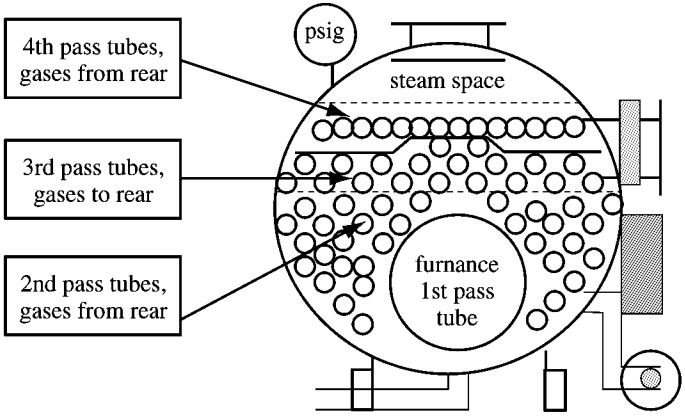


Figure 2.1 Cross section of a "packaged" four-pass FT boiler.

use with the FW pump, controls, and all necessary auxiliaries and appurtenances contained within the overall boiler unit volume.

Most manufacturers supply packaged boilers as skid-mounted units to aid shipping and site positioning. Many designs incorporate a factory-installed, insulated steel jacket, while others are housed in an insulated sheet metal cabinet (only on older FT designs was the shell not insulated).

Options typically include a wide range of pressure ranges and steam outputs, fully automatic operation, full **modulation** (*variable FW or steam supply, rather than on–off operation*), low NO_x burners, and high turndown-ratio burners to reduce cycling and improve fuel utilization.

2.2.2.1 Packaged, Horizontal FT Boilers

A schematic drawing of a modern, packaged, four-pass horizontal FT boiler, indicating the paths of hot combustible gases is shown in Figure 2.2. In common with the SM boiler, the packaged, horizontal FT boiler furnace is a steel heat-transfer tube surrounded by BW and contained within an outer steel shell. As usual, the hot combustion gases flow out from the rear of the furnace tube and are then directed through (typically) either *three-pass* or *four-pass* fire tubes, also contained within the shell.

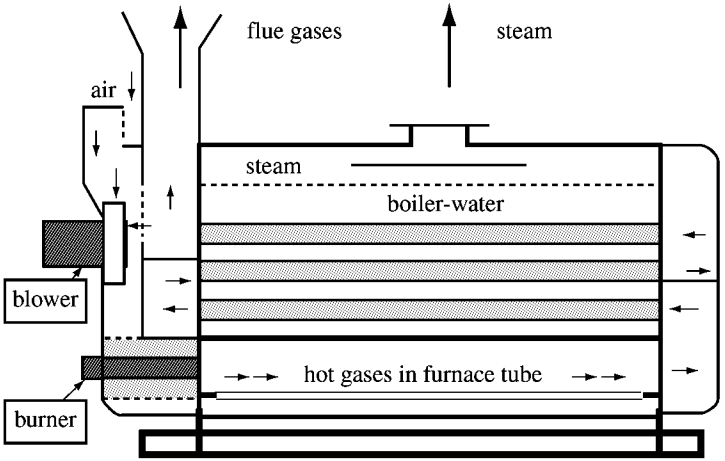


Figure 2.2 Schematic of a modern four-pass, packaged horizontal FT boiler, with low NO_x emission, showing path of hot combustion gas flow, and air/combustion gases recirculation system.

NOTE: Three-pass design boilers have a greater primary heating surface and require less tubes, whereas four-pass boilers have a lower primary heating surface and thus require the extra tubes to achieve the maximum output.

Packaged FT boilers are usually fired by oil or gas using integrated, forced-draft burners and are available as wet- or dry-back types.

Tubes may be arranged in either a *horizontal and vertical alignment pattern* (which provides for easier cleaning and inspection) or in a *staggered layout* (which provides for improved heat transfer) because of the more circuitous flow of water around the tubes).

In modern, packaged horizontal FT boilers, the furnace is the most important heat-transfer component, typically providing 50 to 60% of the total heat transfer from only 30% or so of the total available heating surfaces. This level of heat transfer, coupled with the additional heat extraction obtained by the various multiple-pass designs (four passes is a practical maximum) provide efficiencies of 80 to 83% GCV. As a result, there generally is little additional benefit to be obtained from the use of economizers or air heaters, especially when using oil-fired boilers, which can operate at up to a 3% or so higher efficiency level compared to gas-fired units.

NOTE: Economizers are, in fact, fitted to some gas-fired, packaged FT boilers. The economizer is designed to recover some of the enthalpy lost as a result of the increased water vapor content in the exit gases from burning natural gas.

Although WT boilers are sometimes employed for HW and LP steam duty for space heating, domestic water heating, and similar applications, these functions are normally the province of FT boilers. In particular, horizontal FT boilers of SM or firebox design are specified extremely often.

Some definitions of the different categories of FT boiler by approximate temperature and pressure follow:

- **LPHW systems:** Operate below 250 °F (121.1 °C), equivalent to 29.8 psia (15.1 psig)
- **MPHW systems:** Operate above 250 °F and below 350 °F (176.7 °C), equivalent to 135.5 psia (120.8 psig)
- **HTHW systems:** Operate above 350 °F. Typically the maximum temperature is 450 °F (232.2 °C), equivalent to 424.2 psia (409.5 psig)

- **LP steam systems:** Operate below a maximum allowable working pressure (MAWP) of 15 psig (29.7 psia), equivalent to 249.8 °F (121 °C)
- **HP steam systems:** Operate above a MAWP of 15 psig and 6 boiler horsepower (207 lb/hr). Fire tube boilers for commercial space heating applications seldom operate at above 30 psig (44.7 psia), equivalent to 276 °F (135.5 °C). Fire tube boilers for industrial application may operate at, say, 100 psig (114.7 psia), equivalent to 338 °F (169.9 °C) up to, say, 250 psig (264.7 psia), equivalent to 406 °F (207.8 °C), or even 300 psig (314.7 psia), equivalent to 421 °F (216.1 °C) and with an output exceeding 750 boiler horsepower (25, 875 lb/hr).

As a result of continuous improvements in packaged, horizontal FT boiler design and the use of new alloys, higher furnace heat-transfer rates have become possible. However, the risks of exceeding furnace or tube **critical heat flux** (CFH) at some localized point, due to *sludge* or *scale deposition* have also increased. This risk of deposition also increases the risk of *differential aeration* and *oxygen pitting* corrosion, so that mechanical deaeration is generally an advantageous proposition in HP packaged boilers.

Furthermore, modern boiler shell waterside internals tend to be more inaccessible, and the compact designs make inspections, cleaning, and maintenance more difficult tasks than with earlier designs.

From the preceding notes it can be surmised that, although output and efficiency levels are high, modern packaged horizontal FT boiler designs generally require significantly tighter operational control than earlier models. They are also more demanding in their water treatment programs. High standards of operation and vigilance are required not only to maintain the output efficiencies, but also to avoid problems such as *waterside fouling*, *overheating*, *leaking or corroding tubes*, *bulging furnaces*, *low water*, *carryover*, and so forth.

It is pertinent to note that with older design FT boilers the problem of **silicate scaling** was almost unheard of (although perhaps the problem may have gone unreported or was simply ignored). However, as the risks of glassy silicate scale formation increase with higher boiler heat flux, it is today unfortunately fairly common to find significant silicate-containing scales deposited in the high heat flux, waterside areas of modern packaged boilers. (It also is likely that a general deterioration in the MU sources commonly employed around the world for boiler FW has further contributed to the problem of silica scaling.)

2.2.2.2 Packaged Vertical Boilers

Although the great majority of modern, packaged boilers are of horizontal FT design, *packaged vertical boilers* also are available, and a schematic, cross-sectional drawing of a modern vertical boiler is shown in Figure 2.3.

Vertical boilers are particularly suited for smaller heating and process applications, such as hotels, laundries, food processing, adhesives, plastics, andpharmaceuticals manufacturing, or in standby operations, because steam output is relatively low (usually only up to 100 boiler hp or 3,450 lb/hr) but the time taken to reach full pressure is short.

When boiler aesthetics play some part in the selection process, modern vertical boilers also win, as apart from being highly efficient and compact units, some designs look particularly smart and provide a quality image because of their polished stainless-steel outer jackets.

Typically, modern, vertical boilers are of "tubeless" design. They contain a suspended, dry-back, two- or four-pass, circular water jacket, of pressure vessel construction, about 5/16th inch (7.94 mm) in thickness. The inner tube of the water jacket is in reality the furnace tube, whereas the outer tube is the boiler shell.

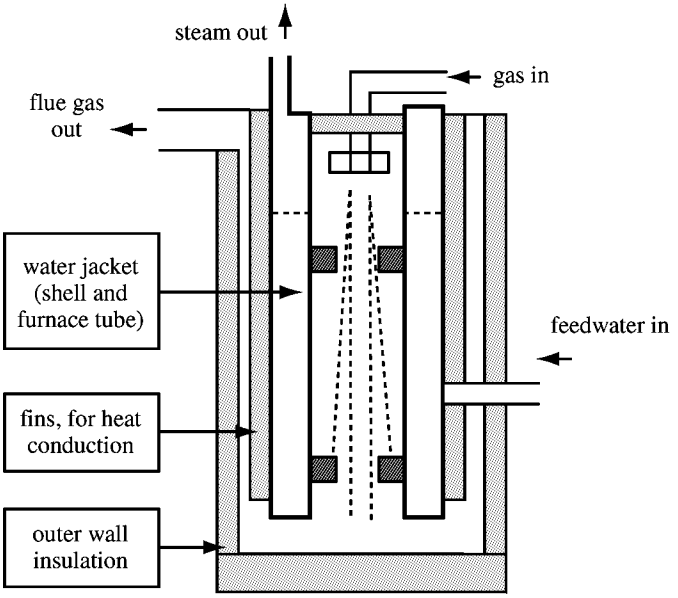


Figure 2.3 Two-pass, vertical, "tubeless" packaged boiler.

A forced-draft, gas-fired burner is seated at the top of the inner tube and produces a spinning **cyclonic flame** that reaches down to the bottom of the furnace tube. The hot combustible gases return over the boiler shell, which is provided with heat convection fins to extract more heat before the upward flowing gases exit the boiler. The furnace tube is fitted with a top and bottom, cast-steel flame retainer. These design features act to increase flue gas residency time and provide improved structural integrity to the pressure vessel.

Because of their compact size, packaged vertical boilers can be custom-designed as a complete boiler plant system and simply shipped to the customer on a steel skid or platform. This type of system may comprise a dual boiler arrangement, with a pretreatment unit (water-softening and chemical-feed system), boiler blowdown and condensate return facilities, and also possibly a dual stack containing an economizer. This type of packaged system may reach 85% GCV efficiency.

Low NO_x emission burners also are available, typically maintaining NO_x to below 20 to 60 ppm CO (corrected to 3% O_2), equivalent to under 20 nanogram (ng) NO_x/J output.

NOTE: Apart from the "standard" packaged, horizontal and vertical boilers discussed previously, other designs of packaged, direct-fired, LP steam generators are commonly available but designed for special industrial applications, such as curing concrete.

Typical designs may provide for a vertical, water-cooled combustion chamber and top-mounted, water-cooled burner. These steam generators may produce up to 105 boiler hp (3,620 lb/hr) or so, available as fixed levels of steam output. This is achieved by employing combinations of air blowers that can provide up to seven steam output stages.

These steam generators are often used for once-through steam processes; as such, they are not usually provided with any form of water treatment program and are not considered further in this text.

2.3 WATER TUBE BOILERS

Water tube boilers convert heat from burning fuel within a central, boxlike open furnace chamber to generate either hot water or steam (often at very high pressure, temperature, and output capacities).

However, contrary to FT boilers, the BW is held within one or more tubes, and heat from hot gases flows across the tube walls from the *outside*. As a consequence, a significant benefit of WT boilers is the fact, that for any given tube diameter, WT boiler tubes have a greater heating surface than FT boiler tubes. This is because the heating surface of WT

boiler tubes is the larger outer wall, whereas in FT boilers the heating surface is the smaller inner wall.

Almost all designs of WT boilers have multiple banks of special-purpose tubes (*water walls*, *boiler bank*, *tube bundles*, etc.), although a particular type of WT boiler, the **coil boiler**, typically has only one coiled tube.

Water tube boiler design and construction provide for much greater capacity, pressure, and versatility than FT boilers because of the subdivision of pressure parts and the ability to rearrange boiler components into a wide variety of configurations. As a result, steam output may be from under 1,500 lb/hr to several million lb/hr. Designers have, over the years, developed WT boilers for many diverse industrial process applications.

As a general rule, WT boilers are safer from explosion than FT boilers because the drum is not exposed to the radiant heat of combustion. If tubes rupture, there is only a relatively small volume of water that can instantly flash to steam.

From a good housekeeping aspect, the ability to gain access for inspection, cleaning, and maintenance is probably comparable for modern WT and FT boilers, but WT boilers tend to require more total hours of operator involvement per year, simply because they are generally physically bigger. Another general rule is that WT boiler systems require more highly trained operators because of their greater complexity.

Water tube boilers are installed in all manner of commercial and institutional buildings, smaller industries, large industrial processors, and power generators. (In fact, the utility power industry is the single largest user of WT boiler capacity in the world.)

Smaller WT boilers are available as shop-assembled packaged units, whereas large boilers are constructed in sections and shipped to site for field erection. The largest field-erected boilers can provide steam, superheated to 1,100 °F (593 °C) and at pressures in excess of 2,900 psig. Some boilers operate at *supercritical pressures* (N.B.: critical pressure is 3,208.2 psia).

The versatility of WT boiler design provides for several broad categories of application:

- **Coil boilers:** Used for small industry, hotel, laundry, food processing, and similar duties, where rapid but intermittent steam demand is required.
- **Industrial boilers:** Typically operating below 900 psig and used for various water and steam heating activities and for process applications.

- **Cogeneration (combined-cycle) boilers:** Typically operating from 450 psig to 1500 psig, providing both electricity and process steam. Smaller cogeneration plants may employ gas turbines or diesel engines for electricity generation and generate only LP steam via waste heat boilers (which recover the heat contained in the plant's exit gases).
- **Utility power boilers:** Most modern plants usually operate at over 1,500 to 2,000 psig and feature some of the most complex engineering available in the world. Older plants may operate at only, say, 450 to 950 psig.
- **Marine boilers:** In the most modern ships, marine boilers have become relegated only to *auxiliary* and *heat-recovery* use because diesel engines have now become the primary form of equipment employed for marine propulsion.
- **Waste-heat** and **other special-purpose boilers:** Special designs provide boilers for *waste heat* and *chemical recovery*, *waste-to-energy*, and *combined-cycle installations*, *pulverized-bed*, and even *biomass* applications.

The serious development of WT boilers began in the mid-1850s, and by the late nineteenth century WT boilers were considered safe and reliable steam generators, able to be used for all manner of applications, both in the industrial world and for marine duty.

Some major steps forward in the development of WT boilers were the invention of bent tube designs, the use of pulverized fuel, the development of integral furnace boilers, and other design innovations.

1. The invention of **bent tube** designs from 1880 (and first used in **Stirling® boilers**) permitted a wide but low head arrangement and the direct coupling of generating tubes between a top-mounted **steam drum (top drum)** and a **mud drum (bottom drum).** Modern boiler designs still make some use of bent tubes because they are more flexible than straight tube designs. Bent tubes permit free expansion and contraction and allow more heating surface exposure to radiant heat than straight tubes.
2. The use of coal in a **pulverized fuel** (PF) form during the 1920s significantly increased the volumetric combustion rate possible and provided for the much greater boiler capacity required in the developing electric utility industry. The majority of high-capacity, cogeneration, and utility power boilers now use coal PF because almost

all coal sources around the world are potentially suitable for pulverizing. Following proper preparation (which includes moisture removal), PF is conveyed to the boiler house and blown directly into the boiler.

3. The development of **integral furnace boilers** during the 1930s allowed walls constructed of banks of vertical tubes welded together to form a continuous membrane (**membrane walls** or **water walls**), which provided for simultaneous heat transfer from the furnace and a furnace water cooling surface. (Earlier WT boilers had completely separate cooling systems.)

   In addition, the use of water-wall design lowered gas exit temperatures, which increased boiler efficiency and reduced the potential for rapid degradation of refractory surfaces caused by the buildup of **slag** (molten ash). All larger WT boilers today employ water-wall membrane designs in their construction.

   NOTE: Modern power boilers are designed for complete water-wall cooling (no boiler bank). They have very large superheaters, employ balanced draft systems, and typically do not have a mud drum.

4. Shop-assembled, **packaged boilers**, developed during the 1940s were designed to meet the significant wartime era demand for high output, mainstream industrial use at lower cost than field-erected units.
5. The development of **critical pressure boilers** during the 1950s came in the post–World War II years amid a growing demand for domestic electricity consumption, especially within fully industrialized countries. The invention stimulated further designs for low-cost electricity generation.
6. The widespread application of **nuclear boilers** by the 1960s went hand-in-hand with the developing nuclear technology of several industrialized countries in both the West and the East. There was an increased use of nuclear power for electric and motive power, on land and at sea.
7. Continuous improvements during the 1970s and 1980s in **radiant boiler** furnace design made significant steps forward in the efforts to further improve operational efficiency and reduce the frequency of offline cleaning cycles for fossil fuel–fired boilers. Additionally, this same period saw the development and growth of modern cogeneration plants.

8. During the 1980s and 1990s, various **quality management** systems (such as total quality management, or TQM) together with **environmental protection programs** emerged. With the rise of politically and socially sensitive issues such as **global warming** and **acid rain**, WT boiler system development continues to center around maximizing overall operating efficiency through the reuse of resources, while minimizing the pollution impact of large WT boilers. As an example of responsible environmental efforts, the use of **fluidized-bed combustion systems**, stringent **emissions control**, and **combined-cycle systems** is rapidly becoming the norm in many industries.

2.3.1 Water Tube Boiler Plant Sections

As noted earlier, WT boiler design provides for significant versatility because of the subdivision of pressure parts and the ability to rearrange boiler components into a wide variety of configurations. Boiler designers tend to divide the boiler into a number of sections and place each of the primary boiler components into one or other of these sections, although there is no universal agreement concerning the specific division of these components. The sections are often described as:

- **Furnace section**
- **Convection-pass section**
- **Exit gas section**

The first two sections also contain part of the steam–water circulation system (which includes all boiler surfaces, such as drums, tubes, and shells). Figure 2.4 shows the first two sections and some of the major WT boiler components.

2.3.1.1 Water Tube Furnace Section

Within the furnace section is the **furnace structural system** (which includes all necessary supporting steelwork, the refractory, and insulation) and the **combustion system** (which includes fuel and air delivery systems, burners, and ash handling components). The combustion system largely determines the basic boiler configuration.

When a boiler design employs a **radiant superheater**, it is located within the furnace section. Also within the furnace section are the water-cooled, **membrane walls** (*water-wall tubes*), **risers**, **headers**, and

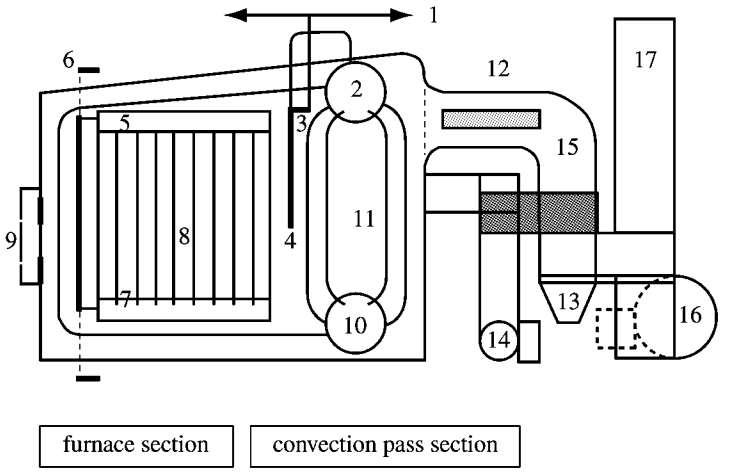


Figure 2.4 Schematic of WT boiler.

Legend: 1 = steam header, 2 = steam drum, 3 = attemperator, 4 = superheater, 5 = top header, 6 = riser and downcomer (note: *downcomer* is outside the boiler), 7 = bottom header, 8 = water wall tube membrane (with *radiant area* inside membrane), 9 = burners, 10 = mud drum, 11 = boiler bank, 12 = economizer, 13 = dust collector, 14 = forced draft fan, 15 = air-heater, 16 = induced draft fan, 17 = stack

where fitted, the **boiler bank** or **steam-generation bank** components of the steam–water circulation system.

NOTE: Some WT boiler designers place or simply designate the boiler bank within the convection-pass section.

2.3.1.2 Water Tube Convection-Pass Section

The convection-pass section contains heat exchangers such as the **convection superheater**, **reheater**, and **economizer**, which are within the boiler proper. Also within the general area of this section are the **attemperators (desuperheaters)**.

*NOTE: Although superheater, reheater, and economizer heat exchangers all contain either steam or water in their respective tube bundles, they generally are not considered by boiler engineers and designers to be part of the **steam–water circulation system's "boiler surfaces."** This distinction typically is reserved for the various tubes, connecting headers (manifolds), and drums that collectively provide the primary heat transfer and steam-generating facility.*

2.3.1.3 Water Tube Exit Gas Section

The exit gas section contains the **air heater** tube bundles, **flue gas dampers**, and the various **emission control systems** such as **dust collectors**, **electrostatic precipitators**, and **gas scrubbers**.

2.3.2 Steam–Water Circulation System

In common with a FT boiler plant, a WT boiler plant contains several steam–water condensate systems and subsystems, although those of industrial and waste-heat WT boiler systems are generally larger and more complex, and power WT boiler systems are even more so.

External to the boiler itself are various **pre-boiler** and **post-boiler water subsystems**. These include the **MU water pretreatment system**, **FW supply system**, and **steam-condensate recovery system**, again of varying complexity depending on the design and size of the boiler.

Within the boiler, subsystems include a **steam–water circulation system** and a **steam delivery system**.

2.3.2.1 Boiler Steam–Water Circulation System

A diagram of a WT boiler steam–water circulation system is shown in Figure 2.5.

The boiler steam–water circulation system is designed to promote the delivery of steam from the various **generating tubes** to the **boiler steam drum (top drum)**. From here the steam is separated from the BW and transferred to the steam delivery system for possible superheating and subsequent use in a turbine generator or other downstream process application.

At the same time, the natural circulation that results from the combustion process provides effective cooling of all tubes, headers, drums, and other *boiler surfaces*.

The water flow route starts with preheated FW, which is supplied via an *economizer outlet header* to the *top drum*, where it enters and mixes with BW in the drum. This FW–BW mixture then leaves the top drum and flows through the external *downcomers* (*downcomer tubes*) to various *bottom water-wall headers* located at the lowest part of the furnace.

NOTE: The downcomers, although part of the boiler steam–water circulation system, are located outside the boiler so that theFW–BW mixture flowing within the downcomers remains cool relative to the steam–BW. Thus, density differences remain and natural circulation continues.

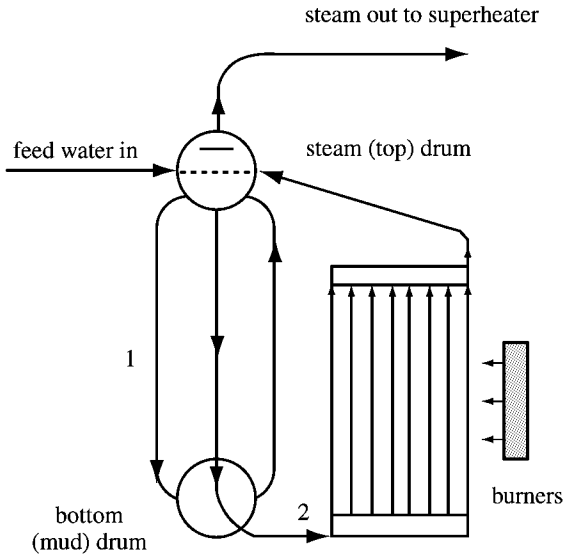


Figure 2.5 Steam-water circulation system.
Legend: 1 = boiler bank circulation system
2 = primary steam-water circulation system

From here the water mixture rises through the *water-wall tubes* (*generator tubes*) that constitute the *furnace membrane* where steam is generated (primarily by radiant energy transfer). The steam–BW mixture is collected in *top water-wall headers* and conducted through *risers* (*riser tubes*) back to the top drum, where the saturated steam separates from the water at the steam–water interface.

The wet steam passes through *steam–water separators* within the top drum. Separated water is returned to the inlet of the external downcomer, while the moist-to-dry steam may pass through a secondary steam–water separator to remove any residual moisture before passing into the *steam header* part of the steam delivery system.

In addition to a top drum, most industrial WT boilers employ a *bottom drum* (*mud drum*) to assist in the steam–water circulation and to provide for the separation of mud and sludges.

A **boiler bank** is also included. The *boiler-bank tube bundle* provides sufficient heat transfer surface area to provide the rated capacity for saturated steam. Boiler-bank tube spacing and dimensions are arranged so that a *steam–water circulation subsystem* connects the top and bottom drums with subcooled water passing down the tubes farthest from the furnace and returning as a steam–water mixture.

2.3.2.2 Steam Superheating and Delivery System

Most larger WT boiler designs incorporate some form of roof cooling by incorporating *roof tubes* supplied with dry steam from a *roof header*. Horizontal and vertical section convection-pass cooling is also provided via membranes supplied with dry steam from headers.

Exiting steam from the roof and convection-pass cooling sections is collected in headers and typically passes through a *primary superheater tube bundle*, where a controlled amount of superheat is provided. In the superheater the steam discharges through an outlet header and across a *spray attemperator* (which provides the steam temperature control) and is then delivered to the control valves for distribution and subsequent use in a turbine or other items of process equipment.

Power boilers usually incorporate a *reheater* and *secondary superheater*. Superheaters and reheaters may be pendant or horizontal, and some boiler designs may use their roof cooling tubes to provide a support for these various tube bundles.

2.3.3 Types of WT Boiler

Four types of various WT boiler are shown schematically in Figure 2.6 a–d. Water tube boilers are widely used in all manner of industries around the world, but they are mostly associated with larger energy applications such as utilities, independent power producers, chemical and petrochemical industries, pulp and paper, and marine duty. However, they are also widely used by governments, institutions, and municipalities in airports, universities, and other large buildings for both HW and steam generation. Smaller general industries also widely use WT boilers, often in conjunction with FT boilers.

This wide range of applications has resulted in an almost innumerable number of design permutations. These designs are normally based on multitube configurations but also include single-tube coil boilers.

Conventional designs for smaller WT boilers typically place a considerable emphasis on energy transfer by **convection** to meet rated capacities. This requires much of the total heating surfaces to be at right angles to the combustion gas currents (or as close to this as possible) so that the gases flow around the tubes. However, the larger the boiler, the less of an emphasis on convection because energy transfer by **radiation** to *water-wall membranes* becomes more important.

Nevertheless, many modern boiler designers defy convention and provide quite small industrial, packaged WT boilers that employ

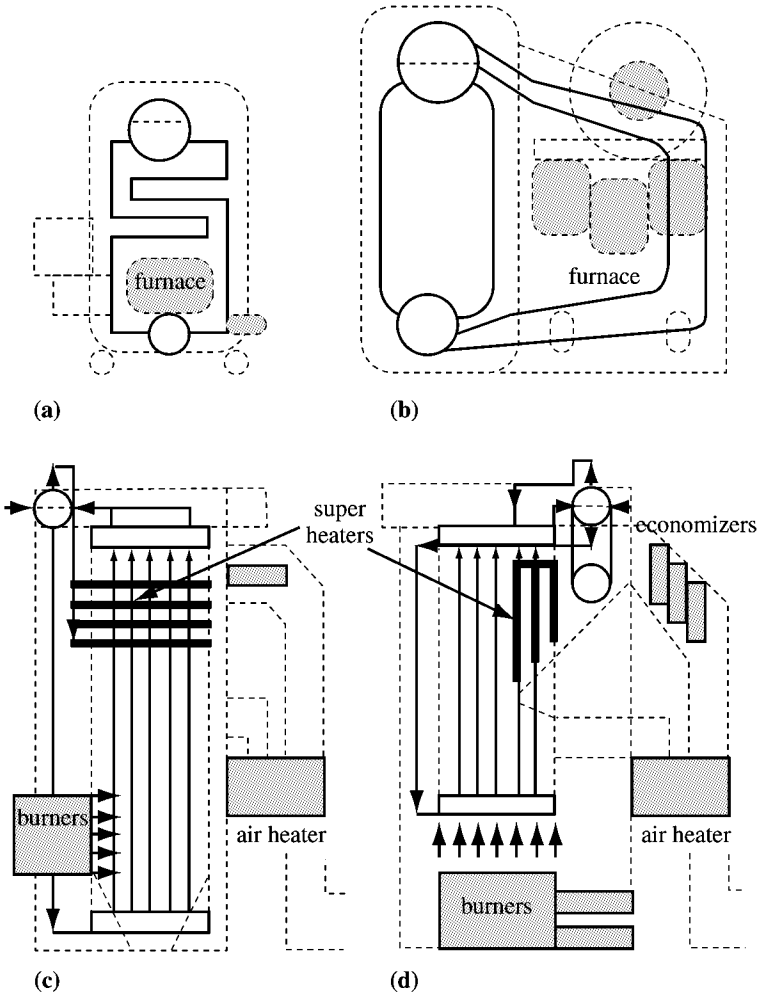


Figure 2.6 (a) Small WT boiler, for HW/steam; (b) large D-type, steam raising, industrial WT boiler; (c) radiant WT boiler for utility power; and (d) pulp mill recovery boiler, burning black liquor.

radiant-heat water-wall membranes. Also, some new WT designs include even smaller boilers, of 1.5 to 9.0 MBtu (36–215 boiler hp) capacity, which incorporate removable, preinsulated side panels for easy tube replacement and annual maintenance. Various WT designs and applications are described in the following sections.

2.3.3.1 Coil Boilers

Coil boilers are available as fully automatic package units, typically ranging in size from 15 to 300 boiler hp (500 lb/hr–10,000 lb/hr). Most designs employ forced circulation and a single, continuous spiral, helical-wound coiled tube that hangs inside the furnace. The coil is subjected to intense heat release from a gas or oil burner.

Coil boilers can come on line quickly, providing full steam pressure within 5 to 10 minutes. This makes them particularly suitable for smaller batch operations and applications that require a rapid but intermittent steam demand. In addition, they can provide a backup in emergency situations.

The primary disadvantage of coil boilers is that any slight fouling or blockage within the coil or accumulation of soot on the furnace side may easily cause rapid overheating and the resultant failure of the coil. As a consequence, high-quality FW and a good internal treatment program are required.

The pre-boiler, FW supply should normally be of demineralized quality, such as may be provided by *ion exchange*, *reverse osmosis* (RO), or similar process. Extremely efficient mechanical deaeration also is required because the path length from the FW tank to the boiler is usually quite short, and thus the contact time is generally inadequate for the sole use of chemical oxygen scavengers (even catalyzed scavengers).

With regard to operational considerations, the recirculation pump pressure gauges (which measure pressure differentials and consequently indicate possible blockage in the coiled tube) require frequent calibration. Regular cleaning and good housekeeping are also required, especially within the furnace area.

2.3.3.2 Industrial WT Boilers

Industrial WT boilers may provide HW or steam generation, Manufacturers normally design for left- or right-hand component arrangements.

2.3.3.2.1 Hot Water Generators Hot water generators can range in size up to 60 MBtu/hr and provide water temperatures as high as 430 °F. They can be installed as single or multiple boiler units to meet HTHW capacity needs. Most HW generators of WT design provide for forced internal BW circulation. (The internal pump is necessary in addition to the water-heating system circulation pumps and the low-water/high-

water level pumps that control the nitrogen-blanketed, HW system expansion tank).

Hot water generator designs normally control the circulating water flow through the generating tubes by means of small orifices. Unfortunately, these orifices sometimes become blocked with rust particles, dirt, or scale. However, some designs now eliminate the orifices (and thus the risk of blockages) and instead employ a jet-induced circulation system that mixes return HTHW with HW generator water in a separate **plenum unit**. This jet-induced design also minimizes the risk of waterside attack from corrosive gases (primarily H_2 and O_2) generated in cause-and-effect fashion as a result of the corrosion that may occur at low flow, resulting in turn from partially blocked orifices.

Some WT designs provide an *automatic safety shutdown cycle* that is actuated in the event of an operational problem. This system can be used to good advantage during boiler commissioning at the preoperational cleaning stage. Thus, if a **preoperational, waterside cleaner** is added to the new boiler and the boiler is fired up with the inlet and outlet valves closed, internal boiler cleaning begins to take place as the pressure of the water–steam mixture builds up. After a time the boiler automatically shuts down well before any possible damage occurs but after the internal surfaces have been washed. This procedure generally provides a perfectly safe method of providing internal cleaning before the initial operational startup.

2.3.3.2.2 Water Tube Steam Generators Steam generators for industrial applications may have internal boiler components such as drums, boiler bank, and membrane wall designed in one of several different arrangements. These arrangements are based on the position of the boiler drum and include the following:

- **D-type WT boiler design:** A top and bottom, two-drum arrangement, with an offset furnace surrounded by a D-shaped membrane
- **A-type design:** A three-drum arrangement with a central furnace
- **O-type:** A two-drum, centrally positioned arrangement

Typically, industrial WT boilers operate at pressures within the 100 to 650 psig range (sometimes up to 900–950 psig) and are rated for steam capacities within the range 40,000 to 200,000 lb/hr (5–21 kg/s) and steam temperatures of up to, say, 900 °F (482 °C). Industrial boiler designs tend to rely on natural, internal steam–water circulation.

They tend to be bottom-supported and can be supplied either as packaged or modular (field-erected) units. Industrial boilers may be designed to burn crushed coal (PF), oil, gas, or a combination of oil and gas with a solid fuel.

They also may utilize by-product fuels, for example:

- **Blast furnace gas** and **coke oven gas** (steel industry)
- **Carbon monoxide**, **refinery gas**, **petroleum coke** (petroleum industry)
- **Bagasse** (sugar mills)
- **Wood** and **bark** (pulp and paper industry)
- **Municipal solid waste** (local authorities)

More modern industrial boiler designs also provide facilities for easy fuel changeover with simultaneous firing, low NO_x burners, high turndown ratios, and low excess air capabilities (down to only 10% excess air).

Designs often include boilers with economizers and pendant superheaters because many of the largest manufacturing operations require additional mechanical or electrical power to process steam and use **combination heating and power services (cogeneration)**.

These large industrial manufacturers (paper mills, steel works, oil refineries, petrochemical facilities, etc.) tend to employ either high capacity (200,000–800,000 lb/hr) packaged D-type boilers, or field-erected, two-drum, single gas-pass **industrial power boilers**, which produce steam at up to 1,800 psig.

All industrial WT boilers require good quality FW, and to ensure a full boiler life span (which may be 60 years or more) the water treatment program and its implementation must be first class.

Typically, for any given pressure, industrial packaged boilers operate at higher heat-flux rates than field-erected boilers, This requires that the package boiler FW quality should be substantially better (i.e., lower overall TDS and lower levels of silica and sodium). Appropriate MU water pretreatment may, for example, necessitate the use of *twin bed* and *mixed bed demineralization ion exchange*, or *RO* and *mixed bed* (in addition to mechanical deaeration and other processes).

A rule for all industrial WT boilers is that they should receive as good a quality of MU water to the FW system as local conditions dictate and the business can economically support. However it is not unusual in some parts of the world to find large field-erected industrial

boilers that do not use as high a quality of MU water as desirable, but instead rely on some lower standard.

The sugar mill or sugar refinery industries of developing industrial countries are common examples of this tendency. Here, operators of large 450 to 650 psig WT boiler plants typically pretreat MU water by softening followed by (but not always) mechanical deaeration. A heavy reliance is placed on simple internal treatments such as phosphate precipitation programs, sometimes without adequate BW sludge control. Under these conditions, without very tight technical control over the water chemistry, the result can be a fouled boiler, perhaps before the end of a sugar campaign.

Where low-cost labor is available, operators can provide intensive manual cleaning during the annual plant shutdown period. However, this is not a model for operational efficiency, and "low-cost" labor is seldom that low when quality and productivity is factored in. In the long run, it usually is far better to aim for a higher operational standard from the beginning.

2.3.3.3 Cogeneration Boilers

Cogeneration WT boilers typically operate from 650 psig to 1,500 psig, providing steam for both electricity generation and industrial process. The basic economic benefit in producing steam for industrial applications and generating electrical power in the same power plant stems from the ability to usefully employ a much larger percentage of the heat supplied by the fuel than when generating electricity alone.

Many cogeneration plants use PF coal, oil, or gas as a fuel, but if blast furnace (BF) gas, sawdust, bagasse, or other low-grade by-product fuels are available, these normally can be used to reduce overall fuel costs. Often a combination of fossil fuel and by-product fuel is employed.

With larger cogeneration plants, the dry HP steam produced from the "cogen" boiler is first fed to a high-speed turbine to generate electrical power. Depending on design, the exhaust steam may be sent back to a reheat system in the boiler convection-pass section for reentry to the turbine at an intermediate pressure (IP) stage. Finally, the exhaust steam is conditioned (adjusted to meet temperature and pressure requirements) and then distributed to the various downstream process users. In this traditional approach to cogeneration, if steam demand exceeds that needed for power generation, an auxiliary boiler is usually is supplied to provide the balance.

If low-cost natural gas is available, a **gas turbine** can be used to generate power. In this case, the waste heat in the exhaust gas is used to produce steam in a **heat recovery boiler** (HR boiler). This approach also is used with some gas turbine plants (as in some high-speed navy vessels). Where an HR boiler is employed, if steam demand exceeds power demand, the boiler is fitted with auxiliary burners.

NOTE: Cogeneration for smaller facilities may be provided in a similar fashion to that described above, with electricity being generated via a diesel engine. The water used for cooling the machine passes through the engine jacket and typically rises to a temperature of 190 to 203 °F (88–95 °C) before providing the feed to a FT HR boiler. Steam generated usually is about 85% of the FW input supply.

The process of using almost once-through cooling water as a FW source for HR is termed ebullient cooling.

Unless adequate BD is provided, these boilers may very rapidly develop severe scale buildup on the external side of the heat-transfer tubes, originating from the total evaporation of the ***ebullient cooling water****.*

2.3.3.4 Utility Power Boilers

Utility operators may choose from several technologies to generate electricity, although the most common approach is via the use of high-temperature, fossil fuel boiler plants. In this case, the boiler (steam generator) itself may be of several different design types.

Designs include the **once-through boiler**, which can operate at *subcritical*, *critical*, or *supercritical pressures* and at all commercial temperatures, and the **radiant boiler**, where heat absorption is largely by radiant energy transfer.

- *Once-through* boilers are **single-phase boilers**. They have no conventional drum and employ forced steam–water circulation. Water is initially pumped through the pressure-part heating surfaces as a **subcooled liquid**. The water absorbs heat, leaving the boiler as steam at the required temperature and pressure. The net effect is akin to operating with a single continuous tube. There is no recirculation of water within the boiler, and heat-flux rates are very high. The boiler furnace section nevertheless employs many conventional *boiler surfaces* such as a water-wall membrane, lower and upper furnace wall headers, roof headers, and tubes. Once-through boilers also employ superheaters and reheater tube bundles. They have completely fluid-cooled furnaces (via the water-wall membrane) and usually are designed for

balanced draft operation. The boiler is regulated in part by matching the water flow to the steam demand. These boilers do not have a water level, do not blow down, and require very high purity FW. Internal treatment is extremely limited.

- *Radiant power boilers* are **two-phase boilers**. Designs typically employ only one drum for the largest installations, whereas smaller power boiler designs generally incorporate two drums. Fossil fuel–fed, radiant power boilers are probably the most common type of equipment employed for large-scale utility power generation.

Power boilers typically produce one kWh of electricity for every 8,500 to 9,500 Btu (8,968–10,023 kJ) gross fuel input, providing a **net thermal efficiency** of ± 34 to 40%. (As a rule, utility power plants are seldom more than 34 to 36% efficient, although some modern designs may go as high as 40%.)

The turbine design may require the utility boiler to provide superheated temperatures within the range 950 to 1,000 °F (510–538 °C) and pressures of 1,800 to 3,500 psig (124–241 bar).

Environmental considerations may require boiler designers to provide units with *low NO_x burners*. Specific designs may also necessitate an enlarged furnace and overfire air or NO_x ports.

Where low-grade coal is burned, **electrostatic precipitators** or **fabric filters** may be required for flue-gas particulate collection and a wet desulfurization system (*gas scrubbers*) to remove *sulfur* from the flue gas.

Water treatment for utility power boilers must be "first class" and generally necessitates extremely sophisticated pre- and post-boiler treatment processes. Internal water chemistry usually rellies on the use of **caustic-free, phosphate treatment** or **all-volatile treatment** (AVT) programs.

Water treatment monitoring and control is often a "knife-edge" operation and must be tailored to the overall operation of the boiler because waterside and gas-side problems usually are interlinked. Consequently (and as with other types of WT boiler), not only should the utility boiler FW be essentially free of dissolved oxygen to prevent waterside pitting corrosion of the economizer and other boiler components, but also the temperature must be high enough to prevent **dewpoint condensation** and subsequent *acid attack* on the gas side of the economizer tubes.

Dewpoints and the potential rate of corrosion vary with various fuel sources, their sulfur content, and the type of burners employed. Different fuel sources create differences in fireside (gas-side) corrosion and fouling behavior, and particular fuels may lead to very specific

types of fireside problems. These problems can reduce heat transfer effectiveness and, on the *waterside* of the tube, promote the localized precipitation and buildup of extremely high concentrations of low levels of dissolved boiler water salts. This buildup in turn creates further cause-and-effect problems. The mechanisms by which this sequence of affairs may occur are various and often interdependent, but the waterside deposition and localized corrosion problems that may result are serious and may shut down a boiler.

Designing and constructing a large utility boiler plant is one of the most complex engineering tasks undertaken in the world today, and designers must consider many factors. In the boiler itself, for example, they must ensure that adequate steam–water circulation takes place throughout the boiler and that areas of low velocity (<1 m/s) and uneven flow distribution do not occur. This factor is especially important where the boiler design involves a **tube bifurcation** (fork in the tube) because the result may be waterside regions of localized **dryout** or **metal wastage**.

2.3.3.5 Marine Boilers

Marine boilers are not merely land boilers adapted for use at sea. They must be specially designed because apart from low head, light weight, room for inspection and maintenance in a confined area, and a wide load range, they are also required to operate in very adverse sea conditions and even during military operations. This means that marine boilers must be extremely rugged and able to absorb vibration and various shock forces.

Top drums are generous in size to accommodate possible heavy listing and high-trip operating conditions. In addition, drums must be located in the fore and aft positions rather than longitudinally to minimize the risk of uncovering tubes as the ship rolls.

Marine boilers currently in operation tend to be oil-fired, packaged, D-type units. However, in many of the latest merchant marine and naval ships constructed, marine boilers have become relegated only to **auxiliary** and **heat-recovery** use because diesel engines and gas turbines have become the primary form of equipment employed for marine propulsion.

Where propulsion is provided by diesel or gas turbine, it is common to use an **auxiliary boiler** in conjunction with a *waste heat/heat recovery boiler* (WH/HR boiler). The steam–HW mixture, produced by passing the exhaust engine gases over the HR boiler tubes, is piped to the auxiliary boiler steam drum and then mixes with auxiliary BW. All steam utilized by the ship is taken from the auxiliary boiler.

Makeup water may be supplied from a *seawater evaporator*, although the use of RO (perhaps followed by *ion exchange demineralization*) is now probably the norm. Where an **evaporator** is used, there is always a small risk of seawater contamination, resulting in high hardness and chlorides. This problem, together with oxygen infiltration to the boiler FW supply, also may occur from possible leaks in the **main condenser**. Careful and regular monitoring is therefore essential because these problems can lead very quickly to serious scaling and corrosion in the boiler.

However, where an evaporator is operating efficiently and there is no problem with the condenser, the resultant water is of suitably high quality. Typically, a two-stage flash evaporator produces MU water containing only 0.25 to 1.0 ppm TDS, with perhaps 0.05 to 0.07 ppm silica (as SiO_2).

Evaporators require the continuous low level (1–3 ppm) application of a suitable antiscalant chemical treatment. Traditionally, polyphosphate has been used (sometimes in conjunction with an antifoam and/or a dispersant agent), but it generally performs poorly because of a lack of thermal stability. Treatments based on **polymaleic acid** (PMA) and other modern organic polymers tend to perform much better.

2.3.3.6 Waste Heat and Other Special Purpose Boilers

Waste heat (WH) boilers are essentially **indirect (nonfired) steam generators** that recover the heat energy present in hot gases of combustion (e.g., from a gas turbine) or from hot process stream gases.

The term *waste heat boiler* is also widely used to cover *heat recovery boilers* (HR boilers), which tend to be **direct-fired steam generators**, albeit employing low-grade by-product fuels such as bagasse, wood bark, corn cobs, peanut shells, blast furnace gas, black liquor, and the like.

NOTE: Solid waste for use as fuel sources in HR boilers generally has a reasonable potential heat content, but typically below 3,000 to 4,000 Btu/lb (as received), whereas the heat content of by-product gases is very low (generally only on the order of 100–1,000 Btu/lb).

Where relatively clean by-product gas is available, WH boilers of both horizontal and vertical FT design are often used. For larger applications WT boilers are preferred, and in fact most WH boilers are of the WT type. However, if the gas is dirty, special boiler designs are required to prevent fireside fouling of the furnace tubes, superheaters, and burners.

There are very many industrial processes for which WH/HR boilers may be required, and during some by-product fuel combustion processes, downstream HR boilers can also recover chemicals for reuse upstream. Some WH and special-purpose boiler applications are briefly discussed in the following sections.

2.3.3.6.1 Steelworks Waste Heat Boilers Steelworks waste heat boilers burn the various by-product gases from coke ovens and by-product works in an integrated steel-making facility. The gases burned are:

- **Coke oven gas**, which has a heat content of only 500 to 600 Btu/cu ft; and
- **Blast furnace gas**, which is a very low-grade gas. It contains 25% carbon monoxide (CO) by volume and free hydrogen and may have a heating value of less than 100 Btu/cu ft. It is heavily dust-laden, and to minimize fouling, the gas is usually cleaned by washing, followed by electrostatic precipitation. Boilers may employ a straight tube design to reduce the potential for fireside fouling.

2.3.3.6.2 Basic Oxygen Furnace Boilers (BOF Boilers) Basic oxygen furnace boilers are commonly employed in the BOF steel-making process. A WH boiler is fitted into the flue gas hood. The WH boiler may be either a steam generator of water-wall membrane construction or a steam-pressurized HTHW boiler. Where a steam generator is employed, the steam is fed to the plant for general use.

2.3.3.6.3 Carbon Monoxide Boilers Carbon monoxide boilers are used to recover waste heat generated from oil refining *fluid catalytic cracking* (FCC) processes. The FCC process produces copious volumes of by-product gas containing 5 to 8% carbon monoxide (CO), which has a heat content of about 150 Btu/lb. A 10,000 barrel (bbl) per day FCC unit produces 60,000 to 150,000 lb/hr of CO.

WH boilers are usually packaged WT types of dual-fire design because a supplementary fuel is also required. The thermal energy is recovered and used to produce medium pressure (600–900 psig) process steam.

2.3.3.6.4 Black Liquor Recovery Boilers Many special boiler designs have been developed around the world for the pulp and paper industry, including *black liquor recovery boilers*.

Black liquor is 13 to 17% strength, rinsed extract from washed and cooked woodchip pulp, produced in the **Kraft pulping process**. This

black liquor is concentrated by passing it through *multiple-effect evaporators* before being introduced into the boiler.

Air is added at different elevations within the boiler to provide various fuel-to-air ratios, depending on combustion requirements. Superheated HP steam is produced and passed to a turbine generator. The resultant LP steam is used for woodchip cooking, furnace air heating, pulp drying, and related processes.

This combustion process results in the reduction of inorganics, leading to a molten **smelt** of *sodium carbonate* (Na_2CO_3) and *sodium sulfide* (Na_2S) on the furnace floor, which is discharged to a tank and dissolved to form **green liquor**.

Various permutations of the black liquor recovery boiler design are used to combust *soda liquors* in the **soda pulping process** and *alkaline earth liquors* and *ammonium liquor* (red liquor) in the **sulfite pulping process**.

2.3.3.6.5 Enhanced Oil Recovery Boilers Enhanced oil recovery boilers provide HP wet steam for enhanced oil recovery. The steam is injected into oil-bearing strata, to heat the oil and reduce its viscosity, thereby increasing the potential for flow.

2.3.3.6.6 Fluidized Bed Combustion Boilers (FBC boilers) Fluidized bed combustion boilers are often conventional boilers but with unconventional, specially designed furnace beds. Fluidized bed combustion boilers are used to burn solid fuels, such as low-grade, high-sulfur crushed coal. The benefit of this process is its ability to provide 95 to 100% combustion (depending on the reactivity of the fuel) combined with reduced emissions of *sulfur dioxide* (SO_2) and *nitrogen oxides* (NO_x).

The process essentially involves passing air through a bottom furnace distributor plate and a fixed bed of sand. As air flow rates increase, the fixed bed becomes more unstable and bubbles of air appear (*minimum fluidized condition*). Above this minimum level, higher air flow rates produce—depending on design—either **bubbling fluidized beds** or **circulating fluidized beds**, and the fuel is introduced onto these beds.

If a *limestone* or *dolomite* **sorbant** is added to the hot sand bed, the *calcium oxide* (CaO) produced reacts and combines with SO_2, thus reducing the emission of the pollutant.

The use of FBC boilers results in lower NO_x emissions compared with conventional boiler designs at the same furnace temperature.

2.3.3.6.7 Sugar Refinery Boilers To burn **bagasse** (sugarcane waste), sugar refinery boilers often have a specially designed furnace area (**Dutch oven furnace**) with a curved radiant arch. Bagasse has a typical heat content of only 3,500 to 4,500 Btu/lb, but because it contains 40 to 50% moisture, the heat content (as measured by weight) may be raised by first producing a drier solid fuel.

2.3.3.6.8 Waste-to-Energy Boilers Waste-to-energy boilers are of various designs and are employed to burn municipal garbage, using either **mass-burning fuel** (unprepared fuel) or **refuse-derived fuel** (RDF). The design of the boiler typically depends on the degree of recycling that takes place and the amount of plastics in the garbage. Newly industrializing countries tend to have garbage with less plastics, more moisture, and a lower heat value. Typically, RDF has a heating value of 3,000 to 6,000 Btu/lb.

2.3.3.6.9 Combined Cycle Boiler Systems These boiler types are used to harness the waste heat from one power source to provide the heat source for a second power source, usually an electricity generator via a steam turbine. They are a form of **cogeneration** boiler plant.

Combined-cycle systems are used in both land and marine applications employing diesel engines or gas turbines (which usually provide the first power source) and by large process industries that produce significant heat-containing, by-product waste streams.

Where, for example, diesel engines or gas turbines are employed to generate electrical power, the cooling water recirculating through the engine jackets is usually at a temperature of > 95 °C. This water passes to a flash tank, where it generates steam in a combined-cycle process. The steam usually is used for industrial processes and commonly produces little condensate return. Consequently, unless the MU water is properly treated, both externally and internally, rapid scaling and deposition problems occur. The flash tank fills with scale and sludge, and steam production falls off dramatically.

2.3.3.6.10 Vyncke Special Purpose Boilers The **Vyncke horizontal FT boiler** is another example of the diversity of design of special-process boilers. It is an industrial process boiler with elements of WT design, but it has a vertical (3–4 meters high) fuel feed box positioned on the front, which necessitates the FT section to be raised significantly off the ground on a strong steel frame. It is employed in wood products processing facilities (plywood, fiberboard, chipboard manufacturing, etc.) and uses waste woodchip as a fuel.

2.3.4 High-Purity Steam Generation

Where small quantities of high-purity steam is required for **electronic chip, pharmaceutical, sterilization, food preparation**, and similar process applications, a small risk of steam contamination may exist. This may be caused directly by the use of amine treatments or indirectly through process contaminants or the transport of iron oxides. Consequently, alternative arrangements for steam generation are made.

Commonly, a multiple-unit LP boiler plant may be supplemented by a small HP steam generator to meet higher purity demands; this is often a vertical FT boiler of perhaps 1,000 to 2,500 lb/hr capacity. However, when special steam requirements are extremely low, very small, stand-alone steam generators may be provided. Some examples are described in the following sections.

2.3.4.1 Kitchen Steam Generators

Kitchen steam generators to provide live steam for steam tables are widely available. They tend to be very small, perhaps only of 150 to 250 lb/hour generating capacity. However, because they typically receive 100% *cold*, city supply as a FW source, and where the boiler vessels are constructed of carbon steel, oxygen pitting and subsequent boiler failure can occur rapidly.

Pressure vessels and appurtenances should be constructed of stainless steel or other corrosion-resistant materials. Ideally, these steam generators should receive hot demineralized FW to minimize chemical treatment requirements. Alternatively, where a main boiler plant is installed, 100% steam condensate provides a good source of FW. In practice, it is very difficult to accurately control the correct amount of chemical feed. Chemicals are typically restricted to potable grade, deposit control agents such as polyacrylates, and other materials listed under the **Code of Federal Regulations**, CFR 21 §173.310, or **National Sanitary Foundation** (NSF International) approval system. These boilers may be electrically heated or gas-fired.

2.3.4.2 Clean-Steam Generators

Where steam is used for sterilization, hospital duty, food and drug manufacturing processes, or steam humidification purposes, there generally is a reluctance (or mandated prohibition) to employ amines as a treatment for steam–condensate line corrosion protection. Clean-steam

generators overcome this problem because they are, in essence, noncontact, nonfired, **steam-to-steam heat exchangers**.

Larger clean-steam generator designs typically employ a pressure vessel (shell) containing a U-shaped tube bundle. The heat source is primary steam supplied to the shell side (which may be amine treated), and secondary "clean" steam is generated within the tubes.

Condensate return is often less than 15% and perhaps nothing is returned. Demineralized FW should be supplied on the clean side. Where FW quality is less than this standard, extremely rapid deposition and fouling take place. Pitting corrosion also is common, even with stainless steel. Where throughputs are high, RO provides an alternative to demineralization, although pretreatment to the RO plant usually is necessary (e.g., carbon filter or softeners). Also, because some TDS remains in the MU and FW, the application of a suitable **deposit control agent** (DCA) is generally required, as is an oxygen scavenger such as **sodium ethorbate**.

Vapor compression, **thermocompression and multiple-effect stills**, and **evaporators** are additional alternatives for the production of high-purity steam and water.

2.4 NUCLEAR REACTOR BOILERS

Nuclear reactor development began during the 1940s, following the demonstration of nuclear fission by Fermi in 1942. Since the 1950s, nuclear boilers have been used increasingly for the generation of electrical power.

Many dozens of industrialized countries now employ nuclear reactors for power generation, and some countries produce more electrical power by nuclear reaction than by fossil fuel combustion (France is an example). The United States, however, has the largest installed capacity of nuclear-powered boiler plants (in the year 2000 there are more than 120 nuclear reactor power plants in the United States). Nuclear power is also widely used for marine duty in both commercial and naval vessels.

The heart of the nuclear reactor boiler plant system is the *reactor core*, in which the **nuclear fission process** takes place. Nuclear fission is the splitting of a nucleus into two or more separate nuclei. Fission is usually by *neutron particle bombardment* and is accompanied by the release of a very large amount of energy, plus additional neutrons, other particles, and radioactive material. The generation of new neutrons during fission makes possible a **chain reaction** process and the subsequent

harnessing of the nuclear reaction for the provision of electrical power generation.

The nuclear fuel required in the reactor varies depending on the technology employed, but includes both *naturally occurring nuclides* such as **Uranium^{232}**, **Uranium^{238}**, and **Thorium^{232}**; and *artificial nuclides*, such as **Thorium^{233}** and **Uranium^{235}**.

The three types of radiation commonly resulting from the decay of specific nuclides are:

- **Alpha particles** (α particles), which are equivalent to the nucleus of a *helium* atom (two *neutrons* and two *protons*)
- **Beta particles** (β particles), which have the same mass and charge as an electron. They are formed from the conversion of a *neutron* into a *proton* and β *particle*
- **Gamma rays** (γ rays), which are high-energy, short wavelength, *electromagnetic radiation particles* that originate from within the nucleus

2.4.1 Nuclear Power Reactors

There are various types of nuclear power reactors, including *boiling water reactors* (BWR) and *pressurized water reactors* (PLWR or LWR), which are both **light-water reactor** (LWR) designs and are cooled and *moderated* by water. There also are **pressurized heavy-water reactor** (PHWR or HWR) designs.

Most earlier units around the world were BWR types, but modern units tend to be PWR types. The designs of reactors have been continuously improved upon since they were first installed in the early 1950s.

- In **BWR reactors**, steam is generated in the reactor and conveyed directly to the turbine. The benefit of relatively low operating pressures must be weighed against the possibility of radioactive carryover into the turbine.
- In **PWR reactors**, the heat generated by fission is transported through a closed-loop **reactor primary circuit** to the steam generator and transferred to the **reactor secondary circuit**, which is the working fluid from which steam is generated. Here, the risk of radioactive carryover is prevented but at the expense of operating the primary water at a much higher pressure to avoid boiling. The exhaust from the steam turbines returns to the boiler via a condenser and FW heater in the conventional way.

Other newer designs include the *advanced, gas-cooled reactor* (AGR), *Canadian deuterium reactor* (CANDUR), *sodium-cooled reactor* (SCR), *sodium-heated reactor* (SHR), and *fast breeder reactor* (FBR). These reactors employ either **natural** or **enriched uranium fuels** that may be modified in some way (e.g., *graphite-moderated fuels*).

Nuclear installations are provided with a *pressure explosion suppression and containment shell* as an accommodation system against any sudden energy release resulting from an uncontrolled *nuclear fission reaction.* The internal air pressure is maintained at a level lower than the external atmosphere.

The nuclear reactor also must be shielded against the emission of radioactive material to the external environment. Suitable radiation controls include both thermal and biological shielding systems. Radiation from alpha particles (α *rays*) and beta particles (β *rays*) has little penetrating power, but gamma rays have deep penetration properties. Neutron radiation is, however, the primary area of risk. Typically, extremely thick concrete walls are used as a neutron absorber, but lead-lined concrete and special concretes are also used.

2.4.2 Nuclear Steam Supply System

Nuclear reactor boiler plants consist essentially of a central reactor core providing controlled energy that is transferred via a pressurized cooling system to one or more steam generators. These in turn provide superheated steam for delivery to a turbine.

A schematic drawing of the nuclear steam supply system is provided in Figure 2.7, and a drawing of a nuclear boiler is shown in Figure 2.8, with the various steam generation zones indicated.

The key components of a PWR nuclear steam supply system are:

1. **Reactor vessel:** Reactors produce intense heat, and those employed in large nuclear power boiler installations (typically 800–1,000 MWh) may have 50,000 to 60,000 sq ft of heat transfer surface area with a heat flux of from 150,000 to 500,000 Btu/ft^2/hr.
2. **Reactor coolant primary circulation system:** Depending on design, this closed-loop cooling system may recirculate high-purity treated water or other fluid at 300,000 to 450,000 US gpm (1,136–1,704 m^3/m), and at velocities of 15 to 16 ft/s 4.5 to 4.9 m/s.

   PWHR primary circuit pressures are typically 1,280 to 1,455 psig (8.8–10.0 MN/m^2), at temperatures of 550 to 600 °F (288–316 °C).

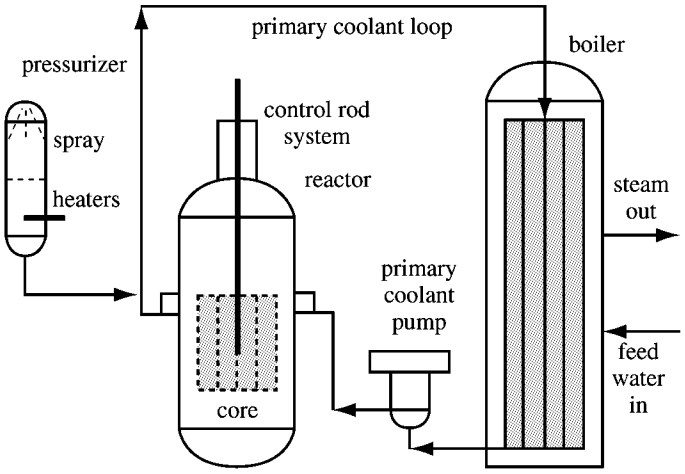


Figure 2.7 Nuclear steam supply system.

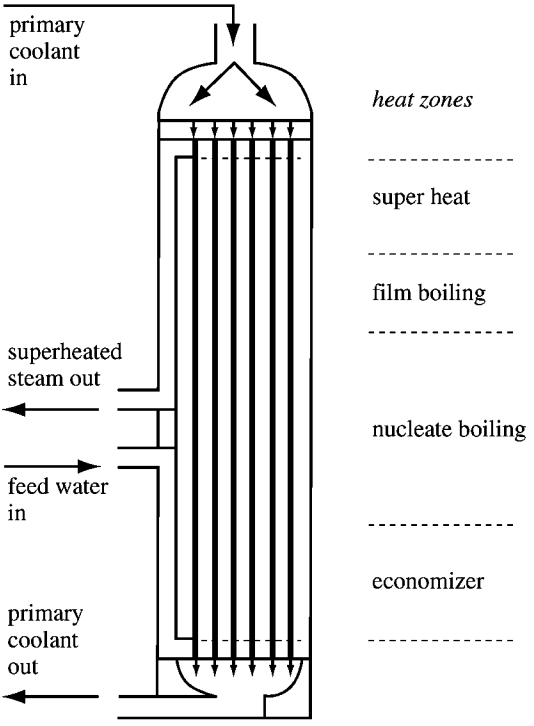


Figure 2.8 Nuclear reactor, straight tube, steam generating boiler.

PLWR primary circuit pressures are typically 1,425 psig for older systems to 2,500 psig or more for newer systems (9.8–17.1 MN/m^2), at temperatures of 480 to 500 °F (251–260 °C) up to 550 to 600 °F (288–316 °C).

3. **Pressurizer:** The pressurizer maintains and controls both the temperature and the pressure in the primary coolant system. It contains a "cold" water spray and electric heater bank as a means of providing the necessary control.
4. **Steam generator(s):** These act as **heat sinks**, and the secondary circuits may produce in excess of 5 Mlb/hr (630 kg/s) of steam at 900 psig (62 bar, $6.2MN/m^2$) and 600 °F (316 °C).
5. **Containment system:** This provides for suitable containment against explosion, radioactive leakage, and other hazards.
6. **Integrated control system:** This includes various safety, monitoring, and control systems, including a reactor protection system.

2.4.3 Principles of Nuclear Reactor Boiler Plant Operation

The energy produced in a nuclear reactor vessel is the result of a *nuclear fission* (atom splitting) process that occurs when sufficient nuclear material is brought together (**critical mass**). Under these circumstances, a chain reaction occurs and an external supply of neutrons is not required. A **nuclear fuel control rod system** raises or lowers the nuclear fuel (which is contained within fuel rods) inside the reactor vessel.

To slow down and control the rate of reaction, a **moderator** is also required. Typically, the moderator is **boric acid**, **graphite**, or **heavy water** (D_2O) and is present in the high-purity water, which also serves as a primary coolant for the fuel and the reactor vessel. The tremendous heat generated by nuclear fission is transferred to this closed-loop coolant, which is contained within a **reactor primary-coolant circulation system**. The high-purity water coolant also contains a suitable pH buffer such as **lithium hydroxide**, which has the additional effect of limiting the corrosion of fuel-cladding and other components.

A **pressurizer** operating within the range of approximately 2,450 to 2,750 psig maintains pressure within the closed-loop circuit. The pressurizer contains the "cold" spray water system, which is typically supplied at around 550 °F (288 °C), and the electric heater-bank system. These systems maintain and control primary-coolant water pressure and temperature. The high-temperature water produced in the primary

cooling system is then circulated to either one or two **steam generators**, where it acts as a heat source for steam generation.

There are different designs of steam generator (see next sections), but the generator is in essence a counterflow, vertical *shell and tube heat exchanger*. The high-temperature water is distributed through the steam generator/heat exchanger via two or more very large, **primary-coolant pumps**.

2.4.3.1 Straight Tube NP Steam Generator

In this design, the (high-temperature) *reactor primary circuit cooling water* flows down from the top of the generator, inside the tubes of a straight-tube bundle. The once-through, *secondary circuit* FW enters from below the middle of the steam generator, where it is heated to saturation temperature by aspirated steam. It then flows down an *entry downcomer* to the bottom of the unit. From here it flows inward, through an *orifice plate* and *baffle* and then up the generator, on the shell side of the tube bundle and within an annulus. On its passage up the steam generator, the FW is converted into superheated steam. The steam then flows outward and down an *exit downcomer*. Finally, the superheated steam leaves the steam generator and is distributed directly to the turbine.

2.4.3.2 Vertical Recirculating, Inverted U-Tube NP Steam Generator

In this design, the *secondary circuit* FW is again on the shell side, but recirculation takes place within the steam generator, resulting in the formation of a steam–water mixture that covers the top of the inverted U-tube bundle. Saturated (but not superheated) steam passes through high-efficiency moisture separators and from here is again distributed to the turbine.

3

BOILER PLANT SUBSYSTEMS, APPURTENANCES, AND AUXILIARIES

Modern HW-generating and steam-raising facilities comprise a number of often complex, interdependent **boiler plant subsystems**, **appurtenances**, and **auxiliaries**, with large process, utility, and cogeneration boiler plants being especially complex. This chapter provides notes on many of the various boiler plant subsystems and types of equipment employed as an introduction to considering the waterside problems that may be encountered therein.

Hot water generators are the simplest systems overall, although many larger institutional and commercial **hydronic heating plants** contain fairly complex distribution systems that may include *high* and *low flow rate subsystems* and *primary* and *secondary piping schemes* in either *series* or *parallel* configurations.

Compared to HW generators, **steam-raising plants** contain additional safety devices and become increasingly more complex as they become larger. Irrespective of size, all steam-raising plant facilities contain interdependent subsystems that are essentially the same in nature and purpose.

Larger steam-raising boiler plants may be physically divorced from factory areas, and the very largest tend to contain systems and equipment housed in a number of separate facility areas or buildings. As a limited example, these facilities may include:

- Water pretreatment plant
- Waste water treatment plant

- Fuel yard
- Fuel preparation area
- Boiler house
- Turbine hall
- Control room
- Condenser cooling system
- Flue-gas scrubber plant
- Bag house
- Chemicals and spare parts storehouse
- Substation

Although the complexity of operating an average industrial boiler plant (with perhaps only two or three FT boilers) cannot be compared to that of a large utility power generating station, the potential for water-side problems, while different, may be just as difficult to control. As an example, consider some differences between a utility and a factory.

Power generators have large diameter but relatively short-run systems, they generate steam at fairly constant rates, and they distribute the same at a limited range of pressures with the primary focus being on efficient power generation. The bulk of the steam is used to power turbines, with the balance being employed in preheaters and the like. The steam is condensed, it returns to the beginning of the system, and the cycle continues.

Most factory boiler plants, on the other hand, while having much smaller diameter systems (because steam volume output is generally much less) usually must provide steam at several different (and sometimes fluctuating) pressure ranges, matching steam output with varying demands and unrelenting production schedules. They typically need to account for many diverse types of manufacturing processes within the same industrial facility and usually cannot have a narrow focus for steam-raising operations. This diversity of applications, pressure ratings, and production demands creates a wider range of steam usage control problems when compared with the power generator.

Larger manufacturing plants may need to distribute steam and collect condensate through an extremely long and complicated network of pipes, manifolds, and valves, often many miles in length and involving remote building distribution and collection requirements. And when factories add new manufacturing areas or processes, the steam distribution and condensate recovery systems must increase accordingly.

Within these tortuous systems there exists considerable opportunity for process contamination, corrosion, and equipment malfunction to occur, with cause-and-effect problems creating further impact downstream and placing additional demands on monitoring and control efforts.

Another difference between utilities and factories is that most industrial facilities tend to operate boiler plants with a lower quality (and often variable) FW compared to power generators. Although boiler **heat flux** is usually lower, this practice nevertheless adds an additional water chemistry control burden, especially because most factories do not employ chemists with specific water chemistry duties.

Additionally, because most factories do not operate steady-state processes, the efforts to match steam output to variable production department steam demands may further tax the boiler plant's generation capacity and manpower resources.

NOTE: As a consequence of the different kinds of operational and management problems associated with raising steam in industrial boiler plants, it often requires a different mindset than that needed for a base-load utility power house, where personnel strive to maintain steady-state (but knife-edge) operating conditions. The differences between industrial plants and power generators is also reflected in the waterside chemistries and monitoring and control objectives of their respective boiler plant systems.

3.1 BOILER PLANT SUBSYSTEMS

3.1.1 Water Pretreatment Plant System

Hot water generators and LP steam-raising plants of below 15 psig are designed to operate with minimal blowdown and to suffer negligible circulatory losses. As a result, clean, sediment-free water of almost any characteristic nature (e.g., *soft* and *corrosive* or *hard and scale-forming*) is likely to be suitable as a source of boiler water makeup.

NOTE: Although the MU water demands of HW-generating plants are typically quite limited, this does not mean that they are totally free from waterside problems and therefore do not require internal chemical treatment programs—they most certainly do face waterside challenges. Dispersion of sludge is important, as is oxygen pitting corrosion control (especially if air enters from leaking pipes or faulty seals, which is common, or if boiler operation is in a daily on–off mode).

However, the source of MU water for higher pressure steam-raising plants is important because it is generally the case that no matter the origin of the water, it will *not* be entirely suitable for the purpose and some form of **water conditioning** will be required. This conditioning requirement necessitates the provision of a (**pre-boiler section**) **water pretreatment plant system** (*external treatment/ external conditioning*) to render the water fit for purpose.

Most usually the pretreatment plant is a capital item fixed asset facility, but the trend is increasingly noticeable around the world today for the supply of properly conditioned MU water to be **outsourced** from a contractor, who either leases a mobile plant to the facility or generates a profit from the direct sale of water to the boiler plant.

The requirements for pretreatment vary considerably from plant to plant, and there is always more than one way to provide the appropriate quality needed. Pretreatment may combine several process steps including:

- Sand, carbon, or other media filtration
- Lime or ion exchange softening
- Dealkalization or demineralization
- Membrane treatments
- Evaporation/distillation
- Magnetic or other nonchemical treatments and devices

3.1.2 Feedwater Supply System

When considering HW generators (as the system water is merely recirculated), the term **feedwater** (FW) is synonymous with **makeup** (MU) **water**. For steam-raising plants, FW is a variable mixture of **condensate return** (CR) and MU water.

The FW supply system is part of the **pre-boiler section**, as is the pretreatment plant. It includes all necessary distribution pipes and valves, the boiler *FW regulator*, *FW pumps*, *FW tanks*, and various forms of *FW heaters*.

In considering smaller steam-generating plants, a low-level (returning) condensate receiver also may double as a FW tank by providing the entry point for MU water.

Similarly, some boiler plant designs may provide only a high-level FW tank (i.e., positioned higher than the boiler) and have returning condensate discharge directly into this tank.

Many steam-generating plants have more than one type of **direct** or **indirect FW heater** to increase the FW temperature, which reduces the potential for boiler thermal shock and increases boiler operational efficiency.

Direct FW heaters include:

- **Electrical resistance heaters**
- **Steam sparge pipe heaters**
- **Open FW heaters** (including **deaerating heaters** or **deaerators**)

Indirect FW heaters include:

- **Economizers**, which are tube bundles located in the exit-gas system
- **Closed FW heaters**, which are specialist shell and tube heat exchangers for utility power application
- **Low pressure (LP) heaters**, typically employed for boiler plant operating at under 900 psig

3.1.3 Boiler Steam Generation System

The boiler steam generation system primarily covers the boiler itself, the **boiler surfaces** (the primary heat-transfer and steam-generating surfaces within the boiler proper), and all necessary **appurtenances**.

3.1.4 Steam Delivery System

The steam delivery system forms a major part of the **post-boiler section** and includes **auxiliaries** such as *superheaters*, *attemperators* (*desuperheaters*), and *reheaters*, plus components such as the various *steam headers*, *steam valves*, *distribution pipework*, *pressure reducing stations*, and the like.

3.1.5 Balance of Plant Equipment Systems

The various *balance of plant equipment systems* (BOP) consist of a wide range of post-boiler section equipment and associated pipework, including *turbines*, *condensers*, *condenser cooling systems*, and related components.

Feedwater heaters also may be considered as BOP equipment (with the exception of *economizers*), especially in utility power plants. *Blowdown receivers* and *flash steam and heat recovery* (FSHR) also may be considered BOP equipment.

3.1.6 Condensate Return System

The condensate return system is a post-boiler section system that includes all *steam traps*, *condensate lines*, *associated manifolds* and *valves*, *condensate receiving tanks*, *save-all tanks*, *condensate pumps*, and other auxiliaries for condensate recovery.

In very large boiler plants, the CR system may include a *condensate polishing plant* (the physical location of this plant may be pre- or post-boiler).

3.1.7 Fuel Management System

The fuel management system includes the various types of *fuel preparation* and *fuel delivery equipment*, *burners*, *ignitors*, *stokers*, *soot blowers*, and *ash handling equipment*.

3.1.8 Air and Flue Gas Management System

The air and flue gas management system includes the various *baffles*, *dampers*, *fans*, *dust collectors*, *scrubbers*, and other *FGD* and *emission control equipment*, and the boiler *flues* and *stack* (chimney).

3.1.9 Waste Water Treatment System

For most smaller operators, the waste water discharge from pretreatment equipment, blowdown receivers, and FSHR equipment typically discharges into a city sewer. Most larger factories, process plants, and power stations, on the other hand, incorporate some form of *waste water treatment facility* to balance the pH level, remove oils and precipitable solids, or otherwise reduce the contamination load before the discharge of water from the site.

3.2 BOILER APPURTENANCES

In almost all countries today, safety codes and regulations exist for the construction, operation, and inspection of all boilers and associated pressure vessels and boiler systems. Both HW and steam-raising plants are provided with several vital boiler **appurtenances** (*appliances* or *fittings*) and various subsystems containing **auxiliaries** (*accessories*) that must be maintained, monitored, and controlled. However, for small HW and LP steam boiler plants the inspection process may be rather cursory with regard to the pressure vessel internals and tends to concentrate primarily on ensuring the proper operation of the various appurtenances that provide for boiler safety.

Appurtenances are primarily the fittings that enable boilers to operate safely. They control the FW supply, boiler pressure, BW level, and steam supply. Appurtenances include:

- **Pressure gauges**, together with any associated test connections
- **Fusible plugs** (where fitted)
- **Safety relief valve**
- **Bottom (main) blowdown valve**
- **Water column gauge glass and gauge cocks** (try cocks)
- **Feedline stop valve and check valve**
- **Feedwater regulator**
- **Boiler vents** (air cocks)
- **Steam line stop valve**
- **Soot blowers**

NOTE: Soot blowers are typically employed only on WT boilers and may be regarded as appurtenances because boiler safety and reliability is directly related to the cleanliness of the heat transfer surfaces. Boiler performance and efficiency also depend on the same heat-transfer cleanliness factors.

The *pressure gauge* and associated *shut-off valve*, the *boiler vent cock valve*, *main steam stop valve*, and *safety valve* can be observed rising above the crown sheet of a FT boiler (the highest point of the boiler), normally in a line running the length of the boiler.

Water tube boilers have a *pressure gauge*, *vent cock*, and *drum safety valve* on the top of the steam drum. Where superheaters are fitted, the steam takeoff line leads to the superheater, which is followed by a *superheater safety valve*, *automatic nonreturn valve*, and *stop valve* with a *pressure-equalizing line and valve*.

3.2.1 Blowdown (Blow Off) Valves

The process of heating water usually produces **sludge** and **sediments** (primarily noncrystalline precipitated salts) in the boiler's waterside drums and tubes. (Sludge production may be deliberately encouraged in certain forms of internal water treatment programs.)

The sludging, sedimentation, and scaling processes may greatly accelerate where steam generation takes place because the continuous supply of MU water (as a replacement for steam and water losses) to

the FW system gradually increases the concentration of BW TDS to the point where solubility limits are exceeded (**saturation point**).

Thus, to control the buildup of sludge and scale (which may include the prevention of these foulants and deposits in the first place), it periodically becomes necessary to **deconcentrate** the BW by physically removing some of it from the boiler (*blowing down* or *blowing off*). This is achieved via a **blowdown valve** (BD valve) usually located at the bottom rear of the boiler vessel or WT mud drum. The BD water lost from the boiler is replaced by less concentrated FW.

Apart from **bottom blowdown valves** (*main BD valve*), other types of valves are often employed. Blowdown valves also can be used to control high water levels, drain the boiler for cleaning or inspection purposes, and maintain chemical concentrations and water chemistry below maximum permitted levels.

On a **FT boiler**, the main blowdown valve is always located at the bottom of the shell towards the rear of the boiler. On a **WT boiler**, blowdown valves may be located in the side of the *top (steam) drum*, the *bottom (mud) drum*, and the *lower water-wall headers* (sides, front, and rear).

Top drum blowdown is usually via a surface (skimmer) blowdown arrangement.

NOTE: Water tube boiler water-wall headers should not be blown down while the boiler is under load because it disturbs the natural circulation and may result in an overheated and bulging or ruptured tube. Usually header blowdown valves are locked closed and are only blown down when the boiler goes offline.

Marine boilers are usually given a high volume BD only once every 3 to 7 days, such as when arriving at or leaving port. Periodic BD may be routed to the **bilges** or overboard, and this supplements a small continuous BD to either the bilges or the evaporator shell.

Coil boilers often use automatic, TDS-controlled solenoid valves to control BD. They are installed following the *steam separator* and *steam trap*.

Vertical FT boilers may employ an automatic TDS-controlled BD system, utilizing an extended length electrode (to reach the BW) inserted through the top of the boiler.

Whatever the design of boiler, good control over a narrow range of BW TDS is required, The use of some form of **continuous blowdown** arrangement as the primary form of blowing down BW is preferred in almost all steam generation facilities.

There are various types of BD valves and valve arrangements, as well as different BD procedures, depending on the boiler design and operational preference. **Gauge glasses** are regularly blown down, which, although providing part of the total BD from a boiler (but only a marginal contribution), *cannot* be considered a substitute for periodic boiler bottom blowdown. It is also possible to recover some of the flash steam and heat available in the BD water (see **heat recovery systems**), although even where FSHR is used, some blowdown water is physically lost. The BD water is passed to a BD pit or a receiver before discharge to a waste water handling facility.

NOTE: Blowdown water from utility or cogeneration boilers is sometimes discharged to the condenser cooling system and forms part of the total MU. This is not a practice to be recommended because, although the BD water TDS level is low (typically below 250 ppm), the temperature is significantly higher than that of the cooling water and it usually contains phosphate, which may precipitate, act as a nutrient, or otherwise interfere with the cooling water treatment program.

The most common blowdown arrangements are described in the next four sections.

3.2.1.1 Main (Primary or Bottom) BD Arrangement

The minimum requirement is for boilers to be fitted with one, slow-opening bottom BD valve. However, most boilers have either two **slow-opening angle valves** (valves having a sliding cylinder with ports) or a **side-action lever**, **rapid-opening valve** (which is connected closest to the boiler shell) followed by a slow-opening angle valve.

Where a rapid-opening valve is fitted, it is opened first and closed last, with the rate of bottom BD water controlled by the slow-opening valve.

NOTE: The minimum regulatory BD requirement for steam-raising land boilers (stationary or trailer-mounted) is usually for a once-per-day opening of the bottom valve. Hot water heating boilers and LP steam boilers employed for hydronic system duty are almost never blown down daily, but should be blown down regularly, albeit usually for the minimum period necessary to ensure the continued safe operation of the bottom BD valve.

Bottom BD valves are designed for manual removal of sludge only. They are not designed to be automated and are of large diameter to ensure the forced removal of accumulated sludge.

Blowdown is generally provided only for a few seconds, or sufficient to drop the water level in the gauge glass by perhaps 1/2 inch (1.25 cm). Where 10 seconds of BD is required, it is much preferable to stagger this over a period of time rather than all at once.

3.2.1.2 Surface (Skimmer) BD Arrangement

Using a skimmer, the BD water is taken from close to the top surface of the BW, either from the side of the FT boiler shell or WT boiler top drum or from a top-mounted sparge pipe extending down 3 to 6 inches below the waterline (but above the top set of tubes in a FT boiler). Blowdown is provided on either a **continuous blowdown** or an **intermittent blowdown** basis.

- *Continuous, surface blowdown arrangements* employ a multistage nozzle valve that permits the BW to expand and flash gradually and safely across each successive orifice and chamber with almost no noise. This effect reduces the flow velocity and virtually eliminates the risk of **wire drawing**. The BD valve is provided with a regulating lever and calibrated dial (or an electric actuator) for either manual or automatic BD rate adjustment. Continuous blowdown arrangements are entirely suitable for incorporation into FSHR systems. They are commonly employed for WT boilers.
- *Intermittent, surface BD arrangements* are controlled automatically and are not very suitable for smaller boilers with high percentages of returning condensate (i.e., those boilers with only a very low blowdown volume requirement).

The use of intermittent BD arrangements employing timers and electrical conductivity electrodes has been standard technology for at least 25 years. Nevertheless, problems still occur that may be attributable to the use of electrodes unsuitable for the temperatures involved or inadequate electrode cleaning and maintenance.

There are several options for the control of the intermittent BD valve:

1. **Timer-controlled intermittent BD.** This is simple, and the arrangement works satisfactorily provided that the boiler is on a fairly constant load.
2. **Timer-controlled with BW electrical conductivity measurement override.** The BD valve only opens when the electrical conductivi-

ty is above a set point. The electrode may be placed in the boiler (not particularly recommended) or in a bypass line. This method is suitable for smaller boilers (below 5,000–10,000 lb/hr).

3. **Continuous conductivity measurement controlled with the electrode placed in the boiler.** This method is not recommended because of potential safety and liability issues. In addition, there are difficulties with cleaning and maintaining the electrode, and the intense heat to which the electrode is constantly subjected may cause failure. FT boiler installations generally provide for the electrode to be placed above the first set of tubes but 4 to 6 inches below the waterline.
4. **Continuous conductivity measurement controlled with the electrode placed in a bypass sampling line.** This arrangement requires the permanent discharge of approximately 0.5 U.S. gpm of sample water to a drain (which is, in effect, continuous BD). This system may be wasteful on small boilers but is suitable for larger boilers (15,000–20,000 lb/hr) and for boilers with high FW TDS, which consequently require a relatively high BD rate (i.e., >15%). This arrangement is improved if the water sample passes through a cooling coil because the electrode is subjected to less thermal stress.
5. **Intermittent conductivity measurement controlled, with the electrode placed in the BD line before the BD valve.** In this arrangement the controller program opens the BD valve for a timed period (≅1 minute), sufficient for "fresh" BW to flow past the electrode and an accurate electrical conductivity measurement to be taken. The BD valve remains open until the conductivity falls below a set point. Again, this arrangement is improved with the use of a cooling coil. It is the most widely employed intermittent BD arrangement for FT boilers.

NOTE: All intermittent BD arrangements require a properly adjusted throttling gate valve on the BD line (and sample coolers) for good results. It may be appropriate to lock the valve or remove the wheel to ensure that the valve position is not inadvertently further opened or closed.

3.2.1.3 Rapid Action Intermittent BD Arrangement

Lever-operated, rapid action, intermittent BD valves are commonly used to provide periodic, full-valve opening, BW BD. The valve is

installed on the bottom BD line. Valves are supplied in various arrangements, including horizontally or vertically installed, spring-loaded and push-down lever operated, rapid-open/ rapid-close, and cone-and-seat valve types.

The lever-operated valve may be opened intermittently, either manually or automatically, for 2 seconds via a timer-controlled diaphragm actuator.

Automatic programmable systems may be designed to incorporate rapid action valves to provide flash steam to condensate tanks and/or HR for various industrial applications.

3.2.1.4 Calculating Blowdown

The required **boiler BD rate** may be expressed in several ways:

1. **The percentage of BW evaporated that is required to be blown down:**
   % BW BD = FW TDS × 100/ (BW TDS − FW TDS)
2. **The percentage of FW supplied that will be lost as BD:**
   % FW BD = FW TDS × 100/ BW TDS
3. **That part of the steam generated lost as BD, to maintain BW TDS:**
   BD = Steam generation lb/hr (or kg/hr)/(COC − 1)
   Where:
   TDS is expressed in ppm or mg/l
   COC = cycles of concentration of BW TDS relative to FW TDS

   Example:
   Boiler steam generation rate is 10,000 lb/hr
   FW TDS is 200 ppm
   BW TDS is maintained at 3000 ppm

   COC = 3000/200 = 15x

   Using expression 1. % BW blowdown = 200 × 100/2800 = 7.14%
   Using expression 2. % FW blowdown = 200 × 100/3000 = 6.67%
   Using expression 3. BD = 10,000/(15 − 1) = 714 lb/hr

NOTE:

- *If the rate of blowdown is too high, heat (fuel) and treated water are wasted and the boiler water chemistry may be less than desirable for optimum waterside control.*
- *If the rate is too low, permitted or agreed water chemistry limits will be exceeded and waterside problems are likely to develop, leading to poor heat transfer and a higher fuel consumption level.*

3.2.2 Boiler Safety and Stop Valves

Apart from the BD valves and drain valves, a boiler is fitted with a **safety valve** (at least one), **stop valves**, and (usually) **automatic nonreturn valves**. As a minimum, these valves must be dismantled, inspected, and overhauled annually.

3.2.2.1 Safety Valves (SV)

Safety valves are spring-loaded valves of various designs, typically with a **steam huddling chamber** feature that increases the total force of the steam, thereby causing the valve to pop up (**pop-type SV**) rather than rise slowly in response to increased pressure. Boilers operating at higher pressures (say, 600–3,000 psig) tend to have super-jet SVs.

Safety valves are matched to a boiler's particular **maximum allowable working pressure** (MAWP), and a boiler failure may result if this pressure is greatly exceeded. Typically, boilers having more than 500 ft^2 of surface area or exceeding more than 500 kW input are required to have two safety valves.

Safety valves are normally manually tested at periods between 1 and 6 months and pressure-tested every 12 months. Boiler operating pressures are typically 5 to 10% less than safety valve set pressures to avoid valve weeping.

3.2.2.2 Stop Valves

Stop valves are fitted to each main or auxiliary discharge steam outlet, close to the boiler (but not in front of a safety valve or superheater connection). They are employed to place a boiler in or out of service. Gate-type stop valves of **outside stem and yoke valve** (OS&Y) design often are employed because they indicate whether they are open or shut by the (out/in) spindle position.

3.2.2.3 Automatic Nonreturn Valves (NRVs)

Automatic NRVs act like *check valves* and cut out the boiler if its pressure falls below the main steam-header pressure. The installation of an automatic NRV may require the provision of a *bypass pressure equalizing line* and a *pressure equalizing valve.*

3.2.3 Boiler Vents

Boiler vents are valves located at the top of a boiler. They are opened to permit air to be bled from a boiler when filling it with water and when initially raising steam. They are also opened during a boiler drain-down to prevent formation of an internal vacuum, which could cause the shell to collapse or other damage to occur. During typical HP boiler warm-up, the boiler vents are kept open until 25 psig steam pressure is registered.

3.2.4 Feedwater Regulators

Feedwater regulators are fitted to boilers as a means of controlling the rate of addition of FW. This is necessary to maintain a consistent water level that, in turn, reduces the risks of thermal shock to the boiler, reduces the potential for BW carryover with the steam, and improves boiler efficiency.

By definition, the FW regulator provides BW level control through the use of various sensing elements at the **normal operating water level** (NOWL). Three types of FW regulator are described in the next sections.

3.2.4.1 Thermo-Expansion FW Regulator

A thermo-expansion FW regulator is employed on larger WT boilers when FW pumps run continuously. The thermo-expansion regulator uses a thermostat located at the steam–water interface NOWL. The device expands when the water level drops because it is surrounded by (higher temperature) steam. This expansion moves a mechanical linkage, which opens the valve.

3.2.4.2 Thermohydraulic FW Regulator

A thermohydraulic FW regulator has a double-tube control element located at the steam–water interface NOWL. The outer tube contains condensate and connects to a bellows. When the water level drops, the

inner tube develops a large steam space and the heat from the steam is transferred to the condensate. This causes the bellows to expand, thus opening the FW regulator valve.

This type of regulator also is widely used on WT boilers. It requires periodically blowdown to keep the tubes free of sediment.

3.2.4.3 Float FW Regulator

A float-type FM regulator type is primarily employed on packaged FT boilers. It has a float chamber located at the NOWL and is connected to the steam–water areas of the boiler. When the water level falls, the float drops and mechanically moves a mercury switch (or electronic switch), which in turn actuates the FW regulator valve.

This type of regulator requires blowdown at the completion of every shift to maintain clean float operating conditions. It usually incorporates a *low-water-level fuel cutoff device.*

3.2.5 Pressure Gauges

Pressure gauges contain a partly coiled, hollow tube (**Bourdon tube**) that further coils or uncoils in response to the pressure of the steam or water contained within the tube. Pressure gauges reading below the steam and water line must be corrected by 0.433 psig per vertical foot to take account of **hydrostatic pressure**:

- **Absolute pressure** (psia) = boiler **gauge pressure** (psig) + **atmospheric pressure** (psiatm)
- **Atmospheric pressure** = 14.696 lbf/in^2 (1.0 std atmosphere, 0.99 bar) at sea level and 62 °F (16.7 °C).

3.2.6 Soot Blowers

The furnace areas of WT boilers require the periodic deployment of retractable soot blowers to remove the buildup of soot and combustion products from water-wall tubes to maintain heat transfer and furnace cooling efficiency, as well as to minimize the interference of flue gas pathways.

Soot blowers also are used to clean particular boiler tube bundles, such as *superheaters* and *economizers*. Steam or compressed air normally is used, and operating practice may require the use of manual boiler control and increased furnace draft or boiler loading during soot-blowing periods to avoid the risks of loss of furnace flame (**flameout**) or small furnace explosions (**furnace puff**).

High-pressure steam from steam soot blowers can easily cut through tubes, so correct alignment of soot blowing equipment is critical.

3.2.7 Water Columns

Water columns serve as fittings to house the water level **gauge glass**, **gauge cocks**, **gauge glass blowdown lines**, and **high/low water alarms**. However, a primary purpose also is to counter BW turbulence, which may occur in the gauge glass, so that a more accurate BW level may be determined.

The gauge cocks provide a backup means to determine water levels. In general, three gauge cocks (*globe valve* type) are vertically installed at spaced intervals, close to the visible gauge glass.

The middle gauge cock is located at the boiler NOWL. Boilers operating at more than 250 psig have either two gauges or one gauge and an electric or electronic level indicator. Low water alarms are either *float* types or *weight* types.

3.3 BOILER AUXILIARIES

Auxiliaries are additional boiler fittings that provide controls for ease of operation. They may include additional valves (such as *check valves* on feed lines, *nonreturn valves* on steam distribution lines, and the various boiler system *drain valves*), gauges, connections, and devices to regulate FW, air, and fuel and to provide for the efficient production, pressure, temperature, quality, and flow of HTHW or steam.

3.3.1 Burners

The combustion of oil, gas, PF, wood dust, and many other types of fuels in a furnace requires specially designed **burners** together with an **ignitor**. Burners use solid state, automatic management systems to proportion and mix fuel, **primary air**, and **secondary air**; prepare the mixture for combustion; and monitor the firing sequence.

*NOTE: **Primary air** is the air provided with the fuel to provide intimate mixing and thus support combustion.*

***Secondary air** is introduced around the burner area and supplies the oxygen required to provide complete combustion.*

Boilers using a **cyclone furnace** design may employ oil, coal, or gas burners. They typically use *high heat-release burners* that burn crushed

coal and are operated in a similar manner to PF coal furnaces. It is necessary to maintain a layer of slag on the inside of the cyclone furnace to trap all larger coal particles (*flypaper effect*) and ensure complete combustion, as well as to reduce problems of furnace area erosion and corrosion.

3.3.1.1 Vaporizing Oil Burners

Vaporizing oil burners prepare the air and fuel mixture by vaporizing the fuel by heating within the burner (**gasification**).

3.3.1.2 Atomizing Oil Burners

Atomizing oil burners prepare the air and fuel mixture by atomizing the fuel so that it vaporizes in the combustion area. Atomization can take place by:

1. Using pressurized steam or air (*air–steam atomizing burner*)
2. Pressurizing the oil and forcing it through a nozzle (*mechanical atomizing burner*)
3. Tearing the drop into droplets by centrifugal force (*rotary cup burner*)

Heavy fuel oils must be heated to provide a suitably low viscosity for delivery to the burner and for atomization. The viscosity of oils at the burner typically should be between 100 and 150 **Saybolt Seconds Universal** (SSU).

3.3.1.3 Pulverized Fuel Coal Burners

Pulverized fuel coal burners (typically *turbulent air burners*, *vertical burners*, or *nozzle burners*) receive hot primary air containing the PF and introduce the mixture to secondary air in such a way that it provides a stable flame. The flow rates of both primary and secondary air are controlled by dampers. An *ignitor* is required to initiate combustion, and the flame front is maintained close to the burner, with the heat of combustion used to ignite incoming PF. A flame safety device electronically scans the flame and initiates corrective action if required.

The method used to deliver the PF to the primary air system is dependent on the rank (grade) of coal used, but usually **bowl mill pulverizers** or **impact mill pulverizers** are employed to produce PF coal.

3.3.1.4 Gas Burners

Gas burners are of various low- to high-pressure (2–25 psi) designs, including *gas-ring burners*, *center-diffusion tube gas burners*, and *turbulent gas burners*.

Gas pressure must be properly regulated, all lines purged before use, and ignitors *proven* to work before initial startup. Also, all gas burning equipment must be regularly inspected for leaks to avoid risks of an explosion.

Gas-ring burners spray gas from orifices drilled in an annular manifold into a controlled-volume air stream. Combustion is initiated by an ignitor.

Other types require a **governor** (*inspirational governor*) to proportion and mix the air and gas, which is then delivered to several burners, where ignition and combustion take place.

3.3.2 Stokers

Solid fuels that have not been pulverized require a **stoker** to introduce the fuel into the boiler furnace at a controlled rate. There are two broad classes of stoker (**overfeed** and **underfeed**) and often several types within each class.

3.3.2.1 Overfeed Stokers

In overfeed stokers the fuel is delivered into the furnace above the stoker. Designs include the *spreader stoker*, where fuel is uniformly thrown across the grate area within the furnace and the fine coal or other fuel burns in suspension, and the *vibrating grate stoker* and the *moving grate (chain and traveling grate) stoker*, both of which are types of **mass feed stoker**.

3.3.2.2 Underfeed Stokers

Underfeed stokers operate by pushing the fuel into the furnace using a *ram feed*, *screw feed*, or similar mechanical means. Designs include the *horizontal feed* or *side ash discharge stoker* and the *gravity feed* or *rear ash discharge stoker*. Primary air is usually unheated and arrives from **tuyeres** (nozzles or openings in the stoker). To protect stoker grates from radiant heat, an ash layer of 3 to 6 inches is typically maintained on the grate.

3.3.3 Baffles

Furnace areas require baffles to deflect the gases back and forth between the tubes. Correct baffle arrangements are necessary to maintain combustion gas velocity, ensure correct temperature differentials, prevent short circuiting of the gas path, and minimize dead spots, which encourage the deposition of **flyash**.

3.3.4 Dampers

Furnace temperatures (and in part, heat transfer rates) are controlled by the opening and closing of **air** and **flue gas dampers** and **burner registers**.

There are various types of damper:

- *Isolation dampers*, which shut off flow to or from certain areas
- *Balancing dampers*, which are employed to balance the flow in two or more ducts
- *Control dampers*, which provide a variable flow restriction

Apart from design type, dampers are also available in different shapes such as *louver*, *round*, and *guillotine*.

3.3.5 Fans

Fans direct air movement within the furnace or combustion area. The two primary fan designs are forced draft and induced draft. **Draft** is the difference between atmospheric pressure and the static-pressure of combustion gases.

3.3.5.1 Forced Draft Fans

Forced draft fans (FD fans) provide a *positive* air and combustion gas **static pressure** *above* that of atmospheric pressure. Almost all boilers have FD fans that force air from boiler inlets through the furnace and convection-pass sections.

3.3.5.2 Induced Draft Fans

Induced draft fans (ID fans) are located near the end of the flue-gas path and provide a *negative* static pressure *below* that of atmospheric pressure (creating a partial vacuum). This induces outside air to infiltrate any openings in the boiler.

Fire tube boilers usually do not have ID fans because they normally can obtain sufficient ID from the stack's natural draft. However, they do employ FD fans, which provide a *positive* furnace pressure.

Large WT boilers generally have a **balanced draft** system (i.e., a combination of both FD and ID fans) and usually operate at *negative* furnace pressure (–0.1 to –0.5 inch of water) to provide for better control of both the furnace flue-gas pressure and the fuel–air combustion process.

Draft is usually measured in inches or centimeters of water using a **U-tube manometer**, with one side connected to the sample point (such as the furnace section, convective-pass section or the boiler stack) and the other side open to the atmosphere. The difference in the manometer column height indicates **boiler draft pressure**, which may be either higher (*overpressure*) or lower (*underpressure*) than atmospheric pressure.

NOTE: One inch of height difference in a U-tube manometer represents 0.0361 psia. A typical draft in a large balanced-draft WT boiler is on the order of 2 to 4 inches.

3.3.6 Economizers and Air Heaters

Economizers are one of several types of FW heaters, all of which are designed to provide thermodynamic gains in the **steam cycle**. They typically are located in the exit gas system, where their use improves overall boiler efficiency, which tends to increase by 1% for every 40 to 50 °F (22–28 °C) reduction in flue gas temperature

Economizers form part of the **boiler (heat transfer) surfaces**, whereas **closed LP/HP heaters** and **open (deaerating) heaters**, although forming part of the overall FW supply system, are often regarded as *balance of plant equipment.*

Economizers are heat transfer tube bundles that preheat MU water or FW flowing within the tubes by extracting waste heat from the flue gas during its exit path to the stack. They typically account for approximately 10% of the total boiler heat transfer surfaces, while absorbing only 7% of the total heat generated in the boiler system.

There are various WT and FT boiler economizer designs, classified as either **steaming economizer** and **nonsteaming economizer** types according to thermal performance. These economizers are constructed in either *bare tube* or *finned tube* (*extended surface*) patterns. They may be positioned horizontally or vertically within the boiler system, in either cross-flow or counterflow arrangements.

Because economizer tube bundles produce very hot FW within the tubes, they may be subject to serious waterside **corrosion** and **deposition** problems, in addition to gas-side dust erosion problems and cold-end **acid attack** from sulfuric acid (derived from sulfur-containing fuels).

A specific waterside problem that affects many economizers is normally one of **oxygen corrosion**. This affects the *internal, carbon steel tube header, first-pass tubes*, and *primary tube bend areas* because these areas first receive cold FW. This form of corrosion commonly results in red oxides, economizer **pitting** and **tuberculation**, and potentially premature tube failure.

*NOTE: Where FW/MU water deoxygenation by chemical oxygen scavenger (such as **catalyzed sodium sulfite**) is employed prior to the water entering an economizer, it is definitely not recommended to add **chelants** at or close to this economizer upstream injection point. Chelant injection here deactivates the cobalt catalyst often used, permitting the FW dissolved oxygen to remain unscavenged and thereby significantly enhancing the risk of oxygen corrosion–induced, economizer damage. In fact, chelants should be added only as far downstream of any chemical oxygen-scavenging injection point as possible.*

The periodic development and use of new steel alloys can improve ferrous corrosion resistance; however, where economizer units are constructed of copper alloys, under certain conditions serious **copper corrosion** problems may result. This occurs when FW having a pH over 8.3 also contains small amounts of ammonia and dissolved oxygen (DO). The ammonia may be present, for example, as a result of the overuse or inappropriate application of certain amines. Further damage may occur from the plating-out of the *copper-ammonia ion* then created as a *cathode* on boiler tubes. This promotes **anodic corrosion** of the immediate surrounding anodic areas.

Economizer corrosion rates are enhanced by higher heat-transfer rates; excessive heat flux may create *localized nucleate boiling zones* where **gouging**, as a result of chemical concentration effects, can occur. **Air heaters** are also located in the exit gas system. They do a job similar to that of economizers except that they preheat combustion air.

Air heater designs include:

- **Convection air heaters**, of *tubular* or *plate* design
- **Regenerative types**, used in large boiler plant installations

3.3.7 Feedwater Pumps

No matter the duty (utilities excepted), most boiler plant systems employ electric motor–driven, **single-stage** or **multistage centrifugal pumps** to supply FW. These may be of conventional design or derivations such as a **turbine pump**. However, steam-driven **reciprocating FW pumps** (steam pumps) are still employed in some countries and for certain smaller applications.

NOTE:
***Feedwater delivery** from a pump varies with the rotational speed of the impeller, so by doubling the speed, the quantity of water delivered also doubles.*

***Head pressure** increases with the square of the speed, thus doubling the speed provides four times the head.*

***Pump power requirements** increase with the cube of the speed, so doubling the speed requires eight times the power.*

However, all pump discharges are subject to friction and other losses, and it is therefore necessary to refer to various pump curves and design data in order to establish the correct pump design and to provide a precise match in terms of pump capacity, FW temperature, head demands, and mode of pump operation.

*The FW storage tank (feed tank) or deaerator storage reservoir must be at the correct height to ensure the proper **net positive suction head** (NPSH) for the pump.*

Some commonly employed FW pumps are described in the following sections.

3.3.7.1 Centrifugal Pumps

Centrifugal pumps utilize one or more *impellers* rotating at high speed within a *casing* to provide centrifugal force to the FW and to convert this force into pressure.

In a *multistage centrifugal pump*, the discharge from the first impeller enters the suction of the next impeller and so on, with the pressure increasing at each stage. The shape of the casing is used to direct the FW discharge. This type of pump can be started with the discharge valve closed.

Centrifugal pumps obviously must be provided with adequate supplies of FW but may nevertheless fail to deliver it to the boiler if the temperature is too high and there is a consequential risk of steam form-

ing in the FW supply. If LP zones or abrupt pressure differences occur in the FW supply (as can happen with too high a FW temperature), **cavitation erosion** of the pump casing and impeller may occur. This form of metal wastage also may happen with highly turbulent FW flow.

When the impeller or casing is made of *cast iron* (common in many designs of FW pumps and other pre-boiler items of equipment), under certain operating circumstances **graphitic corrosion** can occur.

3.3.7.2 Turbine Pumps

Turbine pumps resemble centrifugal pumps but use a combination of a *diffusing ring* and a casing design to direct the FW discharge. The axial clearance between the impeller and casing is less for a turbine pump than for a centrifugal pump.

Turbine pumps are *positive-displacement* pumps: They cannot be started with a closed discharge valve and require the fitting of a *pressure relief valve* to provide overpressure protection.

3.3.7.3 Reciprocating FW Pumps

Reciprocating FW pumps may have either one or two steam cylinders. They are positive-displacement pumps and usually operate at only slow speed. They are efficient but can rapidly lose efficiency when either the steam or water valves are worn.

The exhaust steam can be used for FW heating but must first be passed through a separator to remove oil contamination.

3.3.7.4 Steam Turbine–Driven FW Pumps (FW Pump Turbines)

Instead of using multistage centrifugal FW pumps, larger boiler plants such as utilities or cogeneration plants producing over, say, 300 to 400 MWh, often employ steam turbine–driven FW pumps. These are high-speed rotary devices that are reliable and efficient in operation and can be used with high-speed pumps without the need for any intervening gears.

Feedwater pump turbines typically receive steam from the main turbine (at the IP to LP crossover stage) at 100 to 200 psia (6.9–13.8 bar), and condense the steam to 2 to 3 inches of mercury absolute (0.07–0.10 bar) exhaust pressure, either to the main turbine condenser or to separate condensers.

3.3.8 Superheaters and Reheaters

Superheaters and reheaters are tube bundles located in either the boiler furnace section or the convection-pass section. They are designed to increase the temperature of generated steam prior to its being passed to a turbine. Many larger power boiler designs incorporate a steam reheater in addition to one or two banks of superheaters.

Turbines for electricity generation are limited in their efficiency, in part by moisture present in the steam but also by the partial condensation that occurs during the loss of energy when work is done by steam passing over the turbine blades. Thus, an increase in steam temperature over and above that required for saturation (through the use of a superheater) reduces the potential for condensation to occur and raises the efficiency of the *combustion-to-electrical generation process*, perhaps by 4 to 5%.

NOTE: Typically, ≅ 7,200 Btu are required to provide 1 kWh. At 80% efficiency this requires 9,000 Btu of fuel energy to be supplied. However if the efficiency can be raised by 5% by the use of superheat and reheat, only 8,470 Btu is needed.

The two basic types of superheaters are the **convection superheater** and the **radiant superheater**.

Superheater tube bundles are designed for different arrangements within the boiler:

- *Pendant arrangement:* A suspended series of coils usually shielded against radiant heat
- *Interdeck arrangement:* The tube bundle is located between banks of primary boiler tubes
- *Platen arrangement:* Similar to the pendant arrangement, but the tube bundles are all in one plane
- *Horizontal arrangement:* The tube bundle is supported by lugs, stringer tubes, or convection-pass wall cooling tubes

The formation of superheater deposits in and around the superheater tube outlets and receiving header is a relatively common but serious superheater problem that may occur. These deposits are caused by contamination from BW carryover and also by gross contamination of **attemperation water** used to control the degree of superheat.

Long-term overheating may cause **thermal oxidation** on both the external and the internal superheater surfaces, resulting in a gradual buildup of coarse black magnetite. **Corrosion fatigue** may also occur.

If **dry lay-up** procedures are not carried out entirely satisfactorily (e.g., if a nitrogen blanket is not permanently provided to the superheaters during the lay-up period), atmospheric moisture may condense and oxygen corrosion will ultimately occur.

Finally, if a tube steam leak occurs in a boiler, then depending on the internal arrangements steam may cut into or cause a damaging groove in part of the superheater tube bundle.

3.3.9 Spray Attemperators (Desuperheaters)

The control of superheated steam temperature is achieved by attemperation, using either **surface** (*heat exchange*) or **spray** (*direct contact*) attemperators. The spray type, which requires the steam to be sprayed with water, is the most widely used, and a schematic is shown in Figure 3.1.

The attemperator may be located between banks of superheaters or at the superheater outlet.

High-quality water is required (TDS < 2.5 ppm), and it must not add more than 40 ppb TDS to the steam.

3.3.10 Steam Traps

Steam traps are automatic mechanisms that remove low heat–content air and condensate from the steam delivery system. The lack of steam traps or use of traps that fail to function properly leads to a gradual decline in heat-transfer efficiency, waterlogged heat exchangers, and **water hammer** (which may in turn result in ruptured pipes). When adequate maintenance of steam traps is neglected, this ultimately leads to a serious overall loss of operating efficiency. There are various types of steam traps, each designed for a specific function. Some common variations are discussed in the following sections.

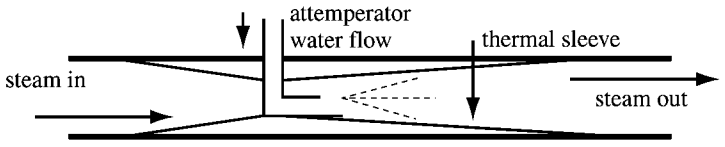


Figure 3.1 Spray attemperator.

3.3.10.1 Thermostatic Steam Traps

Thermostatic steam traps contain a bellows-type element that expands in contact with steam, causing the valve to close, but opens at lower temperatures to allow condensate or air to escape. Typically, thermostatic steam traps are used at up to 150 to 250 psig.

3.3.10.2 Float Thermostatic Steam Traps

Float thermostatic steam traps employ a float valve that rises in the presence of condensate and then opens to permit the discharge of the condensate.

The thermostatic element component only opens if the surrounding temperature is lowered by the presence of air or other **noncondensable gases**. These gases can then escape, but entering steam again closes the thermostatic valve. Float thermostatic steam traps are typically used at up to 125 psig.

3.3.10.3 Inverted-Bucket Steam Traps

Inverted-bucket steam traps contain a small bucket that becomes buoyant if steam is present and shuts off a discharge valve. The presence of condensate causes the bucket to sink and the discharge valve to open. Any entrained air is removed through a small hole in the bucket.

3.3.10.4 Impulse Steam Traps

Impulse steam traps rely on steam to maintain pressure on a piston and valve arrangement. When air and condensate enter the trap, the pressure is reduced above the piston and the valve opens.

3.3.10.5 Thermodynamic Steam Traps (Disc Steam Traps)

Thermodynamic steam traps also rely on pressure differentials for their operation. They employ a *control disc* to open or close a discharge orifice. Both impulse and disc-type steam traps are used in medium-pressure (15–250 psig) steam delivery systems.

3.3.11 Sampling Coils (Sampling Pots/Sample Coolers)

Many boilers are fitted with a heat exchanger–type water sampling coil that permits the collection of a representative and cooled BW sample. The design generally provides for a coil of copper or stainless steel (SS) fitted inside a small SS shell. The unit is fitted with gate valves to control the flow of cooling water and BW.

In general, larger steam-raising boiler installations more commonly tend to employ sampling coils, and the boiler plant design may provide for one or more sampling points per boiler. The sampling coils often function continuously, although the permanent trickle of BW is collected and routed to a **"save all" tank** or other receiver.

Operators of smaller boiler plants, on the other hand, usually open the boiler sampling coil only when it is necessary to take a water sample. In this case, the BW should be allowed to run for several minutes before the sample is taken.

The flow of both the BW and the cooling water should be adjusted so that the temperature of the BW sample ideally does not exceed 30 to 35 °C.

The primary reason for installing a cooling coil is for operator safety when sampling, As the boiler pressure rating increases, it becomes increasingly important to use a cooling coil.

It should also be noted, however, that if a BW sample is taken directly off the boiler (or if there is inadequate cooling when using a sampling coil), some of the BW will flash off as steam. This can, in effect, concentrate the BW sample by as much as 25 to 30%, resulting in analytical results that reflect an apparent serious *overconcentration* of TDS, alkalinity, or other analytical parameter.

The usual response to the apparently high and out-of-specification result is to "correct" the problem by increasing boiler blowdown. The net result is an unnecessary waste of BD water and the heat associated with it. Consequentially, there is an unnecessary increase in fuel consumption.

Given the importance of ensuring proper boiler plant safety and optimum BW quality and treatment, it is surprising how many smaller boilers are not fitted with sampling coils. They are often viewed as an unnecessary expense, but because a boiler typically costs several hundred times as much as a sample cooler, this viewpoint is clearly nonsense. The fact is that sampling coils are a vital fitting on any boiler. The cost usually can be recovered within a few days or weeks as a

result of more accurately identifying the true condition of the BW and managing the blowdown program accordingly.

3.3.12 Blowdown Water and Flash Steam and Heat Recovery Systems

Various designs of blowdown water heat recovery systems, including **flash steam and heat recovery systems** (FSHR), are available and usually are designed automatically into utility and other large steam-generating boilers plants. This is seldom the case with smaller, industrial steam-raising boiler plants (although the position continues to improve globally as the cost of fuel and waste water treatment increases and environmental awareness programs take effect).

Flash steam and heat recovery systems are almost never fitted into hydronic heating and LP steam boilers because of the very limited discharge of boiler water as blowdown. A schematic drawing of an FSHR system is shown in Figure 3.2.

Flash steam and heat recovery systems provide a useful and simple means of recovering both heat energy and steam condensate that would otherwise be lost by BD. The capital cost for an average sized industrial boiler house is relatively low, and capital payback periods are usually within 12 to 24 months.

For any particular FSHR design, capital payback periods are clearly reduced by half if the equipment is installed in a boiler system that

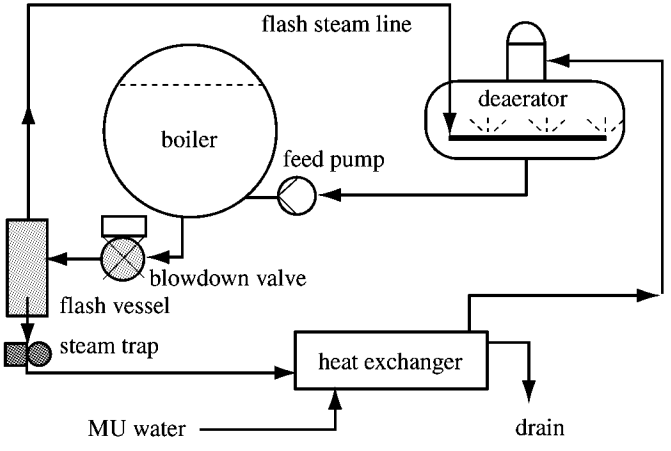


Figure 3.2 Flash steam/heat recovery (FSHR) system.

operates 24 hours per day rather than only 12 hours per day. As with any boiler, the **maximum continuous rating** (MCR) size of FSHR system equipment is exactly the same.

Flash steam and heat recovery systems perform more efficiently if a continuous source of blowdown is provided. Depending on boiler pressure, the potential BW blowdown recovery is up to 25% of the blowdown volume recovered as flash steam and up to 75% of the heat content recovered. The flash steam can be passed to a LP steam line or sent back to a deaerator or feed tank, where it provides both FW heating and a replacement for MU water.

The percentage of BW blowdown steam flashing off is a function of the boiler pressure, as shown in Table 3.1. An example of FSHR calculation is provided at the end of this section.

In many ordinary industrial plants, the arrangement of the various boiler plant systems is not conducive to the optimum use of any flash steam generated. Recommendations to consider include:

- Avoid using unlagged condensate lines because much of the heat available will simply be wasted to the air rather than returned to the boiler FW system.
- Avoid using unlagged and open-top FW tanks. Ensure a good feed tank design (as shown in section 3.3.15), with the condensate return line going fully to the bottom of the feed tank and terminating in a *sparge pipe*.

Table 3.1 Flash steam recovery from a FSHR system

Boiler pressure psig	*Percentage (%) flash steam*
75	9.9
100	11.8
125	13.5
150	15.0
175	16.2
200	17.3
225	18.5
250	19.5
300	21.2
400	24.3
500	26.9

- Avoid overheating FW tanks and the generation of steam in the tank. If the FW temperature is too high and there is inadequate *net positive static head* (NPSH) on the FW pump suction, the pump will not operate and *cavitation* problems may occur.

Flash steam often may be usefully recovered by fitting a flash vessel either in a common condensate return system or after the steam traps, where large volumes of HP steam are used. Flash steam recovered in this way can be discharged to an LP steam delivery system.

The flash vessel should be fitted with a *float* or *inverted-bucket type steam trap* to the condensate discharge line, and also a *pressure relief valve* to prevent excess pressure buildup, as may happen if the demand for LP steam drops below the flash steam production rate.

An alternative way to use flash steam is to provide several, small self-contained FSHR systems, keeping the system pipework to a minimum and lagging the pipes to avoid unnecessary heat losses. Flash steam forms at the point where the pressure drops, which is at the BD valve or the valve seat of the steam trap. From this point the flash steam and condensate travel together until the flash vessel is reached. The vessel then acts as a steam–water separator.

The minimum flash vessel height is typically 3 to 4 ft (1–1.3 m). The maximum steam velocity through the vessel should typically be 10 ft/s (3m/s), and the maximum flash steam exit velocity should not exceed 50 ft/s (15 m/s).

Example of Heat Recovery Calculation

- A facility is an industrial manufacturer, operating 24 hours per day for 355 days per year.
- The boiler plant is operating at 150 psig and producing 40,000 lb/hr (18,140 kg/hr) steam for 8,500 hours per year.
- The BD requirement is 5% of steam generation, which is 2,000 lb/hr (907 kg/hr).
- Recovered steam sent to a MU water tank at 60 °F (15.5 °C).

NOTE:
1 kJ = 0.948 Btu
1 Btu/lb. = 2.33 kJ/kg approx.
1 therm = 100,000 Btu

1. The BD pressure translates to a temperature of 365 °F (185 °C). At this pressure 15% will flash off into steam in the BD valve. The flash steam separates from the BD water in the flash vessel at a pressure of 3 psig (0.2 barg).
2. Flash steam equaling 300 lb/h (136 kg/hr) (15% of 2,000 lb/hr) at 3 psig and 220 °F (104.4 °C) is recovered, with a latent heat of 964 Btu/lb (2,243 kJ/kg), It is passed to the deaerator, where it condenses, thus replacing some MU water and giving up both its latent heat and sensible heat.
3. Residual BD water totaling 1.700 lb/hr (771 kg/hr) at 220 °F (104.4 °C) passes to the heat exchanger. Heat is transferred to the "cold" 60 °F (15.5 °C) incoming MU water.
4. The residual BD water (still amounting to 1,700 lb/hr) flows to a drain at a much lower temperature of 104 °F (40 °C).
5. Latent heat recovered from flash steam equals 964 Btu/lb (from steam tables).
6. Sensible heat recovered by cooling condensed flash steam from 220 °F down to 60 °F equals 160 Btu/lb.
7. Total heat recovered in flash steam is 964 Btu/lb + 160 Btu/lb. This equates to 1,124 Btu/lb (2,615 kJ/kg).
8. The *annual* ***latent heat*** *recovered* in this way equates to:

   300 lb/hr × 8,500 hours × 1,124/100,000 = 28,662 therms or 3,023 gigaJoules (GJ)
9. The sensible heat recovered in the heat exchanger (assuming 100% efficiency in heat transfer and based on the residual BD water dropping from 220 °F down to 104 °F) is 116 Btu/lb.
10. The *annual* ***sensible heat*** *recovered* in this way is:

    1,700 lb/hr × 8,500 × 116/100,000 = 16,762 therms (1768 GJ)
11. The ***total annual realizable heat recovery*** is 28,662 + 16,762 therms. This equals 45,424 therms (4542.4 MBtu, 4,792 GJ). This can be further equated to a *savings in primary fuel input requirements.*
12. The ***total annual condensate recovered*** is:

    (2,000 lb/hr × 15%) × 8,500/ 8.34 = 305,755 US gal (1,390 m^3).

    This saving in condensate can be equated to a *savings in the requirement for treated makeup water.*

3.3.13 Condensate Pumps and Tanks

The **condensate return** (*returned condensate* or *simply condensate*) tank is positioned at the lowest point in a condensate return (CR) system and collects condensate from the various steam heating and process applications. If traps or condensate pumps are installed to aid the return of the condensate (as is usually the case), this is called a **mechanical CR system**. Nevertheless, some parts of the system may return condensate by *gravity* either to a condensate tank or directly to a FW tank.

Some boiler plant designs employ a **vacuum pump CR system** because this type of system requires less steam pressure to flow up a riser. Thus, greater steam circulation can be obtained, giving rise to an increased heat transfer rate.

Condensate tanks are typically sized 25% larger than the boiler MCR (the tank is normally designed to be only 75% full). Condensate tanks should incorporate an *atmospheric vent line* to prevent pressure buildup, although this still may occur in systems with leaking steam traps.

Condensate pumps generally deliver CR either to a *deaerator* or to a *FW tank* (ideally in an *uncontaminated* condition). The condensate pumps are controlled by a *regulator* similar to a FW regulator and may be adjusted by reference to the condensate level as seen through a condensate tank sight glass.

3.3.14 Feedwater Heaters And Deaerators

Feedwater heaters of various types, sizes, and shapes have been employed since the earliest days of boiler plant design. Their primary purpose is to increase the *thermodynamic gains* of the steam cycle and reduce problems of *thermal shock* in the boiler. Typically, they may be classified as HP or LP, open or closed FW heaters. Some types of open FW heaters additionally provide FW *mechanical dearation*.

An **economizer** is a type of FW heater wherein the "cold" FW or MU water gains heat from the exit gas system rather than from steam, which is used in most other types of FW heater.

The number and types of FW heaters employed in any particular system is effectively dependent on the size of the boiler plant. The largest utility boiler plants use up to 20 to 30% of turbine throttle steam to provide **regenerative FW heating** and may have up to six or seven stages of steam heating (each stage rising by 40–50 °F).

The average industrial process plant, on the other hand, has perhaps only one or two stages of steam heating, whereas the smallest steam-

raising plants may not have any form of FW heater or deaerator at all (apart from the FW tank itself).

3.3.14.1 Closed Feedwater Heaters

Closed FW heaters are used widely in large WT boiler plant systems; a schematic drawing is shown in Figure 3.3. It is a horizontal, three-zone, HP, closed FW heater, of a design that is often employed in utility plants.

Closed FW heaters are *shell and tube heat exchangers* typically designed to contain U-tube bundles expanded or welded into a single, stationary *tube sheet* (although some designs replace the tube sheet with inlet and outlet box headers).

Saturated or superheated steam flows on the shell side and FW on the tube side. Closed FW heaters are so called because the steam and water do not come into contact with each other. Most are of a horizontal design although vertical FW heaters are manufactured.

Maximum design flow rates for closed FW heaters vary with the materials of construction but are typically:

- **Carbon steel:** up to 8 ft/s
- **Copper/brass:** up to 8.5 ft/s

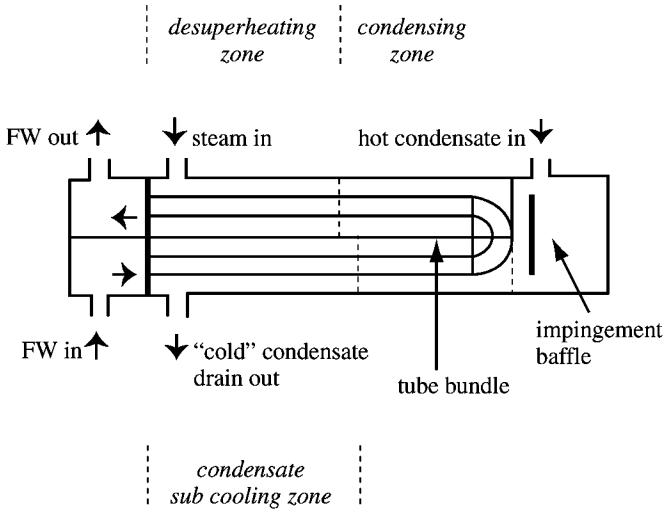


Figure 3.3 Closed FW heater.

- **Copper nickel:** up to 9 ft/s
- **SS/Monel™/Inconel™:** up to 10ft/s

3.3.14.2 Low-Pressure FW Heaters

Low-pressure FW heaters are shell and tube heat exchangers located *upstream* of the FW pump and designed for pressures typically below 900 psig (62.1 barg).

3.3.14.3 High-Pressure FW Heaters

High-pressure FW heaters are shell and tube heat exchangers located *downstream* of the FW pump and designed for pressures typically up to 1,500 psig (103.4 barg).

3.3.14.4 Open Feedwater Heaters

Open FW heaters permit the intimate contact of MU and FW with steam. In doing so, these heaters not only heat the incoming water but also provide for effective mechanical deaeration. They are often called **deaerating, pressure FW heaters** or simply **deaerators** (DAs).There are several different types of DA, including:

- Tray (baffle) deaerators
- Exchange packing deaerators
- Spray deaerators
- Atomizing deaerators

Various deaerators are shown in Figure 3.4 a–d.

Almost all larger boiler plants employ *pressure deaerators* in the pre-boiler FW system. They are available in horizontal or vertical configurations and usually are supplied as packaged units complete with all valves, gauges, sight glasses, and other accessories. Essentially, they comprise a deaerating device mounted onto a storage compartment that holds the hot deaerated FW, which is protected from recontamination by a steam blanket. (**Vacuum deaerators** may sometimes be used but they are not *FW heaters*.)

Small boiler plants often do not incorporate a DA because of the relatively high capital cost of the equipment, although custom and practice in some countries (notably the United States, Germany, and some

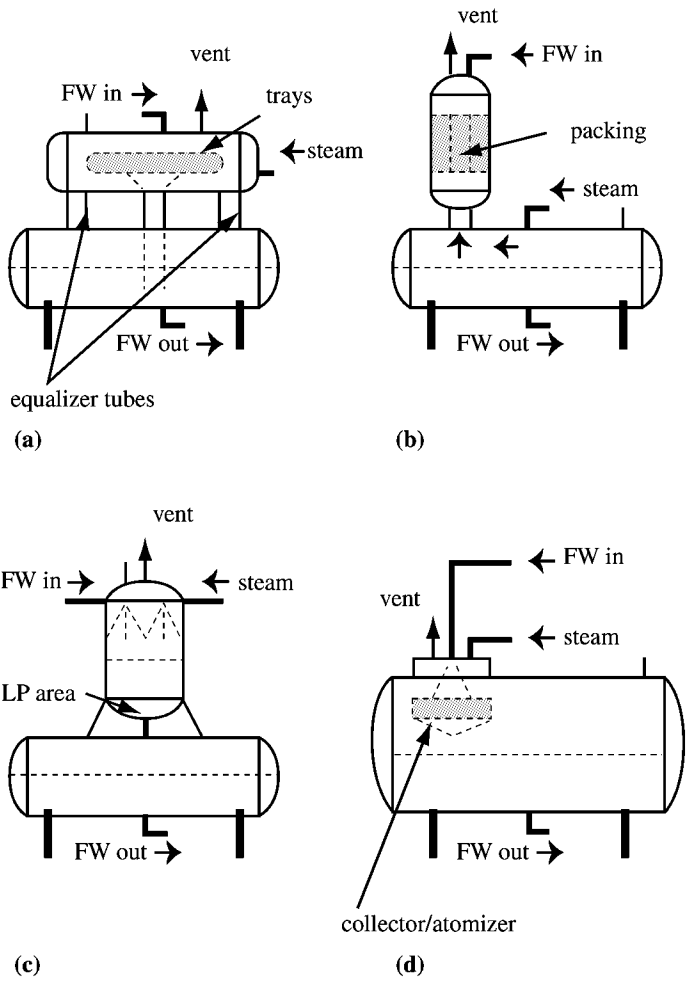


Figure 3.4 (a) Tray type deaerator; (b) exchange packing type deaerator; (c) spray type deaerator; and (d) atomizing type deaerator.

other industrialized nations) often dictates that a DA is installed. This is a practice to be encouraged for all but the very smallest plants because the long-term gains usually far outweigh the initial capital investment. Benefits include:

- Improved steam cycle efficiency
- Savings in fuel
- Reduced risks of thermal shock

- Reductions in **chemical deaerator** (*oxygen scavenger*) requirements, leading to lower FW TDS and some slight reduction in BD requirements

The basic mechanism for deaeration is the same for each type of DA design available; that is, it is the removal of dissolved gases from FW by reducing the **partial pressure** of the gases in the atmosphere surrounding the FW. This condition is achieved either by applying a vacuum to the system (*vacuum deaerators*) or by venting the unwanted gases using steam as a **purge gas** (*pressure deaerators*).

NOTE: The operational efficiency of a deaerator is governed by its potential to reduce the partial pressure of oxygen in the FW to a minimum. The equilibrium concentration of any gas (such as O_2) dissolved in a liquid (i.e., the gas's solubility) is proportional to the partial pressure of that gas in contact with the liquid. This relationship is expressed by ***Henry's Law****:*

$$C_{total} = P \times k$$

where:
C_{total} = *total concentration of the gas in solution*
P = *pressure of the gas above the solution*
k = *a proportionality constant (Henry's Law Constant)*

Thus, because oxygen comprises approximately 20.9% of the atmosphere, the partial pressure of oxygen in air is approximately 0.2 atmospheres (atm). If the solubility of oxygen in "warm" FW is 4 ppm and, by use of a mechanical DA, the partial pressure is reduced to 0.002 atm, the solubility of oxygen in the FW accordingly is reduced to 0.04 ppm.

The corrosive gases removed by deaeration include:

- **Oxygen**, which is particularly damaging to boiler steel components through a variety of mechanisms.
- **Carbon dioxide**, which damages condensate return systems via the formation of carbonic acid.
- **Ammonia**, which damages copper-bearing alloy components.

The mechanical deaeration oxygen removal process is not 100% efficient, however, and all boiler FW must be further deoxygenated by some form of chemical **oxygen scavenger**.

In addition, although **free carbon dioxide** can be removed by deaeration, in practice the process is limited. Most of the available carbon

dioxide is *combined* with water and is released with steam into the steam delivery and condensate return systems. The usual solution to this is to add **ammonia** or some form or blend of **amine treatment**. This process can be quite effective, but if it is not properly controlled, it may give rise to the presence of *ammonia*, which has the potential to attack copper alloys.

Typical pre-boiler FW system arrangements provide for boiler FW (which is a combination of CR and MU water) to be pumped from either the *surge tank* or the *FW tank* and delivered to the DA, where it is sprayed through a spring-loaded nozzle into a steam atmosphere. The FW is heated to within a few degrees of the **steam saturation temperature** and more than 95% of the FW oxygen is released into the steam.

NOTE: The proportionality constant ***k*** *is reduced with increase in temperature. Under these hot DA conditions, the solubility of oxygen is very low (as per Henry's Law).*

The oxygen thus released concentrates in the upper zone of the deaerator with other noncondensable gases, passes through a small **vent condenser**, and then exits the DA through an atmospheric vent together with a limited amount of steam.

The balance of the DO is not readily released to the steam and is removed by a second stage in the DA. This stage is a *gas scrubbing stage*, and the specific mechanics vary with each of the different types of pressure DA.

3.3.14.4.1 Tray (Baffle) Deaerators Tray deaerators spray FW water into a steam-filled first stage section (which provides primary heating and partial deaeration of the water in the usual way). Very hot FW then cascades down through a tray stack, breaking into fine droplets from tray to tray and mixing with incoming steam, which heats the water to full saturation temperature This process removes almost all the remaining oxygen and other noncondensable gases.

3.3.14.4.2 Exchange Packing Deaerators Exchange packing deaerators are very similar to tray deaerators but use a *vertical fill pack* (exchange packing) to provide a high surface area for thin-film water–steam mixing and the easier elimination of dissolved gases.

3.3.14.4.3 Spray Deaerators Spray deaerators pass hot and almost fully deaerated water from the first stage to a separate, lower, second-stage section, where the pressure is dropped. This causes the water to boil and remove the final gases.

3.3.14.4.4 Atomizing Deaerators Atomizing deaerators collect the water from the first stage of deaeration in a conical water collector located within a common deaeration chamber–storage area and then pass it through an atomizing valve. High-velocity steam meets the FW at the atomizing valve, breaks it down into a fine mist, and heats it to full saturation temperature.

The mist mixture strikes a baffle plate that separates water, steam, and other gases. Hot, gas-free water then falls to a lower storage compartment while the steam and noncondensable gases rise and are vented.

3.3.14.4.5 Pressure Deaerator Troubleshooting If pressure DA equipment is properly maintained and carefully set up, operators should be able to produce FW containing dissolved oxygen (DO) levels of less than 0.005 to 0.01 cubic centimeters per liter (cc/l) O_2.

NOTE: 0.005–0.01 cc/l O_2 = 0.0072 to 0.0143 part per million (ppm); 0.0072 to 0.0143 milligram per liter [mg/l]; or 7.2 to 14.3 parts per billion (ppb).

To convert DO in cc/l to mg/l, multiply by 1.433, for 0 °C and 760 mm pressure.

Solubility corrections are needed for different temperatures, pressures, and salt concentrations, but they can be ignored for the low levels of DO considered here.

Nevertheless, manufacturers typically claim that their various pressure DA designs produce FW containing DO at levels of less than 0.005 cc/l, (7.2 ppb) oxygen and 0.0 cc/l carbon dioxide. This level of deaeration is normally reported at a temperature of 227 °F (5 psig nominal). This ultra-low level of DO is, in fact, normally achieved in large, HP utility power generating stations, where operational standards typically require a maximum DO level of 0.005 to 0.007 mg/l (5–7 ppb) oxygen at the economizer inlet, before the addition of chemical oxygen scavenger.

In these kind of facilities, the DO level is measured very frequently to ensure compliance and may often be measured periodically in *real time*, with the results automatically forwarded to a system management monitor located in a central control room.

It is rare, however, that other types of organizations (such as the average industrial facility) can afford this level of DO monitoring vigilance. It is also rare (utility stations apart) that deaerators receive the kind of preventative maintenance and general attention necessary to ensure that they operate constantly at peak performance. The inevitable

reality for most boiler plant systems is that practical DA efficiency is less than potentially achievable.

NOTE: A more usual FW DO performance standard achieved is 0.008 to 0.030 cc/l (0.011–0.043 mg/l, 11–43 ppb) O_2.

If a pressure DA under surveillance does not provide a satisfactory level of deaeration, there are several things to check. These include:

1. **Check the DO analysis.** Repeat the tests and check the reagents, the validity of the sampling point, the validity of the DO method, and the detection limits. Water to be sampled must always be properly cooled (typically below 80 °F/27 °C, although some methods specify 60–65 °F/16–18 °C). Samples should be taken either before any addition of oxygen scavenger or from a suitable scavenger bypass point. Sampling procedures should follow an appropriate method, such as American Society for Testing and Materials (ASTM) D510, D860, D1066, or equivalent. The sampling point must run for a considerable time before the sample is taken (which may range from a minimum of 5 minutes to perhaps an hour or more). The **Winkler method** (with or without modifications) remains a primary "wet" chemistry method (ASTM D888) and requires duplicate samples to be taken from sample water flowing into 500-ml glass sample tubes and with a minimum of 10 changes of water before the stopcocks are closed.

   NOTE: Where samples for DO analysis are taken from a deaerator storage compartment, it should be remembered that a chemical oxygen scavenger is typically added to this compartment (usually via an injector quill located below the water line). It may take several hours for this chemical to be diluted out of the tank.

2. **Employ appropriate test equipment and methods.** The DO measurement methods employed may need have detection limits down to 1 to 2 ppb. Although the Winkler method may be employed, suitable ultra-low-range field DO meters are available, Chemical field test methods include the *Rhodazine D* method using **CHEMets® DO ampoules** and a color comparator (ultra-low-range method) from Chemetrics Inc.

   The CHEMets method utilizes a small sampling reservoir conveniently affixed to a smooth surface and filled via a rubber tube from

a controlled, upward-flowing stream of sample water. The sample point must be absolutely leak-free because the smallest air bubble sticking to the inside of the sampling reservoir will cause erroneous results. The tip of a test ampoule is broken off under the water and the sample is drawn in. This results in a color change that can be compared to permanent color standards.

In practice, the sample reservoir is quite small, and the task is made easier with a larger glass filter funnel firmly mounted to a laboratory stand. The height of the upward flow of water is controlled using a tube grip on the bottom discharge hose.

3. Check the original DA specification and compare it against current performance. Deaerator performance should be checked at least quarterly and perhaps monthly. (This task is almost never undertaken on anything like a regular basis in most industrial facilities.) Check the temperatures and pressures of the steam–water mixture in the deaerator top section and the stored water compartment because problems here are quickly reflected in poor DA performance. The steam/water mixture in the top section should be within 4.0 to 4.5 °F (2.2–2.5 °C) of the saturated steam temperature for the particular DA operating pressure, whereas the difference between the storage section temperature and the DA top section temperature should not be greater than 4.5 to 5.0 °F (2.5–2.8 °C).

   Most DAs are set to operate at 5 psig with an exiting boiler FW temperature of 227 °F (108.3 °C). In practice, however, the stored water discharged from the base of the deaerator drops by several degrees during its journey to the boiler as the result of some heat loss to the surroundings.

   In practice, many DAs operate at only 2.3 to 3.0 psig, although they may be able to operate comfortably at 10 psig (the pressure vessels are rated to 50 psig), which provides both a higher DA operating temperature anda higher FW temperature. The result of raising the DA operating temperature and pressure is to improve the overall efficiency and rate of DO removal, which can lead to fuel savings of up to 2%.

   To check deaerator performance, appropriate steam tables are provided in Table 3.2 and some performance notes are given at the end of this section.

4. **Check the DA original design drawing.** Check the position of all inlets, outlets, and baffles. Check to see if any unauthorized modifications have taken place, such as additional vent openings. The vent

Table 3.2 Steam tables suitable for pressure deaerators

Temp °F	*Temp °C*	*Absolute pressure psia*	*Bar bara*	*Steam pressure psig*	*Enthalpy (Btu/lb.)*		
					Water H_f	*Evap* H_{fg}	*Steam* H_g
212	100.0	14.7	1.01	0	180.2	970.3	1150.5
216	102.2	15.9	1.10	1.2	184.2	967.8	1152.0
220	104.4	17.2	1.18	2.5	188.2	965.2	1153.4
224	106.7	18.6	1.28	3.9	192.3	962.3	1154.8
228	108.9	20.0	1.38	5.3	196.3	960.0	1156.3
230	110.0	20.8	1.43	6.1	198.4	958.7	1151.1
232	111.1	21.6	1.49	6.9	200.4	957.4	1157.8
236	113.3	23.2	1.60	8.5	204.4	954.8	1159.2
240	15.6	25.0	1.72	10.3	208.5	952.1	1160.6
244	117.8	26.8	1.85	12.1	212.5	949.5	1162.0
248	120.0	28.8	1.96	14.1	216.6	946.8	1163.4
252	122.2	30.9	2.13	16.2	220.6	944.1	1164.7

NOTE: H_f *= enthalpy of saturated water,* H_{fg} *= enthalpy of vaporization,* H_g *= enthalpy of saturated steam.*

should be vertical and free of unnecessary pipework or obstructions. The vent plume should be constant and almost undetectable at the point of exit from the vent pipe. (Typically, the vent discharge volume is only ≅ 0.1–0.2 % of the total steam volume supplied to the deaerator.) If the vent spits irregularly, it is a sign of condensation occurring in the pipe, and this limits the steady discharge of steam. Check for any damage to trays, spray nozzles, and the like. Check for *spray patterns*, *internal cleanliness*, *corrosion*, and *deposits*.

Deaerators taken out of service should be completely drained, dried, and provided with a **nitrogen blanket** during the lay-up period. When placed back on line, the DA should be on manual steam control. Heating should be gradual, and care is needed at the point of initial atmospheric boiling because steam flashing may occur in the FW discharge line.

Notes: To calculate DA performance:

DANC = Deaerator nominal capacity (gpm)
DAAC = Deaerator actual minutes of storage capacity available (to overflow)

AVMT = Average mix temperature
CR = Condensate return
MU = Makeup water

NOTE: Deaerator storage capacity is normally sized at 10 to 11 minutes FW demand at boiler full steaming rate (FSR) or maximum continuous rating (MCR).

$$\text{DANC} = \frac{\text{DA capacity (lb/hr)}}{500} \text{ gpm}$$

$$\text{DAAC} = \frac{\text{vessel capacity (to overflow)}}{\text{DANC}} \text{ gall}$$

For a DA with two sources of condensate return:

AVMT = (% MU × MU °F) + (%CR1 × CR1 °F) + (%CR2 × CR2 °F)

NOTE: Total percentage should be 100.

DA steam required (lb/hr) = DANC gpm × [0.5 × (227 – AVMT °F)]

3.3.14.5 Vacuum Deaerators

Vacuum DAs remove oxygen and other gases from water at temperatures *below* the atmospheric boiling point. They bring the water to its saturation temperature by applying a vacuum rather than by heating (as with pressure DAs).

Incoming water is sprayed through a packed column, which provides for an enlarged surface area, and aids the release of gases from the thin film of water produced in the packing. Depending on the DA size and design, the applied vacuum is maintained either by vacuum pumps or by stream-jet eductors.

Vacuum DAs are seldom used in boiler plant systems but are widely used in water distribution systems. They typically reduce the DO content of water to 0.25 to 0.50 cc/l (0.36–0.72 ppm) oxygen.

3.3.15 Feedwater Tanks for Fire Tube Boilers

Thousands of smaller boiler plants around the world (mainly FT boiler plants) have no form of separate FW heater or DA except for the FW

tank itself. For many of these plants this FW tank is primarily a **condensate return tank** (CR tank) or **hot water return tank** (HW tank). As a consequence, the operators rely on the FW tank to fulfill many functions. The tank may act as a:

- **Hot condensate receiver**
- **Cold water MU point in the steam cycle system**
- **FW heating vessel**
- **DA**
- **Hot FW storage reservoir**
- **Receiver for various chemical treatments**

Clearly, therefore, the design and correct utilization of the FW tank and associated FW equipment is of paramount importance in ensuring the continuous, efficient, and smooth operation of the boiler plant system. As an aid to design, a schematic drawing of a FW tank indicating some of the important elements is shown in Figure 3.5.

Although not particularly common, it also is not entirely unknown for some boiler plant systems to have steam generation difficulties as a

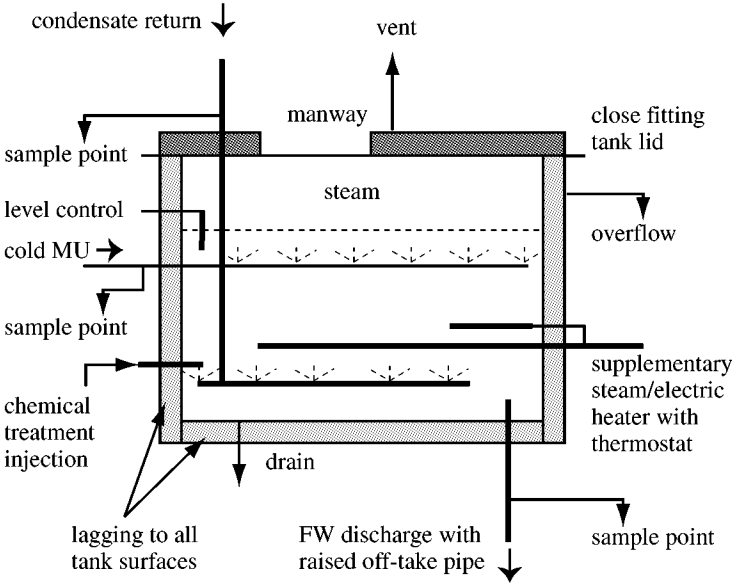


Figure 3.5 FW tank design for smaller boiler plant.

result of badly designed FW tanks, and for poor operational practices to add to the problems. Where this occurs, the kind of problems encountered may include:

- The FW tank may receive only minimal CR and is cold.
- With low CR the demand for MU water is high and this is generally cold also.
- There is no supplementary form of FW heating provided to the tank itself (such as electric heaters or live steam).
- The oxygen scavenger cannot cope with the high volume of inadequately heated FW and chemical deaeration is poor. This condition is further aggravated if the FW tank is sized too small because the oxygen scavenger contact time is reduced.
- No lagging of the tank and associated pipework is present, or poor lagging that gets wet and permits corrosion to develop from the outside.
- Where inhibitor chemical treatments are employed, they may be added daily by hand (*shot-dosed*, *shock dosed*) without any regard to product compatibility, FW needs, or fluctuations in boiler loading during the working day. The effectiveness of the program is therefore compromised under these conditions.

It is therefore not surprising to find that where boiler systems operate under these constraints, they suffer rapid and extensive *oxygen-initiated corrosion* to the internal surfaces of the FW system, the feed lines, the boiler shell, and all internal heating surfaces. With poor oxygen scavenging, heavy **pitting corrosion** and **tuberculation** is found, especially on the tubes and at the waterline of the FW tank and boiler shell.

A fundamental problem that occurs even in fully industrialized countries and large international companies, is that whereas many smaller boiler plant managers purchase well-designed and efficient boilers, pumps, and auxiliaries from recognized quality manufacturers and distributors, the design and construction of FW tanks and even the overall boiler house system may be placed in the hands of persons with inadequate training and experience.

It cannot be stressed too highly, therefore, how important it is to operate with a FW tank of good design and construction. This is especially true for owners or managers of smaller boiler plants where resources are often limited and the extra costs and liabilities incurred can be ill-afforded.

Some considerations for FW tank design are:

1. The tank should be large enough to hold a 1 to 2 hour's supply of FW at boiler MCR.
2. The tank should also be large enough to accommodate peak returns and surges of condensate, and shortfalls in MU water supply caused by softener regeneration.
3. The tank should be positioned sufficiently high off the boiler house floor to ensure that the FW pumps are provided with a satisfactory *net positive suction head* (NPSH).
4. Returned condensate should be discharged through a sparge point to the lowest practical point in the FW tank. The cold MU water supply line also should incorporate a sparge pipe but should be positioned at the highest practical point. This arrangement avoids the problem of poor water mixing because of **stratification**.
5. Adequate venting is required. Typically, the vent pipe diameter should increase by 1 inch for every 120 to 150 U.S. gal (25 mm per $\cong$ 0.5 m^3), and two vents are required for tanks larger than 650 to 700 U.S. gal. ($\cong$ 3 m^3).
6. Feedwater tank temperatures should be within the range of 180 to 190 °F (82–88 °C).
7. Sample points should be provided for the final FW and all sources of water, steam, and condensate that supply the FW tank. All FW tank sample points should incorporate a sample cooler.

Ideally, a **sampling station** should be provided where all necessary samples can be obtained from a single location. This arrangement is very common in large power stations but rare in smaller boiler houses. In fact, in many smaller boiler houses it often is virtually impossible to easily and safely obtain representative samples of condensate from the various collection lines in the CR system.

NOTE: Consider the following logic:

1. *It is generally acknowledged that no matter the size of boiler plant system or quality of FW provided, some form of chemical treatment is always necessary to counter deposition or corrosion problems associated with contaminants present in the incoming FW.*
2. *Thus, to correctly assess initial treatment program needs and to regularly monitor subsequently progress, it is necessary to be able to sample all sources of water that contribute to the boiler FW.*

3. *In most boiler plants, the CR contributes more than 60 to 70% of the total FW supplied. It is clearly unacceptable therefore, not to be in a position to easily and safely obtain samples of returned condensate.*

3.4 BALANCE OF PLANT (BOP) EQUIPMENT

There are potentially many items of equipment that can be described as BOP, and the classification distinctions are not always clear. However, electricity generators (especially turbine generators) and condensers are commonly referred to as BOP, and some notes on these items of equip-

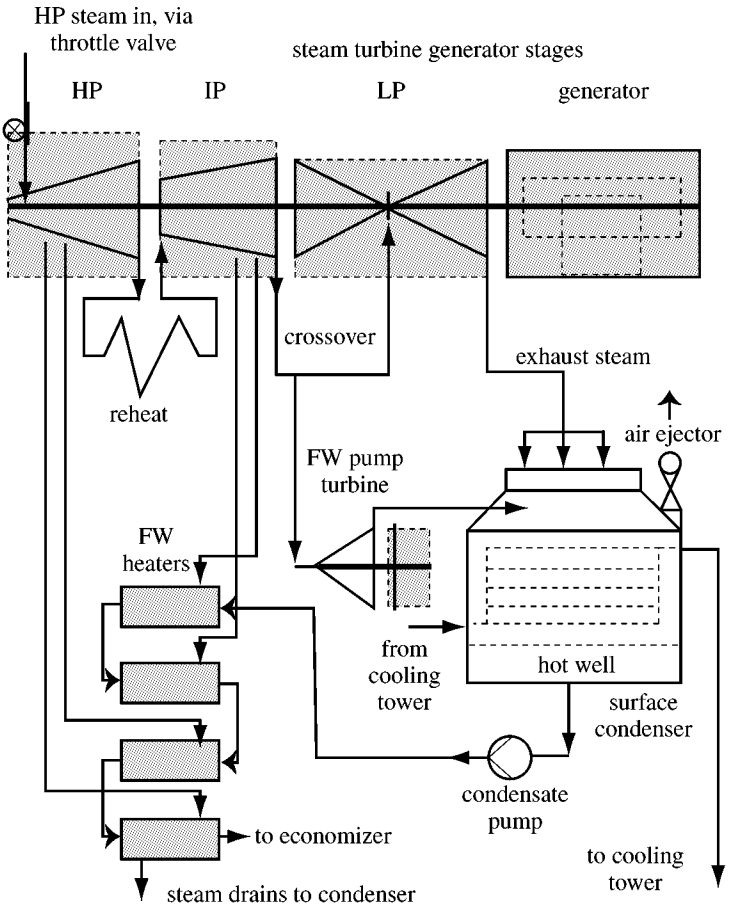


Figure 3.6 Balance of plant equipment.

ment are included in the following sections. A schematic drawing of BOP equipment incorporating a turbine and condenser is shown in Figure 3.6.

The modern global utility power industry typically employs very large turbine generator sets, with each set having an output of perhaps 100 to 500 MW (although generators are available at up to 1,500 MW or so). Utility plant designs carefully balance boiler output potential with fixed turbine set capacity. This normally is not the case with cogeneration plants, and during operation either steam or electricity capacity output tend to become a dominant factor and thus dictate the system design.

For many of the larger cogenerators, such as those in industrial manufacturing or process operations using by-products or waste material as a fuel, a primary goal may be to ensure the generation of sufficient steam to satisfy all industrial demands, or perhaps the capacity to burn all available waste products as a low-grade fuel for the boilers. Typically, under these circumstances, high pressure WT boilers at 900 to 1,500 psig are employed, These in turn pass steam to turbine sets of perhaps 5 to 50 MWh capacity.

Smaller industrial cogenerators may produce electricity only as a secondary function by coupling **back-pressure turbines** (0.2–5MW sets) to their various process operations.

Also, many operators commonly generate electrical power as a *primary* function via gas turbine or diesel engines, and then as a *secondary* function use heat extracted from the cooling jackets and flue gases to generate steam in a **WH boiler** or a **HR boiler**.

3.4.1 Electricity Generators

3.4.1.1 Large Steam Turbine Generators

Large steam turbine generators, as operated by the utility power industry, are usually of a **condensing turbine** or **reheat condensing turbine** design (the latter design incorporating a reheat stage part way through the steam's passage across the turbine). They receive steam at 1,250 to 2,500 psig.

Steam entering the turbine is expanded and does work in several *stages*. As the steam expands through the stages, its volume increases and the length of the rotor disc blade and stage must both increase accordingly to accommodate this greater volume.

The turbine stages may be designed as **impulse stages**, **reaction stages**, or an arrangement that incorporates features of both designs. With large turbines, the *control stages* tend to be impulse-type designs, whereas *LP stages* are of reaction-type designs.

Large generator designs incorporate two or three separate casings. The turbine is broken down into three areas: **high-pressure** (HP)

section, **intermediate-pressure** (IP) **section**, and **low-pressure** (LP) **section**. *Exhaust steam* from the HP stage is normally returned to a boiler reheat stage before passing to the IP stage.

Most large generator designs also incorporate a **regenerative FW heating facility** where from 20 to 30% of the **throttle steam** may be withdrawn from the turbine at various points to provide the necessary heating. In addition, the primary steam requirement for the *FW pump turbines* is extracted from the main turbine at the IP to LP crossover point.

These turbine units finally exhaust the steam at considerably less than atmospheric pressure to a **condenser** (in most circumstances a **surface condenser** is employed). The condenser is designed to raise turbine operating efficiency by reducing the turbine back-pressure to an absolute minimum. This is achieved by condensing the exhaust steam into a smaller volume of condensate, thus creating a substantial vacuum.

3.4.1.2 Impulse Stage Turbines

Impulse turbine design employs a stationary, circular diaphragm onto which a large number of fixed-position, tear-shaped nozzle blades (vanes) are mounted. High-velocity steam moves across the vanes and produces steam jets that are directed into waterwheel-type buckets, mounted onto discs around the turbine rotor. The pressure of the steam in the buckets forces the shaft to rotate. The kinetic energy of the jets is translated into mechanical work as the shaft turns.

Turbine efficiency must be maintained over a wide range of Mach numbers and pitching, and efficiency depends in part upon a balance of rugged nozzle construction and the aerodynamic properties of the bucket blade profiles.

3.4.1.3 Reaction Stage Turbines

Reaction turbine design also makes use of steam jets (which are produced by steam flowing across static vanes), although the turbine has rotor discs that incorporate movable blades rather than buckets. The design utilizes the reactive force produced by steam accelerating through a nozzle (created by the combination of a stationary vane and a moving blade) to rotate the shaft.

3.4.1.4 Smaller Steam Turbine Generators

Smaller turbine generators are used by the process and cogeneration industries. They typically produce electric energy at rates of 2,500 to

30,000 kWh and usually are **extraction** or **induction turbine** types. These smaller units may be **noncondensing** or **condensing turbine generators**.

Manufacturing industries often utilize condensing extraction turbines and employ the *extracted steam* for staged FW heating and industrial process applications.

In addition to condensing turbines, manufacturing industries widely use **noncondensing** (*back-pressure*) **turbines**. These back-pressure units are of various designs and are employed for electricity generation, typically within the range 600 to 30,000 KWh at 115 to 1,250 psig, and for a variety of process applications.

In the United States (and increasingly in Europe and elsewhere), with the rise in **outsourcing**, it is now possible for manufacturing industries to obtain electricity via transportable, trailer-mounted, packaged turbine generators. Here the steam is supplied from outsourced mobile boilers, which in turn receive FW from mobile water treatment plants.

3.4.2 Steam and Water Problems Affecting Turbines

The *salt deposition* and *corrosion* problems that may occur in turbines are similar in nature to those affecting superheaters and are essentially a result of **BW foaming, surging (priming)**, and **carryover**.

In typical cause-and-effect fashion, these particular problems stem from less than satisfactory boiler waterside conditions and have their origins in any of several, often interrelated, mechanical, operational, or water–steam chemistry irregularities.

Carryover may cause serious problems where turbines are installed. Factors that can lead to BW carryover include:

- Excessively high, or rapidly changing *firing rates* and *steam release velocities*
- Maintained levels of BW TDS, alkalinity, or chloride above that which can be tolerated by a particular boiler design or set of operating circumstances
- Boiler operated with *dirty steam separators* or *incorrect water levels*
- *Periodic boiler restarts* or *frequent load changes* that lead to **boiler cycling**; this inevitably produces carryover problems

Excessive boiler cycling may result in the **exfoliation of high temperature oxide scales** from *superheater* and *reheater tubes*, and from *steam outlet piping*. The particles and flakes of exfoliated scale may

become entrained in the HP steam flow to the turbine, thus causing **solid particle erosion** to the blades and nozzles in the turbine HP and IP stages. *Water droplets* entrained in the steam also lead to turbine blade and nozzle erosion, especially when you consider that the velocity of a steam jet may reach 2,000 ft/s (610 m/s). Boiler cycling and regular low-load conditions also promote **corrosion** in the turbine LP stage.

If silica (in the form of volatile **silicic acid**) is present in steam at concentrations greater than 0.02 ppm SiO_2, **turbine deposit** problems result. In some cases, volatile silica appears not to significantly affect superheaters but certainly will always form deposits in turbines. Silica appears in different forms, depending on the steam pressure, and affects *all* turbine surfaces, It is most noticeable on the blades, which eventually results in **rotor unbalancing**.

Additional problems are **sodium salt carryover** and **copper oxide steam distillation** at very high pressures. **Turbine blade fatigue cracking** may occur, although this develops gradually over a long period.

3.4.3 Condensers

Most boiler plants with electrical power generating facilities employ *surface condensers*. These are shell-and-tube heat exchangers in either one-, two-, or four-pass configurations. Surface condensers typically receive cooling water on the tube-side and steam on the shell-side of the heat exchanger. The LP turbine steam generally is received at the top of the condenser and proceeds through the condenser in a downward flow, while the FW turbine exhaust steam enters at the side.

The functions of a surface condenser are:

1. **To maximize turbine efficiency** (by minimizing turbine back-pressure). This is achieved by condensing steam and creating an adequate vacuum. The level of vacuum created by the reduction in steam-to-water volume is typically on the order of 26 to 29 inches of mercury and is in large part a function of the cooling water inlet temperature. A contribution to the maintenance of the vacuum is obtained through the mechanical pumps and air ejectors, which form part of the condenser system.

NOTE: The standard atmospheric pressure of mercury (Hg) is 760 mm Hg (29.92 in) at 0 °C. Thus, ignoring barometric or temperature differences, it can be seen that the condenser back-pressure is usually in the range of 29 to 29.92 inches down to 26 inches, which equals 1 to 4 in mercury absolute (3.4–13.6 kPa).

2. **To remove oxygen, carbon dioxide, and other noncondensable gases from the condensate** to maintain the necessary vacuum and to minimize the potential corrosion problems that these gases can cause in the condensate return system.
3. **To serve as a collection point for all condensate drains** in a bottom **hot well**, thus recovering high-quality condensate for reuse as the primary boiler FW component in the steam cycle.

Apart from surface condensers, other condensers are occasionally employed. These include:

- **Direct contact condensers**, which spray cooling water directly into the steam flow and are only used in certain limited applications
- **Air-cooled steam condensers**, which are used primarily where adequate supplies of cooling water are not readily available, as in desert and scrubland areas, and where water resources must be shared with sizable local populations.

3.4.4 Surface Condenser Operational Problems

Condenser design usually calls for thin-walled tubing with high *thermal conductivity* characteristics plus a high degree of resistance to biofouling and the many forms of corrosion that may occur. (These forms include **crevice** and **pitting corrosion**, **biocorrosion**, and **erosion-corrosion**).

Today many designers favor the use of particular grades of *stainless steel* and *titanium alloys*, but older condensers are often constructed of *copper alloys*, which may provide a source for **copper corrosion**, the products of which can be transported back to the boiler.

The efficiency of the condenser is reduced by **poor air removal** (and the presence of other noncondensable gases), so surface condensers usually are equipped with *vacuum pumps* but also may incorporate older style, single or multistage multielement, *steam-jet air ejectors*. Under most normal operations, the residual oxygen level is below 20 to 40 ppb O_2.

As noted previously, the degree of vacuum created is in large part a function of the *cooling water (CW) inlet temperature*, and high condenser inlet temperatures or poor heat transfer (as a result of *plugging*, *scaling*, or *general fouling* on the cooling-water side of the condenser) lead to reduced efficiency.

Similarly, **blocked intake screens** caused by *aquatic weeds*, *mussels*, or *floating debris* reduce the heat transfer potential of the condenser.

With a clean CW system the **condenser back-pressure** is a function of the condenser inlet temperature, so that:

- An incoming temperature of 55 °F (13 °C) should provide a low back-pressure of approximately ≅ 1.5 in Hg (5.1 kPa)
- An incoming temperature of 75 °F (24 °C) increases the back-pressure to ≅ 2.5 in Hg (8.5 kPa)
- An incoming temperature of 95 °F (35 °C) provides ≅ 3.5 in Hg (11.9 kPa)

Back-pressure also increases as generator load increases. Where scale deposition takes place on the condenser cooling-water side, a similar increase in back-pressure can be observed. The level of increase is based on a combination of deposit thickness and the particular mineral present.

As an example of the effects of a scale deposit, assume a copper-alloy tubed condenser operating at 70 °F inlet temperature, 2 in Hg back-pressure and in a clean condition:

- The deposition of 0.010 in of *calcium carbonate* scale results in an increase in back-pressure of 6 inches
- The back-pressure increase is to 7.5 inches for a similar thickness of *calcium sulfate* deposit
- This back-pressure further increases to 8.5 inches for *magnesium phosphate*

Other causes of loss of efficiency include:

- **Leaking tubes** resulting from seal failures
- **Fatigue** or **stress-induced cracking corrosion**

Poor condenser performance is ultimately reflected in the need for higher boiler firing rates, and thus higher fuel costs. Where condenser performance falls below the design specification, there are several checks that can be made, including:

1. Check the **condenser temperature terminal difference** (CTTD) and compare with design specifications. This is the difference between the *LP exhaust steam temperature* and the *CW outlet temperature*. Changes here will reflect one or more of the problems dis-

cussed earlier. A slight rise or fall in the CW inlet temperature typically does not affect the CTTD in a *clean* condenser.

2. Check the **temperature drop across the cooling tower** (ΔT). The cooling tower itself may not be operating efficiently. However, a higher than normal cooling tower basin or pan temperature (equivalent to the condenser inlet water temperature) may simply indicate higher-than-design condenser outlet temperatures that cannot be compensated for because of limitations on tower cooling capacity.
3. Check the **recirculating CW flow rate**. A decrease in flow rate results in a temperature rise.
4. Check the **recirculating CW pressure**. An increase in pressure drop indicates fouled or plugged tubes, or a fouled tube sheet.
5. Check the **condenser absolute pressure**. An increase in the condenser back-pressure, relative to design, is a sign of fouled tubes, air leakage, or poor overall cooling tower system performance.

3.5 BOILER PLANT OPERATIONAL AND WATER TREATMENT BASICS

Boiler operational management processes vary considerably in their degree of complexity. At larger facilities these processes are controlled by managers who are always qualified engineers (usually mechanical or electrical) and their operators are typically also appropriately qualified and licensed.

For smaller facilities this is not always the case, and many boiler houses will not necessarily require the presence of permanent operators, which can sometimes make the smooth implementation and seamless operation of a water treatment program quite difficult to achieve.

Boiler operational management processes provide for various daily procedures, maintenance routines and checks, including attending to BD, ash removal (where solid fuels are used), and the monitoring and control of fuel and MU water consumption, steam production, operating pressures, air and flue-gas temperatures, and FW and CR flows.

In larger facilities much of this monitoring work is carried out in *real time*, with the data transmitted to a remote control station. Increasingly, the corrective actions necessary may take place automatically through a computer modem.

For smaller boiler plants all relevant information is recorded in **logbooks** that provide a permanent operating and control record. The full and correct completion of logbook entries is mandatory.

Apart from daily routines, periodic boiler housekeeping, equipment lubrication, inspection, testing, maintenance, and cleaning, overhaul and repair work becomes necessary.

No matter the size of facility, some form of water treatment program is required and although it may form a relatively small part of the overall boiler plant operation, it is important. Effective boiler water treatment always requires some degree of capital investment for external treatment and the provision of an internal program appropriate to the boiler design and circumstances. Implementation of the program requires regular monitoring and trend analysis, experienced interpretation of all cause-and-effect aberrations, and a proactive, results-oriented approach.

3.5.1 Boiler Plant Mechanical Operational Functions

Boiler plant operational duties occasionally necessitate starting up boilers from cold (**cold plant startups** or **dead plant startups**), bringing a boiler online to support other operational boilers (**live plant startups**), and taking boilers *offline*.

Online boilers may be idle or may run on low- or high-fire and may operate under a variety of conditions, such as steady-state, peak-load, or lead and lag arrangements.

A **boiler lay-up** is provided when the plant is out of service for some period. The lay-up may be a *wet lay-up*, wherein water remains in the boiler and is intended only for short periods; or a *dry lay-up*, which is for extended periods.

Routine work typically includes monitoring and reporting load changes, unusual occurrences, machinery failure, steam leaks, and the like. In addition, boiler plant personnel carry out a number of other specific functions, including those tasks described in the following sections.

3.5.1.1 Water–Steam Appurtenance Checks

Water–steam checks include monitoring boiler NOWL and operating steam pressure, and the periodic testing of low-water cutoff controls, pressure gauges, and the FW regulator valve.

Operating without sufficient water remains the most common way to destroy a boiler. If there is any doubt about the ability to provide sufficient water, the boiler must be shut down.

3.5.1.2 Feedwater Supply System Checks

Feedwater supply duties include checking and recording the demand for FW makeup and maintaining correct FW temperatures to prevent risks of pump cavitation and boiler thermal shock. Periodically checking deaerator performance and inspecting the FW pumps and lines for any signs of fouling or corrosion is also required.

3.5.1.3 Fuel Management System Checks

Operators are required to maintain correct fuel pressures and ensure that the combustion equipment (burners, stokers, soot blowers, ash handling, etc., as appropriate) is in good working condition.

Operators also need to test flame failure controls, check the fuel delivery equipment (pumps, fuel lines, regulators, etc.), and keep adequate fuel consumption records.

3.5.1.4 Air and Flue Gas Management System Checks

Checks to the air and flue gas system include visually inspecting the furnace and periodically monitoring all fans, levels of draft, furnace pressure, excess air demands, and combustion efficiency.

3.5.1.5 Condensate Return System Checks

Condensate system requirements are to check the condensate pumps, steam traps, and overall condensate return system. A loss of condensate return necessitates an increase in MU water to compensate for the shortfall in the FW system.

3.5.1.6 Interlock Systems Function Checks

Inspecting and maintaining the interlock system is a vital function. It is required to ensure general safety and to avoid risks of boiler explosion. Interlocks provide for the safe sequence of boiler startup and shutdown procedures.

3.5.1.7 Instruments and Control Systems Checks

Annual checks of all instruments, recorders, and controls are required. Recalibration of some instruments may be required at more frequent intervals.

- **Boiler control systems** include combustion controls, superheat steam temperature controls and FW controls. Control systems are used to maintain steam pressure, boiler load, drum water levels, and fuel-air ratios.
- **Instruments** include pressure gauges to measure steam drum pressure, superheater outlet pressure, FW pressure, inlet and outlet draft pressure, and fuel supply and burner pressure.
- **Recorders** measure steam flow, air flow, FW flow, drum water level, steam temperatures, flue gas temperatures, flue gas analysis and smoke opacity.

3.5.1.8 Periodic Chemical Cleaning

Utility boilers generally require waterside chemical cleaning of all *boiler surfaces* every 300 to 500 days of operation, and this work may be carried out by specialist contractors. It is regarded as a "routine" function, irrespective of water chemistry, laboratory involvement, or the quality of FW treatment and water management provided. Chemical cleaning of utility boilers is designed to permit the boilers to operate at peak performance and within knife-edge control parameters.

Industrial WT and FT boilers, on the other hand, usually tolerate some limited degree of waterside deposition (but not corrosion), and with proficient operation, proper attention paid to chemical treatments, and good technical support services, may (almost) never require internal cleaning.

However, a problem common to some smaller facilities is the failure of operators to provide a **boiler wash-down** of the warm/hot internal waterside surfaces when draining a boiler (for, say, an *annual internal inspection*). When the boiler is not washed down, suspended sludge present in the BW quickly settles on the outside-top of FT tubes or on the inside-bottom of horizontal WT tubes and bakes on, thus creating a "dirty" boiler. This situation leads to a reduction in heat transfer and increased fouling, which may in turn interfere with natural circulation, and it also provides a rough surface for the collection of further sludge during the next boiler operating cycle. The sludge never becomes as hard as crystalline scale deposits, but after baking becomes far more difficult to remove.

Hot water and **LP steam heating boilers** generally accumulate some bottom sludge as a result of infrequent BD schedules. The sludge results either as reaction products of chemical treatments

added to the boiler, or from the precipitation of supersaturated MU water salts. In those boilers in which significant steam losses or HW leaks occur, the volume of sludge generated is significantly higher because the level of MU also is high. This scenario is very common, despite protests to the contrary—the difficulty is trying to confidently calculate the amount of MU used because in most cases there is no water meter on the MU water line. Often some *iron corrosion* debris is also present in the sludge as a result of unintended air infiltration or on–off heating cycles.

Because, for whatever reason, these boilers almost always have some level of sludge present after a winter heating season, they benefit from an annual **"boil-out."** This is a program in which the boiler is provided with a strongly alkaline, short-cycle cleaning program before being drained, washed down, and thoroughly flushed out. The boiler normally is subjected to a dry lay-up in preparation for the next heating season.

3.5.1.9 New Boiler Work

Following the completion of a new boiler installation, it must be inspected and any remaining debris must be removed, It is then subjected to hydrostatic testing and chemical cleaning prior to startup.

Preoperational cleaning (POC) of new boilers is always required but is often a last-minute item and not given the necessary attention it deserves, which may lead to operational problems down the line. A POC work program is needed to provide for:

- **De-oiling**, typically using a blend of chemical materials such as **caustic** and **alkaline phosphates** together with **nonfoaming surfactants**; the phosphates employed are generally either *trisodium phosphate* (TSP) or *tetrapotassium pyrophosphate* (TKPP)
- **Derusting**, typically using *gluconates* or other *chelants*
- **Passivation**, typically using *phosphates*, *hydrazine*, etc.

Immediately following the cleaning and passivation program, the boiler should be refilled and an **initial-fill dose** of suitable chemical treatment inhibitor(s) provided. The amount of treatment added is a function of the volume of water required to fill the boiler, whereas during boiler operation the feed-rate of chemical is proportional to the demand for MU water.

3.5.1.10 Off-Line, Safety and Other Appurtenance Valve Checks

Vital periodic testing and maintenance of safety valves, pressure relief valves, stop valves, and other items is usually carried out on a 12-month cycle. Boiler plant equipment fitted with such appurtenances (and thus requiring regular checks), include *boilers*, *heaters*, *deaerators*, *evaporators*, and *economizers*.

3.5.1.11 Boiler Inspection Work

Inspection of boiler pressure vessels is generally required every 12 months, but this period may be extended to 15 to 18 months under certain specific circumstances.

Preparing a boiler for inspection requires the operator to first follow a sequence of specific **boiler shutdown procedures**, including cooling the boiler slowly to prevent undue stress to the metal and refractory. The primary purpose of the inspection process is to ensure continued boiler safety, and therefore a thorough inspection of all appurtenances is mandatory.

Larger boilers are also regularly subjected to an *internal* physical inspection. This is not generally the case with HW and small LP steam boilers simply because they may be too small to enter. Consequently inspections of small boiler internals may be cursory or perhaps not carried out at all. Typically the process is relegated to a simple affair of removing lower **mudcovers** and peering in for a few seconds with the aid of a flashlight. This kind of inspection is of limited value because the observations are generally very subjective and generally fail to include the taking of photographs or some form of semiquantitative comparison with previous inspections.

Formal inspection programs present a good opportunity for the water treatment service company representative to undertake an *informal* internal inspection to observe the various *boiler surfaces* first hand, perhaps undertake some limited *nondestructive testing* (NDT) work, and record the results of the previous 12 months' water treatment management program.

Where such internal inspection work is carried, out a *safety checklist* and processes for *confined space entry permit system* and *tag-out/lock-out* MUST be undertaken before any person enters the boiler. The inspection of waterside surfaces should be carried out by a suitable qualified person and will benefit from employing either an *instant* camera or a video camera (**Boroscope™** or similar fiberoptic-based device) to record any parts of the boiler where corrective action is needed.

3.5.2 Water Treatment Program Management

As part of the overall boiler plant operational management process, various items of water treatment equipment must be periodically checked, tested, back-washed, regenerated, or otherwise maintained. Such equipment may include *filters, ion-exchange softeners and demineralizers, the RO plant, chemical feed tanks*, and *condensate polishers.*

In addition, attention must be paid to the BW internal treatment program. Such programs involve the dosing of small amounts of **"polishing" chemical treatments** to specified points in the water–steam cycle system, often continuously and proportional to water flow or steam demand, to provide a desired inhibitory or protective effect.

Also, the particular boiler plant water–steam chemistries must be reviewed and interpreted at regular intervals. The specifics and complexity of this work depend on the type of boiler plant involved and the respective chemical treatment programs employed. The frequency of testing may range from hourly to perhaps monthly, again depending on the type of boiler operation.

For larger plants some water analysis, results interpretation, and recommendations for operational changes may be carried out by a boiler operator, water treatment plant technician or a laboratory analyst (or even by an outsourced subcontractor); these recommendations complement similar work undertaken by the water treatment service company representative.

3.5.2.1 Chemical Treatment Additions

Traditionally, boiler house operational duties include the monitoring of day tank chemical treatment levels and the top-up of additional chemicals as required. Also required is the checking of consumable inventory stock levels and the inspection of chemical feed pumps, injection points, automatic controllers, and other items of dosing and control equipment.

3.5.2.2 Chemical Treatment Testing and Interpretation

Some of the chemical treatment testing work may fall to a boiler plant operator or laboratory analyst, and such involvement generally is a good idea because it stimulates interest in the boiler-related treatment processes and the chemical programs provided to a site. However, irrespective of the level of technical qualifications held by site personnel,

training in the *interpretation* of analytical test results is a must because it is a special skill. Mastery of this function is key to attaining good long-term waterside results.

NOTE: In practice, the skills required to correctly and comprehensively interpret the various water analyses and provide suitable recommendations for action are not widely available outside the ranks of the service companies. When selecting a water treatment service provider therefore, this element should factor significantly in the vendor evaluation process.

If full and correct interpretations are not provided, any subsequent advice, instruction, or actions are unlikely to be fully beneficial, and boiler waterside problems may occur and magnify very quickly. The cause of the problems that develop undoubtedly will have a long-lasting and eventually deleterious or seriously expensive effect,

Unfortunately, in the field it is not particularly uncommon to find that incorrect conclusions may be drawn or perhaps inadequate attention be given to particularly vital analytical results. Alternatively, there may be a slavish adherence to written control limits without due regard to the practical operation of the boiler plant and economic implications. It is therefore worth reinforcing that, irrespective of the size of the boiler plant under consideration, proper water treatment training and relevant experience (especially with regard to results interpretation, assessment of trends, periodic review meetings, and preemptive management) is *essential* to the success of a water treatment program and the benefits it provides.

3.5.2.3 Water Treatment Management Reviews

A periodic review of ongoing water treatment programs with regard to suitability, economic benefit, training needs, and technical objectives also is required.

Water treatment technical service representatives must develop relationships with boiler plant operators and managers and formally meet on a periodic basis so that all involved understand what must be achieved and work in concert toward reaching common, agreed-upon objectives. The frequency of meetings depends on the size of the boiler plant, but essentially, informal communications should take place (up and down the line) very regularly, with a formal program review taking place perhaps every three to four months.

Senior facilities managers should never abrogate responsibility for final review of water treatment programs. Such programs may be com-

monplace, but they typically protect hundreds of thousands or millions of dollars of investment and remain a critical component in the successful operation of any boiler plant. If the boiler or an auxiliary shuts down as a result of inattention to the waterside conditions, then no heating is available, no steam is produced, no electricity generated, and industrial production comes to a halt.

3.5.2.4 Full-Service and Outsourcing Programs

In the world today there is there is a clear trend in almost every market sector for companies and organizations to focus their activities on enhancing core-competencies and build national or global market brands to advance their respective market leadership positions. As a result, many noncore activities are often subcontracted to a service company rather than being undertaken by the organization's own employees.

This development has for some time involved many aspects of the boiler water treatment market but has recently extended further into the overall utilities sector. There are perhaps three levels of extended services now available: the water treatment full-service program, the provision of contract labor to run a company's boiler plant, and the outsourcing of utility components or the entire facilities.

- **Full-service programs:** The demand for a wider variety of *added-value (value added)* services at a customer's facility has led to the provision of full-service programs by many water treatment service companies. Full service is replacing the more traditional **technical supervisory service** provided by the company's technical representative. Full-service work may include the delivery of chemical products, refilling of storage tanks, and the removal of empty containers (**drumless delivery service**). Also, the regular inspection of chemical dosing facilities including chemical product mixing and addition to tank operations, and the review of chemical storage and spill containment facilities. Such work may additionally include all technical aspects of the job, equipment inspections, malfunction corrections, and some specific cleaning and maintenance work.

  This type of service is clearly beyond the scope of a single technical representative, and typically the job has grown in complexity so that the representative now has become a service manager for his or her customer. As such, the representative is responsible for ensuring the smooth and seamless provision of a wide variety of specialist technical services, not merely the chemical water treatment aspect.

Full-service programs require that the water treatment account representative be part of a larger sales and services and technical support team. When such a team subscribes to quality work standards and environmentally responsible practices, they present a formidable taskforce and a valuable partner to their customers.

- **Utilities plant contract labor:** Today these chemical water treatment–based full-service programs may be further enhanced by the supply of various boiler plant mechanical and electrical maintenance and repair work, plus energy management services, all from a single supplier source. In fact, many customers are now replacing their entire utilities staff with contract labor under a utilities service contract. The utilities plant contractor usually subcontracts the water treatment full-service component to a specialist water treatment and environmental services company.
- **Utilities outsourcing:** The complete outsourcing of utilities, such as the provision of steam and water, is the next level. In fact, many organizations around the world have purchased steam from a neighboring manufacturing facility or from a utilities supplier for many years, but today there are many permutations on this theme. For some time it has been common to hire a boiler or even a turbine generator on a temporary basis. Now it is easy to hire the water treatment plant, or simply to buy the MU water needed to run the plant. Under these schemes, contractors may provide trailer-mounted water treatment equipment, which is simply driven in and hooked up directly to the customers deaerator or FW tank.

  The latest **outsourcing** development is for giant services companies to bundle their services together to provide a **"one-stop shop."** A services contractor may provide some form of permanently installed utilities plant under a **build, own, operate, maintain program** (BOOM), so that the customer merely pays a contract fee to receive water, steam, electricity, and other services. Thus, the entire responsibility for the provision of utilities can be passed to a contractor, and not merely at one facility, but globally!

However, for most smaller industrial and commercial or institutional facilities around the world today, the concept of outsourcing just about every aspect of the requirement for utilities is not on the agenda, but it undoubtedly will come when the time is right. In fact, the added cost of full services is often prohibitive in those countries where in-house labor rates are low; thus, much of the boiler plant preventative

maintenance and good housekeeping work remains in the hands of the facility's own operators or laboratory personnel. Nevertheless, the demand for full-service water treatment programs will continue to grow, and new types of control and technical support services are likely to be offered periodically to the marketplace. These service programs will doubtless be aided (if not fueled) by the continuous developments in global communications and the rapid accessibility of *real-time* monitoring and *online* information.

4

WATERSIDE AND STEAMSIDE PROBLEMS: THE BASICS

All boiler plants require the application of some type of water treatment program and water–steamside chemistry control to meet the owners' and users' specific **strategic**, **operational**, and **economic objectives**. In many cases, the objectives may be limited and the treatment simple, but some form of program and control over water chemistry is required. Even with the smallest hot water (HW) boiler in which a magnetic device may have been installed to "condition" the makeup (MU) water, control over the ingress of oxygen is required to limit internal pitting corrosion. Similarly, an indirectly fired waste heat (WH) boiler recovering heat energy present in hot gases of combustion will require suitably treated FW if it is to function effectively with minimal maintenance year after year.

At the *strategic level*, boiler water treatment practice is essentially the planned, actioned, and documented management of the waterside of pre-boiler, boiler, and post-boiler plant equipment and systems. A key objective is to identify, obtain, and maintain operational and economic benefits for the plant owners, including maintaining the cleanliness and structural integrity of the boiler, its various water–steam cycle auxiliaries, and other components for a specified (long-term) period and to some quantifiable standard.

To achieve this objective at the *operational level*, consistently good water treatment practice is required on site. However, achieving this objective cannot and should not be the sole prerogative or responsibility of any one person. Rather, if success is to be attained and maintained, it requires a proactive approach with joint participation, support, and communication by the water treatment service company and the owners and/or operators of the boiler plant.

In each and every boiler plant around the world, almost without exception, the absence of a decent water treatment program most certainly will ensure that these operational and economic benefits are not attained. Cooperation is required between all parties, and in practice the necessary water treatment functions are inextricably interwoven within the daily mechanical operation of the overall boiler plant.

The design and provision of an appropriately innovative and cost-effective water treatment program generally falls squarely upon the service company, while some of the basic operational functions of the program such as *producing day-tank batches of treatments*, *testing various water samples*, or *adjusting treatment dose rates* often are carried out in part by boiler house, maintenance or laboratory personnel. (However, the rise in the supply **of outsourced utility services**, **drumless delivery systems**, **real-time remote monitoring**, and the like, as discussed in Chapter 3, is evidence of a significant change in thinking in this traditional approach to applied water treatment.)

In addition to supplying the various water–steamside conditioning equipment, chemical treatments, and periodic cleaning or other specialist services, service companies are expected to provide advice, practical expertise, and general support for their program in a proactive manner, to prevent waterside and operational problems from occurring.

When problems do arise, detection and identification of the causes, together with suitable remedies that will prevent reoccurrence, are required.

4.1 HOT WATER AND STEAM SYSTEM CYCLES

4.1.1 The Hot Water Heating System Cycle

At its simplest, a *HW heating cycle* is the circulation of HW from a boiler (or heat pump or similar device) through a supply and distribution piping system to various appliances and then back to the boiler. Hot water systems are **hydronic systems** and, when of any size, are designed to operate via various primary and secondary circuits. These circuits are provided with their own circulating pumps of different capacities to provide proper layout flow, usually to perimeter-wall *fin-tube convectors*, *fan coil units*, or other **space heating** equipment.

Apart from meeting space heating demands, many HW (and LP) steam boilers provide a heat source for domestic HW systems by the incorporation of a bank of finned copper coils located within the top section of the boiler. From these coils indirectly heated water is deliv-

ered to *calorifiers* or other domestic HW storage systems, or continuously circulated in a loop back to the coils, with take-offs providing supply points to individual users. The indirect loop typically contains a mixing valve for cold water (CW) top-up and temperature control.

In *heating, ventilation, and air-conditioning* (HVAC) *system* designs, the hydronic heating systems also may incorporate cooling or chilled water circuits, laid out as **two-pipe** or **four-pipe** systems. These terms typically refer to:

- **Two-pipe system:** This system uses a HW heating supply (pipe 1) and return (pipe 2). Two-pipe systems also may refer to **dual-temperature** (dual-temp) systems, whereby the same distribution piping is also employed for *chilled-water cooling*. Typically, there is a changeover from heating to cooling in the spring and back again in the autumn. However a drawback of basic dual-temp designs is that they tend to fail to cope with cool mornings and warm afternoons. Today, digital electronics are employed to solve the practical workability issues of the two-pipe systems, with flow transmitters providing information on system total flow and tons of heating/cooling demand, and microprocessors controlling boilers, chillers, and pumps to meet that demand. In some countries, "two-pipe" may simply mean two one-pipe systems (HW flow and CW flow).
- **Four-pipe system:** This layout uses HW supply and return pipes for space heating (pipes 1 and 2) and chilled-water pipes for space cooling (pipes 3 and 4). Effective building climate control by conventional means is easier with a four-pipe system, but the piping costs obviously are much higher.

In an ideal HW heating cycle, there is no loss of recirculating water and therefore no regular requirement for MU water. In practice, no HW systems operate as fully sealed **closed loops**, and there are always some unplanned water losses from leaking pump glands and other factors, despite protests to the contrary from some operators. (In some cases, this water loss is very significant and is a prime cause of the waterside scale and corrosion problems that subsequently develop.) There is also some minimal requirement for the periodic blowdown (BD) of sludge generated within the HW system, primarily in the boiler. These water losses introduce fresh water containing oxygen and other contaminants into the system, providing the potential for problems such as corrosion to occur. A water treatment program.is necessary for these applications.

4.1.2 The Steam System Cycle

The steam system cycle is a regenerative *water heating*, *steam generation and delivery*, and *condensed steam recovery* cycle. It involves the operation and management of a boiler(s) and some or all of the auxiliaries and balance of plant equipment discussed in Chapters 2 and 3.

The complexity of the steam system cycle varies enormously; in its simplest form, where the steam is used to provide *space heating* (via radiators) or *process heating* (via a steam coil), it is essentially equivalent to a HW heating system cycle.

When steam in the cycle is lost or used in a process, the reduced volume of returning condensate is compensated for by introducing some level of MU water. The loss of water or steam from a steam system cycle may vary from 1 to 100%. The supply of MU (and to a lesser degree the addition of chemical treatments) provides a source of dissolved solid contaminants that can concentrate in the boiler until some predefined limit is reached. At this point, BD is required, the loss of which is also compensated for by the addition of further MU water.

Primarily it is the demand for MU and its quality (by which we mean the level of natural and introduced contaminants present in the water), coupled with the boiler and support equipment design and materials of construction under consideration, that collectively provide for a unique set of potential waterside problems in any individual steam system cycle.

As a precursor to discussing the fundamental waterside problems, two schematic drawings of steam cycles are provided. These examples (Figures 4.1 and 4.2) display the water–steam path and the key items of equipment in a **FT boiler plant steam system cycle** and a **WT cogeneration steam system cycle**.

4.2 THE SCOPE OF BW TREATMENT AND CONTROL OF STEAM/WATERSIDE CHEMISTRY

Proper BW treatment is largely concerned with the management of boiler plant and steam system internals through the practical implementation of appropriate treatment programs. These programs are designed to counter the omnipresent risk of waterside problems developing, to support and add value to production processes, and to help control the demands and costs of maintenance within agreed limits.

As a minimum, such boiler water treatment programs typically require:

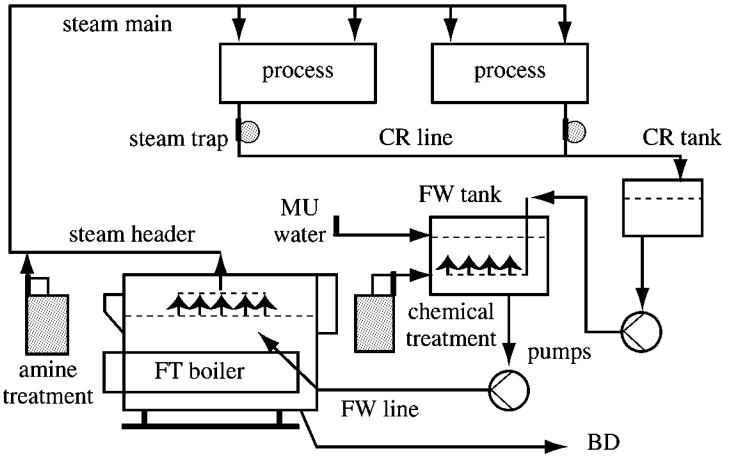


Figure 4.1 Steam cycle path in FT boiler plant.

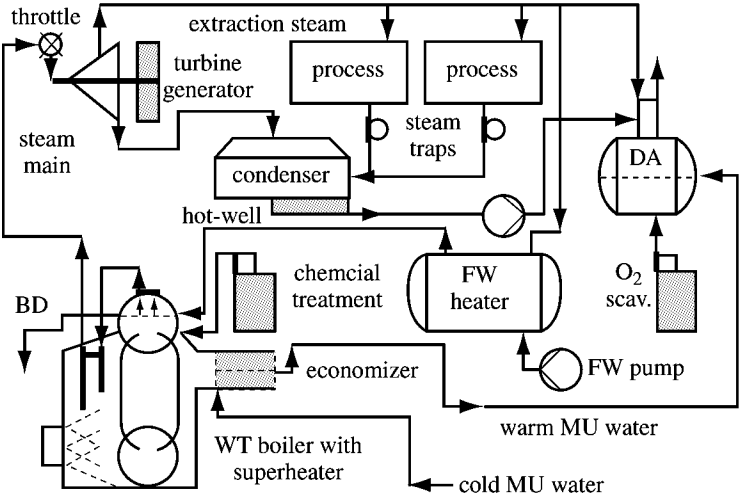


Figure 4.2 Steam cycle path in WT boiler congeneration plant.

1. The selective utilization of *external* water conditioning equipment
2. The addition and monitoring of small amounts of *internal* specialty "polishing" treatment chemical formulations
3. The control of steam–water and internal surfaces chemistry within closely defined parameters
4. The interpretation and communication of the results obtained, together with practical advice on corrective actions and waterside management

The initial cause of many waterside problems is the various dissolved solids, gases, and other impurities introduced into the boiler from the MU water, the atmosphere, and associated industrial or other processes. These impurities may produce **scale** and also lead to **corrosion** and other operational problems.

Crystalline scales and other minerals may form **deposits** that reduce the effectiveness of the boiler as a *heat transfer device* or cause **fouling** that can impede the flow of water and cause overheating by reducing the level of furnace cooling below design specifications. The presence of *process contaminants* also leads to fouling.

Corrosion anywhere within the steam-water circuits results in **metal wastage** and possible **equipment failure**. And if the boiler plant is not operated correctly or if the water chemistry is not maintained within certain control parameters, the generated steam may contain contaminants in a **cause-and-effect process** that ultimately affects the utilization of the steam, reducing quality in a number of areas, and increasing fuel, manufacturing, or maintenance costs.

Where problems develop, there is almost always a chain of cause and effect rather than any single cause, so that problems originating, for example, in the *pre-boiler FW system* may produce additional problems in the *boiler* itself, or perhaps the *post-boiler condensate system*, or in any *balance of plant equipment* such as a turbine.

There are several fundamental waterside problems that may occur, each involving a combination of *physicochemical* reactions. Some of these problems are specific for particular boiler system types and designs, while others are more general in nature and have the potential to cause trouble to all manner of HW and steam-raising plants.

In addition, some waterside problems occur partly as a natural result of operating very complex steam generating and mechanical processes and as such can never be totally eliminated. Nevertheless, a failure to adopt best operating practices or to strictly control the steam–water

chemistry throughout the *entire* steam cycle will rapidly increase the rates of reaction and the development of problems. This in turn raises operating costs and hastens the onset of costly maintenance and repairs.

Most waterside problems develop insidiously. Over time, *scale* and other types of *deposit* are gradually formed on internal heat transfer surfaces, which gradually raises the cost of providing heat energy. Some types of deposition can be very difficult and costly to remove. *Corrosion* wastes away the fabric of the plant (sometimes very quickly) and may produce an unexpected and untimely boiler plant shutdown, with a consequential loss of space heating, electricity, or process manufacturing capability. Likewise, *fouling* reduces the size of waterways and increases boiler operational problems.

Thus, the entire thrust of a water treatment program requires a *proactive approach* to potential problem identification and resolution. The scope of the program should therefore be wide enough to include not only all relevant conditioning equipment and chemical treatments but also a variety of technical and operational support services.

Service company representatives and other personnel involved in implementing a BW treatment program must regularly attend to a number of basic operational functions, including:

- Analyzing water samples (from all parts of the plant not just the boiler)
- Cross-checking and interpreting the various results obtained against predetermined specifications and norms
- Monitoring logbook events, gauges, recorders, day tanks, and chemical stock levels
- Inspecting all associated pretreatment equipment, pumps, tanks, and valves; also, all internal water surfaces whenever a boiler, condenser, FW heater, or other item of equipment is opened
- Reviewing with the customer's operators and management the current waterside status and new problems identified, current treatment program progress, and future objectives

The scope of any program for BW treatment and steam–water chemistry control necessarily includes surveying, monitoring, and possibly treating or otherwise conditioning various types of water.

Typically, there are several different types of water or steam commonly employed in most HW heating and steam-generating plants. In a large, complex steam system there may be a dozen or more different

streams that may eventually pass through the boiler proper, including those listed below.

- Raw water
- Externally conditioned, preheated, or intermediately treated MU water
- Finally conditioned or treated MU water
- Chemical treatment batch dilution water
- Feedwater
- Boiler water
- Boiler water blowdown
- Steam–water recovered from a flash steam and heat recovery (FSHR) system
- Steam–water recovered from a process reaction
- Circulated HW
- Generated steam
- Superheated and reheated steam
- Condensed steam
- Save-all system water
- Filtered or polished condensate or return HW
- Attemperator water

In addition to *external* conditioning processes and the need to provide *internal* chemical treatments to some or all steam–water circuits within the steam cycle, the scope of boiler water treatment includes, as mentioned earlier, the provision of suitable technical resources sufficient to control the steam–water chemistry within defined limits appropriate for the boiler plant under consideration. Because these **steam–water control limits** tend to narrow considerably with increase in *boiler pressures* (and *heat-flux densities*), suitable monitoring and control procedures may require implementing actions with knife-edge precision.

As part of the overall boiler plant design or water treatment program, some form of **pre-boiler conditioning** is almost always provided, such as through the use of *filters*, *ion exchange equipment*, *evaporators*, or *reverse osmosis (RO) plants*. Sometimes **post-boiler conditioning** is also provided via *condensate polishers* or *magnetic particle separators* for the removal of ferromagnetic iron.

For the most part, these various forms of **external treatment** involve the use of "capital expense" equipment, whereas the term **BW treatment** is ordinarily employed to indicate the addition of various types of "maintenance expense" **internal treatment** specialty chemicals.

*NOTE: Simple HW heating and LP steam boiler treatment apart, the term **BW treatment** is unfortunately often something of a misnomer. The practice is, in fact, generally recognized to be primarily concerned with adjustments to the boiler FW chemistry and the addition of "polishing" chemicals to compensate for deficiencies or potential problems associated with the FW rather than with the recirculating BW.*

Thus, it is the combination of both external conditioning and internal treatments, together with some level of associated technical and support services, that most properly comprises a comprehensive BW treatment program.

Large utility boiler plants may be considered an "industry," with one of their primary manufactured products being steam (electricity is the other). As a consequence, most utilities possess considerable internal technical resources and have additional access to specialists to support their primary industrial focus, and many utilities can therefore manage their water treatment needs in-house.

However, most other types of organizations (such as the millions of commercial, institutional, and industrial buildings and facilities globally) do not produce water or steam as a primary product. Rather, they focus on their own market arenas, with the result that, by and large, they lack adequate skilled water treatment expertise and resources internally. These industries therefore employ water treatment service companies as specialist contractors.

Service company contractors generally can provide a wide range of BW treatment programs, with each program having a certain degree of flexibility in design and utilization. As part of the program, dozens of blended chemical formulations are potentially available for utilization. For any particular customer's facility, selections are based partly on economic considerations but also on ensuring compatibility with each pre-boiler conditioning process installed and to counter anticipated problems that may arise under the particular operational circumstances.

Thus, in practice, most treatment programs are specifically tailored for the boiler plant in question. The program must then be properly and quickly integrated into normal day-to-day operating practices in order for the boiler plant owner to gain long-term economic and operational

benefit and for the service company provider to begin to generate a sustainable profit.

Apart from the provision of various permutations of (chemical-based) boiler water programs, it is common to find water treatment companies supplying *value adding* chemicals and services in other boiler plant–related areas where their expertise in **applied chemical technology** can deliver additional economic benefit. Such areas typically include *cleaning services* for boiler waterside and fireside and the provision of *fuel treatments* and *combustion additives*, *dust suppressants* (for coal and ash handling), *acids*, and *cleaner products*.

4.3 FUNDAMENTAL STEAM–WATERSIDE PROBLEMS AND WATER TREATMENT OBJECTIVES

In any boiler system, there are several fundamentally different problems that may develop. Some problems may specifically affect only the waterside *boiler surfaces*, economizers, or condensate system, but *all* will ultimately adversely affect the overall HW or steam-system cycle and raise the cost of doing business.

These various problems may arise under several different circumstances. For example, difficulties may result from consistently poor operational control of the boiler plant or from enforced operating conditions that fall outside generally accepted procedures. Alternatively, problems may stem from malfunctioning equipment, from equipment design flaws, from inadequate water treatment programs, or even as a result of poor interpretation of monitored results and bad water treatment advice.

Not all the problems that arise are clear-cut; in fact, one problem may often mask another problem– or several minor problems may prove to be interdependent—providing a chain of cause and effect. As a result, different authorities may not always agree on the fundamental cause of a particular problem or even the precise chemistry involved. Terminology and problem definitions also may vary from country to country.

This book proposes that in **two-phase** steam–water systems, there are *four* fundamental waterside problem areas:

- **Deposition**, which limits heat transfer
- **Corrosion**, which damages and eventually destroys metal
- **Fouling**, which impedes steam–water flow
- **Contamination**, which adversely affects steam purity

The distinction between a **foulant** and a **deposit** is not always clear. For example, although a settling sludge may have a *fouling action*, it also may settle onto a horizontal heat transfer surface and bake hard—for all intents and purposes acting as a deposit and insulating the heat transfer surface. Similarly, **scaling deposits** often have a rough outer surface that can cause a *fouling action* by increasing drag and reducing the natural BW circulation flow.

In practice, both fouling and deposition actions are likely to occur simultaneously to some degree or other in a boiler system. Furthermore, **corrosion processes** and the entry of **contaminants** into the steam–water system usually results in some form of *deposition* occurring elsewhere in the system.

As a further example, **process contaminant** materials such as *oil* can commonly enter the steam–water circuit. Unfortunately, oil has a strong *binding action* and can attach to corrosion debris suspended in the water to form adherent deposits that may initiate **"hot spot" scaling**. In addition, where hardness salts enter the boiler, contaminating oil can produce a secondary fouling action by binding with freshly suspended calcium or magnesium sludge.

Thus, each of these fundamental problems may manifest itself as either a stand-alone problem or a compound problem. They can also support or promote the development of other problems. Each fundamental problem can in turn be subcategorized and may arise in the boiler plant by any number of different mechanisms, ultimately affecting a wide variety of equipment.

These scenarios are borne out in practice, and where boiler waterside problems are identified, there almost always is more than one contributory factor. Investigation usually reveals a chain of cause and effect. Typically, any specific causative agent identified (such as oxygen) affects more than one part or component of the overall system.

Also, in any particular area of a boiler plant system under investigation, it is common to be able to identify two, three, or more discrete, but interdependent, problems developing at the same time. This is especially noticeable in systems where evidence of both deposition and corrosion exists. The deposit may contain corrosion products, and the corrosion can often be traced to other problems originating further back in the steam–water cycle. For example, corrosion of **low-alloy steel** boiler tubes may occur as a result of the presence of **copper** plating out in the boiler. The copper typically originates from a corroded heat exchanger. The resultant corrosion product is swept into the boiler with returning condensate, providing the causative agent for a secondary problem.

Finally, although the basic development and nature of boiler water plant problems may be similar to those arising in other types of water systems (such as cooling water systems), the extremely high steam–water temperatures and heat-flux densities generally encountered impart a much higher level of intensity. This in turn creates the need for more highly focused and effective solutions to boiler plant problems.

4.3.1 Treatment Objectives

The practical objectives of BW treatment are:

1. To maintain all boiler surfaces and other waterside surfaces in the HW and steam-system cycles in a structurally sound and clean condition, properly protected against the operational and economic problems associated with deposition, corrosion, fouling, and contamination
2. To promote waterside conditions that permit the efficient delivery of HW or good quality, uncontaminated steam
3. To provide technical and other support services to add value to boiler operations and production processes
4. To create an awareness of the program objectives and their importance, and to establish customer confidence in the program's operational strategies through training, mutual cooperation, communication, and management review

For any boiler plant under consideration, the selection of appropriate programs and the application and control methods employed should be consistent with these objectives.

4.3.2 Basic Interrelationship of Waterside Problems with Boiler Design and Operation

Most HW and LP steam boilers (i.e., those that operate below 15 psig) and many smaller high-pressure (HP) steam-raising boilers employ, at best, relatively simple methods of FW pretreatment and a basic internal chemical treatment program. Many times no pretreatment is provided.

This limited sophistication in the provision of water treatment typically is a reflection of:

- The relatively low heat flux of such boilers
- The lack of importance sometimes attributed to the detrimental effects of many waterside problems

- The perceived need to keep external and internal treatment costs in line with either the output of the boiler or its original capital cost; in other words, "if it is a small boiler it does not require much in the way of water treatment," which is seldom true!

It also is true that certain design limitations imposed by the small physical size of such boilers may mean that more sophisticated treatments will, in practice, provide no additional benefit to the operator. Nevertheless, there are exceptions, and some designs of low output but high heat-flux boilers (such as most of the makes of HP vertical FT boilers available) in fact require quite sophisticated programs and must be controlled within very tight parameters to maintain optimum output and operational efficiency.

As a general rule, however, the following is true:

Where MU requirements are high, irrespective of absolute boiler output, more sophisticated water conditioning is usually warranted than would otherwise be provided. Also, as boiler output and operating pressures increase and heat and mass transfer issues become more critical, so the demand for more exacting water treatment programs, monitoring, and control activities increases in importance.

Under higher waterside pressure conditions, consideration of **bulk water** *turbulent flow*, the thickness of the steam–water *laminar flow* **sublayer film** at the heat transfer surface, and the general waterside **physicochemical operating conditions** that exist are important issues in reviewing the potential risks of deposition, corrosion, and other problems that may occur within an operating boiler.

The *sublayer film thickness* and its chemistry are functions of boiler design, FW pretreatment, and boiler operating conditions. This film essentially provides the primary source of resistance to heat transfer from the metal wall to the bulk water that circulates within the boiler. Under boiler operating conditions, the water solution undergoes a concentration effect as a result of the temperature gradient, with the degree of concentration *decreasing* from the metal wall out to the edge of the film.

For most HP boilers, the sublayer film temperature gradient is more important than the bulk boiler water chemistry in determining the risk of deposition of salts. If a local overconcentration of salts occurs, waterside scaling and deposition are the inevitable results.

In typical cause-and-effect mode, where **chlorides** penetrate the deposit or where a localized overconcentration of **hydroxyl ions** occurs, the magnetite film is disrupted and particular forms of very damaging corrosion occurs. In addition, where localized heat flux exceeds design limits within a boiler and may be accompanied by **departure from nucleate boiling** (DNB) conditions, overheating and metal failure may also occur.

Thus, the proper control of deposition, corrosion, and fouling and boiler structural integrity are interdependent functions, and all these phenomena are directly related to boiler design and real-time operating conditions.

Some of these areas of control are individually discussed in the following sections but should be considered in the context of the interrelationship that exists.

4.4 DEPOSITION

Deposition involves the formation and precipitation of both **crystalline** and **amorphous** (*noncrystalline*) **scales** and the ultimate adherence of these **mineral salt scales** onto a heat transfer surface. Problems of deposition have the deleterious effect of *reducing* the rate of heat transfer, thus *increasing* the heat input requirements and raising the costs of operation. In addition, deposition reduces the efficiency of cooling the fabric of the boiler (especially the heat transfer metals), which leads to long-term problems of **fatigue failure**.

Corrosion may also occur under deposits, and the removal of a deposit from a heat transfer surface typically may expose a pit or other form of metal wastage.

Scales may originate at some distant point within the steam–water circuit and only deposit at a point of high heat transfer. Or they may simply originate and concentrate locally on **boiler surfaces**, especially if the boiler is *highly rated.*

Deposits found in boilers and other steam–water circuits tend to originate from several possible sources, including the following:

1. The most common source is the **supersaturation** and subsequent scaling of minerals originating in the MU water. Insoluble **calcium carbonate** in the form of **calcite** ($CaCO_3$) resulting from the thermal decomposition of soluble **calcium bicarbonate** [$Ca(HCO_3)_2$] is a classic example. Calcium carbonate quickly forms a white, friable deposit. In addition, the hydrolysis of excess bicarbonate increases

the concentration of hydroxyl ions, resulting in the precipitation of **magnesium hydroxide** [$Mg(OH)_2$].

The precipitation of **anhydrite** (*anhydrous calcium sulfate*, $CaSO_4$) may also occur. Under ambient temperatures, anhydrite is much more soluble than calcium carbonate, but because calcium sulfate, in common with other calcium salts such as **calcium phosphate** (also known as *tricalcium phosphate* [$Ca_3(PO_4)_2$]), has an **inverse-temperature solubility**, it deposits more rapidly on the hottest heat transfer surfaces.

In addition, naturally occurring **silicates** may form hard, insoluble deposits such as **quartz** (SiO_2) and **analcite** ($Na_2O{\cdot}Fe_2O_3{\cdot}4SiO_2$).

2. A further source of boiler deposits is the potential for the localized overconcentration and deposition of water treatment chemicals added to the system, and the scaling and sludging that may subsequently occur in the BW as a result of reactions initiated by the presence of the water treatment chemicals. An example is the deposition that may result from the use of standard, phosphate-based precipitating treatments that are employed to remove residual calcium hardness. If phosphate is added to FW lines or tanks and the FW pH level is relatively low (say, below approximately 8.3), a phosphate precipitation reaction typically occurs and results in the formation of *calcium phosphate*, a hard, dense scale. However, under higher pH level conditions (such as in the boiler water itself) the reaction produces **hydroxyapatite** [$Ca_{10}(OH)_2(PO_4)_6$], which is more desirable, being a relatively soft flocculant sludge, that in the presence of a suitable dispersant can be easily blown down from the boiler. Thus, to avoid the risk of FW system deposits, phosphates are generally added directly to the BW, especially with HP boilers.

   Nevertheless, even if phosphate is added directly to the boiler, if this sludge is not removed by BD it eventually settles and acts as a foulant to impede flow in the boiler waterways. Furthermore, without adequate dispersants during boiler operation, or if the boiler is not flushed out when drained down, the sludge may bake onto a heat exchange surface and generate an adherent, heat transfer–resisting deposit.

3. Another source of deposits is materials in the steam–water circuits. Acting separately or collectively as *foulants* and *contaminants*, these can pass to the boiler and combine to form deposits that stifle heat transfer. Corrosion debris from corrosion processes occurring at other points in the steam–cycle system can certainly form deposits, and the corrosion product *ferric oxide* (in the form of

hematite, Fe_2O_3) has a natural binding action similar to oil and other contaminants found in the steam–water circuits.

Foulants and contaminants may originate virtually anywhere in the overall steam–water circuit. Some may be derived from pre-boiler systems (such as an *economizer* or *deaerator*) or post-boiler systems (such as a *steam trap* or a *condensate line*), but they inevitably find their way into the boiler and cause significant damage and expense.

The tendency to form boiler waterside deposits is partly dependent on factors such as the solubility of the particular mineral species and the strength of physical adherence involved. As a general rule, the rate of deposition tends to increase with higher levels of BW dissolved solids. Also, the rate of deposition increases with increase in heat-flux density and with the inadequate dosage, inappropriate feeding, or otherwise usage of **antiscalants** and other **deposit control agents** (DCAs).

Deposits also are commonly formed as a result of corrosion processes. For example, at *lower* FW temperatures and *higher* oxygen concentrations (conditions often found in food processors, laundries, or dye houses, where small low-load FT boilers generate steam for batch operations), the corrosion product **hematite** is often formed.

Magnetite (Fe_3O_4) may also be found in deposits, although under the reducing conditions strived for in BW treatment, magnetite naturally occurs and is *desirable* in that it forms a tough, protective film on the metal surface.

Smaller amounts of various other metals and their oxides are also commonly found in deposits including **copper**, **zinc**, **nickel**, and **aluminum**.

4.4.1 Mechanisms of Deposition

High heat-transfer rates at *boiler surfaces* promote rapid nucleate boiling and other forms of convective boiling, which in turn may cause **steam blanketing**.

Under these conditions, localized mineral supersaturation will lead to the precipitation of various scales and their ultimate deposition on the heat transfer surface without the possibility of **scale resolublization**. This is because surface washing by bulk BW (with or without the presence of water treatment chemicals) cannot take place due to the presence of the insulating steam blanket.

As a consequence, *highly rated boilers* require higher quality, pre-boiler water treatment and *very careful* attention to the internal chemical treatments used and the overall internal water chemistry.

*NOTE: In practice, **"higher quality, pre-boiler water treatment"** generally means the use of FW with significantly lower levels of dissolved solids than typically employed in lower rated boilers. Additionally, it implies the reduction of certain specific minerals, ions, and noncondensable gases to meet very low, or extremely low, concentration specifications.*

Low heat-transfer rates at *boiler surfaces* generate only low steam outputs. Under these conditions, the mechanism of deposition is different from that of highly rated boilers.

With an inadequate BW treatment program, the resultant water chemistry may permit the very gradual (but persistent) formation of scaling deposits, the development of which may go unnoticed for some considerable time.

In WT boilers, if the resultant gradual decline in operating efficiency is not recognized, operators may find boiler tubes partially or totally blocked. This can prove expensive because the boiler will have to undergo extensive cleaning and probably some retubing work.

Under the same conditions of low heat-flux density, poor water chemistry, and gradual scaling circumstances, FT boilers may easily lay down from 1/16 to 1/4 inch of scale (6–12 mm) or more during a 12-month period. Tubes may become bridged by scales and sludges. Again, cleaning is required and the extra costs incurred for wasted fuel can never be recovered.

The mechanics of deposition in a boiler are often a cycle of cause and effect, wherein an initial low level of scale deposited on *boiler surfaces* causes a rapid localized rise in wall temperature. The temperature increase leads to localized steam blanketing, which in turn prevents the deposit from resolubilizing. Consequentially, conditions then exist for the further buildup of deposit on the heat transfer surface.

Deposit morphology is very important in determining the origins of mineral deposition. The analysis of the deposit may reflect a chain of cause-and-effect problems, and these problems may stem from any of several points within the steam-cycle system.

Analyses of deposits from lower pressure boilers may vary widely and may comprise several major constituents from a wide spectrum of minerals, although typically there are one or two dominant materials present such as *calcium and magnesium hardness salts* and *iron oxides*.

The potential for hardness salts to represent a dominant part of any deposit usually is reduced with an increase in boiler pressure. This is because higher pressure boilers generally have additional and progressively more sophisticated pre-boiler treatment processes installed,

which, apart from other functions, eliminate calcium and magnesium salts from the boiler MU water.

Thus, the principal components of deposits from higher pressure boilers (say, over 350–650 psig) are more likely to consist primarily of iron oxides, plus some copper, nickel, and small amounts of silica, rather than calcium carbonate.

Additionally, at higher pressures, the coefficients of **thermal conductivity** of these deposits gives increasing cause for concern because scales such as **serpentine** ($3MgO{\cdot}2SiO_2{\cdot}2H_2O$) may be present and often have particularly poor heat transfer rates.

Nevertheless, in general, it is of little practical benefit to dwell too much on the thermal conductivity of individual minerals because most deposits obviously contain a mixture of several different materials. What is more important is to consider the significant reduction in heat transfer properties that can develop when a clean steel (or copper) surface becomes dirty and to concentrate efforts on implementing protocols that minimize the risk of deposition from the very beginning of a steam generation campaign. All deposits are potentially damaging and all increase operating costs.

As a comparison, Table 4.1 lists the coefficients of thermal conductivity (at room temperature) for some metals employed in heat exchangers, together with some minerals commonly found in boiler deposits.

Table 4.1 Coefficients of thermal conductivity for some heat-exchanger metals and boiler deposits

Material	*Btu ft/h ft² °F*	*W/m² °C*
Alloy steel	21	36
Carbon steel	32	55
Copper	240	420
Analcite	0.76	1.31
Calcium carbonate	0.56	0.97
Calcium phosphate	2.20	3.81
Ferric oxide	0.35	0.61
Magnetite	1.80	3.11
Serpentine	0.63	1.09

4.5 CORROSION

Corrosion is essentially an **electrochemical process**, wherein the oxidation of metals or alloys to their (*lower energy state*) oxides or cations takes place.

The corrosion of steel or other metals in a boiler plant system takes place when an electrochemical cell is established. This occurs when *two* different metals (**anode** and **cathode**) are coupled together in water, which acts as the **electrolyte** in any steam–water circuit.

NOTE: Electrolytes differ from metallic conductors in that the current is carried by ions, not by electrons (ion: from the Greek word meaning "to go"), so the passage of an electric current through an electrolyte is always accompanied by the transfer of matter.

Corrosion also occurs where only one metal is involved. Here variations in **oxidation potential** caused by surface chemistry differences (such as irregularities in the metal's crystalline structure or stresses caused during the finishing stages of manufacture) create **microanodes** and **microcathodes**.

4.5.1 Mechanisms of Corrosion

It is at the **anode** that **oxidation** takes place, with the anodic metal suffering a loss of negatively charged electrons. The resulting *positively charged* metal ions dissolve in the water electrolyte and **metal wastage** occurs. In the corrosion cell, the metal or metal area having the lowest electrical potential becomes the anode.

At the **cathode**, a variety of **reduction** reactions take place, including the reduction of hydrogen ions (the gaining of electrons) to produce hydrogen gas.

The relevant important corrosion reactions are shown below:

Anodic half reactions:

1. $Fe \rightarrow Fe^{2}+ + 2e^{-}$
2. $Fe^{2}+ + 2OH^{-} \rightarrow Fe(OH)_2$
3. $4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$

Cathodic half reactions:

1. $1/2\ O_2 + H_2O + 2e^{-} \rightarrow 2OH^{-}$
2. $2H^{+} + 2e^{-} \rightarrow H_2\uparrow$
3. $Cu^{+} + e^{-} \rightarrow Cu$
   (copper deposits on boiler steel)

Corrosion mechanisms in boiler plant systems take many forms. They always result in metal wastage and usually result in a loss of mechanical or structural strength as well.

Each metal or metal area will develop an electrode with a measurable electrical potential. This potential can be referenced to that of a **standard hydrogen electrode**, which by convention is set at zero. Thus, all metals have either a higher or lower potential compared to hydrogen, and a comparative list of metals can be produced indicating their relative nobility. This list is the **galvanic** or **electrochemical series** and measured as an electromotive force (EMF).

In general, the baser the metal, the *lower* (more negative) the electrical potential at the anode and the *higher* the potential rate of corrosion. Carbon steel and low-alloy steels (which are widely used in boiler plants) have a relatively *low potential* with respect to the standard hydrogen electrode and can therefore be expected to corrode readily unless active prevention measures are taken. Copper and brasses have a relatively *higher potential.*

NOTE: The EMF of boiler steels with respect to the standard hydrogen electrode is typically –550 to –400 mV, whereas the EMF for copper and brasses is –50 to +50 mV (compared to hydrogen at 0 mV).

The real electrical potential of various metals and their alloys may, under practical boiler operating conditions, be considerably different from their standard potential under ideal conditions. Thus, a **reversal of potential** may take place in the boiler plant system, with unexpected forms of **galvanic corrosion** occurring.

The cathodic reactions normally are slower than the anodic reactions and are therefore the **corrosion rate–determining steps**.

As boiler metal corrosion products build up at the anodic sites and a film of *monoatomic adsorbed hydrogen* develops at the cathodic sites, so the difference in potential lessens. This voltage change is called **polarization**.

Thus, a useful method of corrosion control is to slow down the driving force of the corrosion cell by reducing the difference in potential at the cathode (**cathodic polarization**). In practice, this can be achieved by maintaining *reducing conditions* at the boiler surface (typically by dosing an oxygen scavenger), which increases the rate of cathodic polarization and drives down the corrosion rate.

In a boiler, the rates of corrosion reactions may increase very significantly with changes in operating conditions. Corrosion rates tend to increase with:

1. A rise in boiler plant *operating temperature*

2. An increase in BW *electrolyte conductivity*
3. An increase in *circulatory flow rate* (which can sweep away the hydrogen film and depolarize the cathode)
4. A high concentration of boiler water *sludge*, *sodium*, *chloride*, or *sulfate* ions, or dissolved gases

Chlorides, in particular, can present a problem because they are **cathodic depolarizing agents** (depolarizers) and thus negate the effectiveness of cathodic polarization techniques.

Anodic polarization also may occur. Typically, this begins with the formation of a thin, impervious oxide film, *chemisorbed* at the anode (as on the surface of stainless steels). However, for most metals used in boiler plant systems this **chemisorption** process must be aided by anodic corrosion inhibitors to reduce corrosion rates to tolerable levels. An example is the application of **nitrite-based** inhibitors, widely used in HW heating systems.

NOTE: Nitrite-containing inhibitors are also widely used in LP steam-raising plants where MU requirements are small. Care is required because shock doses of inhibitor or too high a concentration in the BW may easily cause carryover problems.

Corrosion rates depend not only on the differences in EMF (and the resultant current flow) but also on **current density**. For the *same* current flow, current density is greater on a small electrode.

- Small cathodes promote a *high* current density, which tends to retard cathodic depolarization mechanisms.
- Large cathodes (relative to anode size) concentrate the corrosion current flow onto the anode area and *deep pitting* occurs.

4.5.1.1 Influence of Dissolved Gases in Corrosion Mechanisms

The potential for corrosion as a result of the reactions of **noncondensable gases** present in steam–water circuits is a major area of risk. The *dissolved oxygen* (DO) content of MU water is recognized as a primary source of gas entering a boiler system, and effective deaeration of MU and FW is therefore critical.

Oxygen (O_2) may corrode the steel in pre-boiler equipment, particularly *economizers* and *FW lines*. Also, where oxygen reaches the boiler,

it may corrode *steam–water separators* and *boiler surface components* such as drums and tubes.

Even where effective external mechanical deaeration and/or internal oxygen scavenging is provided, oxygen still may present a serious risk as a consequence of air ingress into leaking pipes, steam traps, and air vents.

- Under **general corrosion and some galvanic corrosion conditions**, oxygen acts as a **cathodic depolarizer**. During this process, hydrogen gas forms and eventually blankets and polarizes the cathode, slowing down the corrosion reaction. Where oxygen is present, it reacts with the hydrogen and produces water; thus, the removal of this **hydrogen blanket** permits corrosion rates to rise.
- Under **localized corrosion conditions**, high localized concentrations of cathodic oxygen can exist. Thus, any points of lower oxygen concentration in the surrounding boiler metal area may become anodic, relative to the point of high oxygen concentration. This difference in oxygen concentration is measured as a current flow, and the current reflects the rate of corrosion taking place.

Oxygen is not the only noncondensable gas found in boiler circuits, Problems occur due to the presence of **carbon dioxide** (CO_2). Carbon dioxide is steam-volatile and reacts with condensing steam to produce **carbonic acid**, which attacks steel condensate return lines.

Ammonia (NH_3) also may be present in some boiler systems, either by design or by the breakdown of amines, hydrazine, and other organic compounds. It attacks components and equipment constructed of copper and brass.

4.5.1.2 Influence of Fouling and Deposition in Corrosion Mechanisms

Corrosion may be associated with **fouling**. For example, *oxygen corrosion* of a steam–water separator typically results in corrosion debris that builds up and fouls the separator device, thus preventing the effective separation of steam from BW.

Corrosion often results in **deposition**. Thus, under certain conditions, *sodium hydroxide* can concentrate in parts of the boiler and eventually precipitate to form localized deposits with an extremely high caustic content. The effect of this caustic deposit is to subsequently stimulate the generation of **caustic gouging corrosion** at the boiler tube surface.

Also, corrosion may result in **contamination** at some downstream point in the steam–water cycle. For example, *iron* and *copper ions* often may be present as corrosion products in steam and condensate and consequently will reduce the purity of the steam. This may render the steam unsuitable for certain industrial processes or applications where **"live" steam injection** is required.

Economizers are not usually designed to generate steam, and any deposits found in them therefore are not likely to be a result of *carbonic acid corrosion* or contamination from steam. Rather, the transport and buildup of corrosion debris within an economizer tends to originate from corrosion processes occurring either in the economizer itself or in some upstream part of the *pre-boiler system*. Economizer deposits typically develop in the presence of oxygen and possess a high iron content.

Uniform rates of corrosion such as **general etch corrosion** seldom occur in steam–water circuits. Rather, **pitting**, **tuberculation**, and other complex types of corrosion tend to predominate. These forms of corrosion often result directly or indirectly from reactions occurring in particular areas of the system where fouling and deposition may be present.

Where corrosion takes place, the origins of the metal oxides and salts formed from corroded boiler system metals should be traced in a systematic fashion to establish cause and effect and avoid misclassifying the fundamental waterside problem. Occasionally however, it is difficult to positively confirm the starting point of a corrosion problem because it is common for corrosion products to be transported from their point of origin and deposited elsewhere in the steam–water circuit, or alternatively to act as binders and contribute to fouling and contamination of the overall boiler plant system.

The presence of corrosion products is not always a negative event; some small degree of surface corrosion of all steel heat exchanger surfaces is generally beneficial. Under the *reducing conditions* normally found on the surfaces of *pre-boiler FW heaters*, *FW lines*, and *boiler surfaces*, black **magnetite** naturally forms by the direct thermal reaction of water with steel. The development of this self-limited magnetite film is most desirable, and optimum formation is achieved at pH levels of 10.5 to 11.5.

4.6 FOULING

Fouling produces dirty and inefficient steam–water systems, impeding the natural or forced circulation within a boiler, limiting the flow in

other steam–water circuits, and exhibiting other detrimental effects such as reducing the rate of heat transfer.

Fouling, like deposition and corrosion, also takes many forms but generally involves the physical adherence to waterside surfaces of materials such as *oils*, *process contaminants*, *corrosion products*, and *settled boiler sludges*.

Contaminants such as **oil**, **magnesium phosphate**, and **hematite** have a natural binding action that exacerbates the fouling problem and may result in the rapid agglomeration of *tube deposits* in WT boilers and *fire-tube bridging* in FT boilers.

Innocuous sludges such as those resulting from using **phosphate precipitation programs** may cause severe fouling problems, especially when oil, **saponifiable fats**, or other deposit binders are present in the boiler.

Oils or fats generally are introduced into the boiler from steam that has been contaminated by an industrial process. Although a high percentage of condensate return usually is a desirable objective, where contamination takes place, the returning condensate transports these contaminants throughout the steam–water system, clearly making a seamless boiler operation much more difficult.

4.7 CONTAMINATION

Contamination in this context refers specifically to the **debasing of the purity of steam and condensate**. Contamination may occur in the presence of unwanted steam volatile materials (such as **silica volatiles**), minerals carried over with BW, oil and process materials infiltrating the steam–water circuit, or by the results of corrosion processes.

Operational problems, such as BW **foaming** and **surging** (**priming**) all ultimately lead to BW carryover and the resultant contamination of steam and condensate lines.

4.7.1 Foaming

Foaming occurs when steam bubbles arrive at a steam–water interface at a rate faster than that at which they can collapse into steam vapor. It is essentially a BW surface chemistry problem and develops from many different causes including:

- High boiler water alkalinity
- The presence of colloidal materials
- Saponified oils or fats

4.7.2 Surging (Priming)

Surging or priming is the phenomena of wildly fluctuating and spouting BW levels as a result of poor operational or water chemistry conditions. Adverse conditions include:

- Too high a water level
- Uneven heat distribution
- Variable load swings and steam demands
- Too high a steaming rate
- Too low a steam pressure
- Excessive steam velocities
- Excessive suspended or dissolved solids, alkalines, chlorides, etc.

The maintenance of any reasonable degree of boiler steam generating stability under surging conditions is impossible and typically leads to the discharge of "slugs" of BW into the steam. Surging is also closely associated with problems of **foaming** and **misting** as part of a chain of cause and effect, all of which may lead to the **carryover** of BW into the steam, especially in FT boilers.

In WT boilers operating at very high firing rates, the risk exists of steam bubbles developing in *downcomers*. Where this occurs, it causes a temporary halt in the natural steam–water circulation and instantly leads to surging or priming followed by carryover.

4.7.3 Carryover

Carryover refers to the **entrainment** of BW (and the contaminating solids contained in the water) into the steam. Contamination of steam from entrained water may lead to deposits in superheaters, on turbine valves, and in steam traps, valves, and flash vessels.

NOTE: Oil and process contaminants may lead to steam–condensate system deposit problems in a fashion similar to entrainment.

Contamination from entrained BW and solids may render steam unsuitable for process operations, including food preparation, sterilization of surgical equipment, textile dyeing, hydrolysis reactions, vulcanizing, and the like.

4.8 LIMITING THE POTENTIAL FOR WATERSIDE PROBLEMS

4.8.1 Effective Water Treatment Practice

Effective BW treatment practice is not a stand-alone function. To achieve good waterside results, at least as much emphasis must be placed on the mechanical operation, cleaning, maintenance, good housekeeping, and overall management of the boiler plant system as on modifying and controlling water chemistry, training, and results interpretation.

4.8.1.1 Training and Experience

Training is important in understanding basic water chemistry and for creating an awareness of the chain of cause-and-effect waterside problems. Appropriate experience, background skills, and a positive attitude are also key requirements. Boiler plant operators do not need a degree in chemistry or chemical engineering, but they do require some training and regular involvement in water treatment. Boiler plant waterside problems are most likely to develop in those situations in which insufficient training in basic water technology has been provided.

Similarly, although the benefit of good industrial experience cannot be underestimated, service company representatives who lack appropriate technical qualification will always be limited in their ability to fully interpret analytical results and trends and provide authoritative recommendations.

By and large, the provision of adequate training and potential problem awareness is less of a problem in large WT utility, process, and cogeneration boiler plants. Here the supply of high-purity steam is a primary "product"—staff are trained accordingly and possess a better awareness of the process technologies involved.

By far the greatest number of boiler plants around the world, however, are found in general manufacturing industries and large residential, institutional, and commercial buildings; for these organizations, the generation of HW or steam is a secondary concern. As a result, adequate technology and problem awareness training is not always provided or reinforced. In these smaller operations, additional or reinforcement training in basic water treatment is a particularly useful mechanism for limiting the potential for costly waterside problems.

4.8.1.2 Understanding Cause and Effect

In fossil fuel–fired WT boiler plants, **boiler tube failure** is perhaps the leading cause of forced outages, so identifying the chain of cause and effect is particularly important.

For example, if tube failure occurs due to **caustic gouging corrosion**, the root causes are most likely related to the effects resulting from the availability of *free sodium hydroxide* in the BW, coupled with the development of *localized caustic concentration*. Control generally requires a twofold approach to remove the causes of this particular problem:

1. The limitation of free caustic in the boiler by modifying the water treatment program and maintaining the FW and BW chemistry within new, close-range parameters
2. An operational change because caustic concentration typically results when high-firing cycle operations permit **departure from nucleate boiling** (DNB) to occur

A further example is the effect of tube failure resulting from **long-term overheating**. Here it is likely that the principle contributing causes are a combination of *deposit formation* and *stresses* resulting from mechanical operation of the boiler in excess of design limits. To minimize or eliminate the risks of deposits and the subsequent effects they produce within the boiler, control again requires a twofold approach:

1. Modifying FW and BW chemistry and maintaining the improved conditions through effective analysis and results interpretation
2. Developing a *fundamental* change in boiler operating practices to prevent high stress conditions

4.8.1.3 Control of Water Chemistry

Most "standard" operating problems associated with higher pressure WT boilers (as in the preceding examples) are well recognized and suitable precautions are routinely taken. Where tube failure occurs, the root cause may be caustic gouging or long-term overheating or the result of very specific and obscure combinations of water chemistry and mechanical operating factors. If the latter is the case, because of the individual nature of higher pressure WT boiler plant system designs, the solution to the problem and the prevention of any reoccurrence might require a particularly esoteric mix of actions.

Notwithstanding the preceding notes, the fact is that whether large boilers or small boilers are involved, the starting point for the proactive reduction in operational risk is *effective control of water chemistry.*

Although close attention to all aspects of the chemistry of the various water and steam–water circuits and the impurities they contain is clearly vital, control is more than simple analysis. And apart from the smallest HW boilers (and LP steam boilers with low MU requirements), control of water chemistry typically requires that some form of **external conditioning** is required, not merely internal treatment.

To limit the potential for waterside problems throughout the steam–water system cycle a balance of water treatment processes is required with *external* items of capital equipment providing primary duty for FW pretreatment and *internal* specialty chemicals providing a supporting, "polishing" function.

Interestingly, it is also found that, because of the complex water chemistry and mechanical operation interrelationships that exist in many larger steam boiler plants, any individual action taken to limit the potential for a particular problem may have an additional and cumulative beneficial effect. For example, actions taken to limit the potential for sludge deposition through a more effective BD regimen usually provide for cleaner boiler tubes and thus produce additional benefits by both reducing the risks of pitting corrosion and improving heat transfer efficiencies.

4.8.2 Need for Water Treatment Capital Equipment

Almost all larger FT and HP boiler plants employ some form of external capital equipment for MU water and FW treatment. The rationale for installing capital equipment is to eliminate (or at least minimize) the level of *mineral impurities*, *process contaminants*, and *noncondensable gases* entering the boiler via the FW system to reduce the potential for the development of waterside deposition, corrosion, steam contamination, and other waterside problems.

External treatment is by no means the only method of limiting incoming contaminants. Where the percentage of steam condensate returning to a boiler can be increased (perhaps by FSHR or by the use of indirect-heating coils rather than "live" steam injection), the consumption of MU water is lessened, which consequently reduces the total input contaminant load.

Nevertheless, when designing a new boiler plant system, upgrading an existing facility, or simply reviewing a particular steam cycle process, it is vitally important to fully consider the requirements for and

the benefits of external capital equipment such as filters, softeners, demineralizers, and other components.

In general, equipment selection should be based on obtaining the *highest quality* boiler FW possible, consistent with boiler duty and with due regard to the cost–benefit circumstances at hand.

NOTE: Although it is desirable to consider the overall water treatment program at the design stage and match both external and internal treatments at the same time, this seldom happens in practice. In most circumstances, because of the many permutations of internal chemical treatments generally available, a suitable program can be developed at some later stage that will enhance and synergise the pretreatment equipment system.

In many cases, the specification for FW quality is higher for medium pressure industrial boiler plant design projects (of, say, over 250–350 psig) than it was 10 or 15 years ago. This is due to a number of factors, including the higher heat-flux ratings of modern boilers and the lower costs of pretreatment resulting from the use of RO and other developing technologies. This trend probably is a particularly good move given that there also is a developing trend to utilize alternative raw water sources, which often are of lower quality.

The more extensive use of pretreatment equipment generally is a commendable approach, although it is difficult to externally "overtreat" boiler MU and FW, it also is pointless to spend limited capital resources installing sophisticated equipment to provide high-purity water and then to subsequently add dissolved solids back into the FW or BW with an inappropriate, internal chemical program. Both external and internal water treatment programs must be compatible and mutually beneficial!

In practice, higher specification MU water usually diminishes somewhat the volume requirements and scope for internal chemical treatments.

When considering the need for capital pretreatment equipment, sufficient care should be taken not to propose any particularly sophisticated external or internal water treatment regimen that of itself creates restrictive operational BW control limitations—where boiler design, steam usage, and common sense dictate no necessity for such limitations to be imposed. The overall water treatment program should not be overdesigned but should properly match the needs of the project.

Unfortunately, at many smaller industrial and commercial facilities, the viewpoint that specifying and installing more than the absolute minimum external capital equipment provides a good return via reduced preventative maintenance and boiler operational benefits is not

widely endorsed. As a result, many owners and operators simply do not achieve the best waterside conditions possible and end up spending considerably more than strictly necessary each year in additional fuel and maintenance costs. For example, it is not uncommon to see the following kinds of problems:

- Vertical boilers operating at 75 to 125 psig without benefit of a water softener
- Water tube boiler plants lacking a deaerator
- Boiler plants using considerable quantities of highly alkaline MU water without some form of dealkalizer, but also providing considerable BD to keep BW TDS under control and with no FSHR equipment to mitigate this loss

In many cases, boiler owners have run for years without appropriate pretreatment plants and therefore have unduly low expectations for boiler cleanliness, steam quality, and fuel consumption. But the fact is that recent changes in technology have brought down the costs of pretreatment equipment and increased quality and output so that even a relatively modest expenditure almost always results in significantly improved operational control and boiler plant efficiency.

It also is likely that when considering the steam–water cycle, expenditure on water conditioning equipment at the "front end" will result in savings in chemical treatments, fuel, and loss of good-quality hot water at the "back end"!

4.8.2.1 Need for Water Softening

Given that the primary source of waterside deposition is almost always **hardness salts**, good operational practice dictates that (HW heating boilers aside) all boiler plants, wherever located and no matter how limited their output or pressure rating, require *softened* MU water as a *minimum* form of pretreatment.

The position is slightly different for LP steam-heating boilers, and a softener normally is not required if requirements for MU water do not exceed a minimum level of 5% or if heat-flux densities are low.

Where LP steam boiler MU requirements are in excess of 5% or heat-flux densities are high but the source of MU water is a naturally low-hardness lean water (as in New York City, where total hardness is often below 20 ppm as $CaCO_3$), it is still advisable to install a water

softener. However, many LP boiler owners do not install a softener, and the reason often given is that by relying on a MU water source with only perhaps 15 to 20 ppm (mg/l) of total hardness, there is no need to incur the additional cost of installing and operating a softener. In these "good quality water" areas, it also is common to find complacent attitudes that result in poor BD practice (generally too little, too infrequently) and a failure to apply and control internal water treatment with the care and attention needed. Such concepts are folly, especially when returned condensate is limited and the MU water demand is high.

A failure to install a necessary softener is ultimately reflected in higher bills for maintenance, repairs, and water treatment chemical products and services. Scaling can still occur with soft, lean waters, and the cost of additional fuel over a year probably would pay for several water softeners. In addition, the control of internal water chemistry becomes more difficult than it might otherwise be, which places an additional operational burden upon the facility.

Hot water heating boilers almost never require softeners (oxygen corrosion and sludge buildup are the most common problems) because MU generally is minimal.

Around the world, the most common form of softening is by means of a *cation resin*, **sodium-cycle ion-exchanger** (*base-exchange softener*, or *BX*). In large, integrated industrial facilities, **lime-soda softening** is sometimes provided and acts as a **hardness roughing treatment**, which is followed by BX softening.

4.8.2.2 Need for Deaerators and Other Equipment

In almost all industrial circumstances, a **deaerator** is a cost-effective oxygen-removing proposition that complements primary pretreatment equipment such as water softeners.

Deaerators not only effectively remove dissolved oxygen and other noncondensable gases but also provide the benefit of FW heating. Also, deaerators do not add dissolved solids to the FW, as happens with sulfite-based oxygen scavengers.

The use of deaerating FW heaters is recommended for all types of boiler plants and is preferable to relying solely upon oxygen scavenging chemicals.

A pre-boiler treatment process such as **dealkalization** (DA) to reduce the alkalinity content of a naturally high alkaline water source may also be suitable. There are various methods of dealkalizing MU water: A common process is by **weak acid, hydrogen-cycle cation**

exchange, and this usually is followed by **degassing**, (limited) **caustic addition**, and **BX softening**, in the form of an integrated pretreatment plant.

*NOTE: Where **chloride-cycle DA** is employed, it is typical for the BX to precede the DA unit.*

The use of **reverse osmosis** (RO), **electrodialysis reversal** (EDR) and other membrane techniques, and **evaporation** or **demineralization** may be applicable when a reduction in the TDS content of the MU water source is required.

In some circumstances (say, where *copper* and *iron pickup* occurs), it may be appropriate to use post-boiler treatment equipment such as **condensate polishers**.

There are many types of external water treatment equipment technologies available, and a boiler plant may employ several different processes, either on a stand-alone basis or in combination. For any particular boiler plant system, however, a point is clearly reached at which further external treatment ceases to be cost-effective. At this point, the necessary supplementary or "polishing" treatment is provided by the use of internal specialty chemicals.

4.8.2.3 Need for Silica Removal

Typically, high-pressure WT boiler plants (say, over 650–900 psig) require some degree of MU water silica removal. Most commercial and general industrial facilities however, operate boiler plants at pressures below 300 psig, and irrespective of whether FT or WT boilers are employed, a silicate removal process usually is *not* provided or deemed necessary.

It usually is considered that at pressures below 300 psig (or thereabouts) the additional capital and maintenance expenditure required for silica removal is unwarranted. This argument is generally true because, although almost all sources of MU water contain some level of dissolved or colloidal silica (perhaps 5–10 ppm as SiO_2), the risk of mineral deposition normally may be minimized within the boiler by controlling the BW chemistry. Typically, a maximum silica content and number of cycles of concentration is specified (and then maintained by providing more or less BD), and appropriate alkalinity–silica ratios are employed. Specific **silica dispersants** (*silica deposit control agents*) may also be used.

Where MU water sources contain relatively high natural silica levels (i.e., above 30–40 ppm SiO_2) or a high ratio of silica to TDS (say, > 25–30% of TDS present as SiO_2), this reasoning is often invalid. And in those boiler plants that use high-silica waters but operate without benefit of external silica removal equipment, extremely careful control of BW chemistry with *very tight* control parameters is vital to avoid risks of serious silicate deposition.

If BW silica levels increase above 180 to 200 ppm, it may not, in fact, be possible to totally control silica deposition by water chemistry means alone. Also, as boiler pressures, temperatures, and heat-flux densities increases, so does the need for external silica removal equipment.

All boiler plants providing steam for electricity generation must be provided with silica removal pretreatment equipment. Pretreatment technologies for silica reduction and removal include:

- Demineralization
- Reverse osmosis (RO)
- Evaporation
- Coagulation (with ferric sulfate or magnesium hydroxide)

4.8.3 Limiting Deposition

Around the world today there are still countless numbers of operating boilers that are more than 70 or 80 years old, and there probably are many operating HRT, locomotive, or firebox boilers that were built a century ago. These and other similar low heat flux–density designs were built by the thousands (primarily in Europe and the United States) to generate steam for hospitals, hotels, textile mills, food processors, tanneries, motive power, and the like. At that time the available water treatment technology was limited, and boiler plants were routinely supplied with relatively poor quality FW and equally poor water treatment programs, thus requiring extensive annual maintenance work and high annual fuel costs. The situation has changed somewhat over the years, and although many old boiler plants still operate, archaic chemical treatment programs no longer exist, and the relative improvement in chemical treatment program efficiency is sufficient to stave off the need to expend capital in boiler replacements.

Nevertheless, it was perhaps only 25 to 30 years ago that significant improvements in limiting deposits through improved water treatment were made available to general industry. Until then many operators in hard-water areas had to contend with no pretreatment softening of MU

water and low-quality (and often difficult-to-dissolve powdered) internal chemical treatments such as **carbonate control programs**.

Arrangements for chemical feed and control also were limited. In these boilers, 1/2 inch to perhaps 1 inch (12.5–25 mm) of multilayered scale could easily deposit during the period between waterside inspections. It was often assumed that these operating conditions were the norm, that regular acid cleaning was a way of life, and that nothing better could be expected.

This level of deposition cannot be tolerated in any modern boiler design, irrespective of where in the world a boiler operates or the type of duty required. Even limiting the maximum acceptable thickness of boiler waterside deposition to an **eggshell thickness** "standard," as once proposed by many people in the industry, is not satisfactory today. Indeed, under modern higher heat-flux density conditions, operators of industrial WT boilers working to this standard would have to contend with frequent disruptions because of ruptured tubes or worse, while FT boilers might eventually suffer from a collapsed furnace and need to be written off.

Nevertheless, current boiler designers do provide some tolerance for the gradual accumulation of waterside deposits, although these usually are not formally presented. There are many variable factors to considerm including:

- Operational boiler pressure and rates of water circulation
- The use of widely differing types of fuel with various heating values
- Boiler metals used and heat-flux density requirements
- The nature and respective thermal conductivities of the many possible waterside deposits

Typically for any boiler design or type, any tolerance for deposition can be expected to decrease with increase in operating pressure. A practical tolerance limitation for the thickness of boiler deposits on heat transfer surfaces is given in Table 4.2.

NOTE: For any boiler, the maximum recommended ***tolerance for deposit thickness*** *can be related to a weight of deposit per unit area; clearly, the weight will vary dependent on the density of the deposit. Typically, deposit densities vary between 2.3 and 5.7 g/cm^3. The densities of calcite and magnetite (which are two common mineral components of deposits) are 2.71 and 5.17 g/cm^3, respectively. Table 4.2 assumes an average deposit density of 3.5 g/cm^3.*

Table 4.2 Boiler heat transfer surface cleanliness

Pressure rating	*Clean condition*	*Dirty condition*
Below 300 psig	3.0 to 5.0 mil	10 to 15 mil
300–1,500 psig	1.5 to 3.0 mil	5 to 10 mil
1,500–3,000 psig	1.0 to 1.5 mil	2.5 to 5 mil
Above 3,000 psig	<1.0 mil	>2.0 mil

NOTE: 1 mil = one thousandth of an inch, 10 mil = 0.25mm. Very approximately: Eggshell thickness = 1/32 in, or 31 mil. 10 mil = 100 mg/cm^2 deposit, or 93g/ft^2, or 3.3 oz/ft^2.

Deposition can be minimized by a combination of good operating practice and overall program management, together with the use of appropriate external conditioning equipment, internal chemical treatments, and proper chemical feed and control methods.

Some areas of operating practice that aid in minimizing waterside deposition include:

- Avoiding operating a boiler plant at its **maximum continuous rating** (MCR)
- Good firing practice by matching fire rates to steam demand
- Correct burner positioning and the elimination of hot spots
- Maintaining correct and steady water levels
- Providing the right amount of BD at the correct intervals

In all cases, and irrespective of the types of pretreatment equipment employed and the degree of boiler operational control provided, additional and complementary support through the use of suitable **internal chemical water treatment programs** is *always needed* to limit waterside deposition.

Today, almost all chemical treatments are liquid, which (profit motives apart) simply enables the chemicals to be fed and controlled more easily and with greater precision than with the use of powdered products.

Chemical treatment programs are often individually designed for particular boiler plant systems but usually contain *oxygen scavengers*, *pH boosters*, and *corrosion inhibitors*. In addition, the formulations employ materials specifically designed to limit the degree of deposition and control the mechanisms of deposition.

Traditional **deposit control agents** (DCAs) such as *phosphates*, *chelants*, *polyacrylates*, *lignins*, and *tannins* continue to be used to some degree in FW chemical treatment product formulations from every water treatment vendor, but modern technology is focused on the development and application of novel, problem-specific **deposit control polymers** (for cooling systems, process applications, etc., as well as for boilers). There are many dozens of polymers available in the marketplace for limiting the risk of waterside deposition; some are for general application, but most are employed for fairly specific duties such as controlling iron or phosphate deposition.

For the most part, DCA chemistries are researched by large international chemical corporations, but the various in-field uses and applications generally are developed by service companies, often in cooperation with "friendly" end-user customers.

The different polymers employed as DCAs for BW treatment function in a variety of ways and usually are blended in a formulation, where they may act in concert for better effect.

Deposit control agents may function as:

- **Dispersants**
- **Crystal modifiers**
- **Precipitants**
- **Threshold agents**

NOTE: The same polymer chemistries employed in the BW deposit control treatment market sector are also made available to other markets such as waste water, cooling water, potable water production from brackish or saline supplies, metal finishing, paint and coatings, electronics, pulp and paper, and more.

The trick is to find the precise way to use and apply the polymer in a particular market sector to add value to a process or to produce cost-effective benefits. Thus, any particular polymer chemistry may be made available to the market in several different derivative forms, in several strengths, and at various prices to suit the particular market conditions.

In the BW market, many of the modern polymers have demonstrated their ability in controlling specific waterside deposition problems. Use of the materials has led not only to cleaner boilers but also to higher customer expectations and the all-round confidence to operate boilers at higher heat-flux densities than in the past (especially in the medium pressure ranges of, say, 250 to 900 psig).

4.8.4 Controlling Corrosion

The corrosion of steel and other metals in a boiler system takes place when an electrochemical cell is established, although the rates of corrosion and the types of corrosion mechanisms involved are highly dependent on the particular circumstances that develop during the operation of individual boiler plants. A failure to adequately control corrosion ultimately leads to the failure of *boiler surface* components or other components and items of equipment in the system.

Both the rates and the mechanisms of corrosion processes can be limited by the judicious selection of materials of construction. Considerable effort goes into this particular function during the boiler plant system design phase. Nevertheless, appropriate materials selection as a stand-alone, primary corrosion control protocol will *not* prevent corrosion problems from occurring during boiler operation; therefore, various secondary measures are always taken. These measures include installing equipment such as deaerators, feeding chemical corrosion inhibitors, and employing best-practice operating procedures.

4.8.4.1 Corrosion Control Through Cathodic Protection

In addition to the careful selection of structural metals, the **cathodic protection** of water-wetted parts may also be specified. For most boiler plant systems, however, because of the tortuous and extended waterside surfaces involved, the use of cathodic protection is only a partial solution to controlling corrosion and should never be the sole secondary protocol. Rather, cathodic protection functions well when employed as part of a more comprehensive program that includes appropriate internal chemical treatments.

Cathodic protection apparatuses are well proven, widely used devices and are not to be confused with **magnetic devices** (*"gadgets"*) or other similar but generally less than satisfactory items of capital equipment. Cathodic protection devices reverse the tendency of a metal to go into solution at the anode (corrosion) by the application of a *counter-potential.* This counter-potential or **electromotive force** (EMF) is provided either from a permanent external source such as a battery or rectifier or from the installation of a **sacrificial anode**.

Where sacrificial anode technology is employed, typically **zinc** or **magnesium anodes** are provided, although zinc anodes cannot be employed at over 140°F because of a reversal of potential above that temperature. In the boiler waterside circuits, they preferentially corrode,

liberating electrons during the electrochemical cell reactions. The degree of corrosion protection offered to the metals of construction is proportional to the applied current density up to that level required for complete protection.

4.8.4.2 Control of Oxygen

Oxygen is almost always a contributing factor to corrosion mechanisms; therefore, the effective removal of dissolved oxygen (DO) is of paramount importance in controlling the rate of boiler system corrosion, irrespective of the size, design, or pressure of the plant.

All large boiler plants and many smaller units employ mechanical *deaerators* to remove oxygen. In addition, various *oxygen-scavenging chemicals* are employed as consumable treatments such as sodium **sulfite-bisulfite**, **hydrazine**, various **novel chemistry organics** (hydrazine replacements), and certain **tannins**.

Normally, a small reserve of oxygen scavenger is maintained in the BW to preserve satisfactory *reducing conditions* within the steam-water circuits.

NOTE: In large HP WT boilers, corrosion actually can be controlled down to a minimum level by adding oxygen to the FW rather than by removing it. The process is called ***oxygenation treatment*** *(OT) and is designed to ensure that sufficient oxygen is always present in the FW (typically ≅ 5 ppb O_2) to ensure no disruption to the passivated magnetite films on the waterside of economizers and feed lines.*

Oxygenation treatment also reduces the risk of erosion–corrosion problems and limits ***iron transport*** *to other parts of the boiler system where fouling could take place.*

Where feed lines have short pipe runs, where hot wells or FW tanks are of small volume, or when FW is too cold, there often is insufficient time for full DO scavenging to take place, even when using **catalyzed scavengers**. The inevitable result of this lack of contact time is the formation of *oxygen-induced corrosion products*, which by various secondary mechanisms may settle out to form permanent deposits within the boiler system. These deposits may develop in several forms (e.g., where DO removal is particularly poor, they often appear as reddish tubercles of **hematite** covering sites where pitting corrosion is active). Active pitting corrosion combined with the presence of waterside deposits ultimately may lead to **tube failure** in a boiler or other item of system equipment and result in a system shutdown.

Equally, *boiler surface* failure may result solely from poor operational practices or other indirect problems, although more usually it is due to a combination of waterside and operational problems such as **corrosion fatigue** and other **stress corrosion cracking** (SCC) mechanisms.

Thus, the effective control of corrosion requires not only limiting the presence of oxygen but also minimizing the risks of waterside deposits. These measures in turn require good management of waterside chemistry and competent mechanical operational practice.

4.8.4.3 Control Over Salinity and Adverse Chemical Reactions

Some measure of control over corrosion also is obtained by limiting the **salinity** in the boiler (primarily the ions of **sodium**, **chloride**, and **sulfate**). These ions all increase the conductivity of boiler water electrolyte and thus enhance corrosion reaction rates. Also, chloride and sulfate ions affect the passivation process.

Strict limitations on the salinity content of BW become increasingly important as boiler pressure or heat-flux density increases. This is primarily effected by:

1. Reducing the FW TDS to a practical minimum
2. Controlling the maximum concentration of BW TDS within narrow ranges appropriate to certain boiler design types

In practice, control over BW TDS more usually is provided by placing limits on electrical conductivity.

- **Sodium:** The FW sodium (Na) content is clearly a factor in the formation of sodium hydroxide in BW and an excess may promote various forms of **caustic-induced corrosion**. Also, high sodium levels may lead to the **depassivation** of steel surfaces caused by high pH generation, which reduces the corrosion resistance of boiler steel.
- **Chloride:** Chloride ions are strongly adsorbed by steel, making it difficult to **passivate**. High chlorides in steam–water circuits increases the risk of **stress corrosion cracking** of *austenitic* steels (type 300 stainless steels) and increase the rate of **pitting corrosion** under sludges and deposits.
- **Sulfate:** Sulfate ions have reactions similar to chloride. They are also *depassivation agents* (especially if allowed to concentrate sufficiently) and can greatly accelerate the risk of stress corrosion

mechanisms. Sulfates act as *corrosion causitive agents* for the various types of **concentration cell corrosion** (similar to oxygen and hydrogen) that result in *pits*, *crevice attack*, or *tuberculation*.

The presence of high BW salinity can increase the risk of corrosion, and good control is therefore vital. Where salinity is high and some corrosion occurs, the corrosion debris may act as a binder, fouling *boiler surfaces* and forming sludges and deposits. The presence of these sludges and deposits can, in turn, induce **pitting corrosion**, and a cyclical chain of cause and effect may take place. Therefore, good operational practice provides for effective BD to limit excess salinity and assist in controlling corrosion and boiler waterside deposits.

Certain internal chemical treatments employed also need strict control to avoid risks of adverse chemical reaction and resultant corrosion. In particular, *nitrogen*-containing chemicals such as **hydrazine** and **amines** require effective monitoring to limit the concentration of **ammonia release** into steam because the presence of ammonia may, under certain conditions, cause **stress corrosion cracking** of **copper** and **brasses**.

4.8.4.4 Passivation

Passivation is a necessary and natural initial corrosion process that occurs on all hot waterside surfaces. It is the conversion of a *reactive* metal surface into a lower energy state that does not readily further react or corrode, and it involves the development of a **passive oxide film** on a clean surface.

Under the hot *deaerated* (reducing) conditions normally found on the surfaces of pre-boiler FW heaters, FW lines, and *boiler surfaces*, a dense, passive, black, iron oxide film of **magnetite** (Fe_3O_4) naturally forms.

This oxidation reaction of steel is self-limited and takes place by the direct reaction of FW (or BW) with steel, which in effect is accomplished by the reduction of hydrogen ions supplied by the water. The reaction is shown here:

$3Fe$	+	H_2O	$\rightarrow$	Fe_3O_4	+	$4H_2\uparrow$
iron		water		magnetite		hydrogen

If oxygen-scavenging capability and boiler loading conditions fluctuate (as may occur during periods when boilers are idle), the magnetite

formed is often coarse and porous, permitting some level of corrosion to continue unabated. This process also may be associated with the presence of some red **hematite**, as shown in the reaction:

$2Fe$	+	H_2O	+	O_2	→	Fe_2O_3	+	$H_2\uparrow$
iron		water		oxygen		hematite		hydrogen

All boiler system waterside surfaces need the protection given by the smooth, hard, tenaciously adherent magnetite layer. The magnetite film sometimes may sparkle because of the precipitation of fine magnetite crystals onto the metal-oxide surface. Magnetite film formation is best achieved under stable, low-oxygen content operating conditions at a pH level of 10.5 to 11.5 (possibly up to 12.0).

At lower pH values, hydrogen ions are discharged, whereas at higher pH values, the magnetite layer thickens coarsely, becomes porous, and may peptize. Hydrogen blistering also may occur.

The magnetite film may, under some circumstances, be layered. For example, in power boilers, under conditions of high steaming rate and low steam–water velocity, a secondary film of precipitated **particulate iron oxide** may form over the original magnetite film.

If the passivated surface is damaged (perhaps following an offline cleaning procedure, welding, system expansion, or general repairs), it becomes necessary to restore the damaged area to a passive state. This generally is undertaken *before* the boiler goes online, and for larger boilers under these circumstances, **nitric acid** is commonly specified. Nitric acid provides restorative preoperational passivation because it generates the required *oxidizing* atmosphere.

When the boiler is placed back online, certain types of **anodic inhibitors** (which are generally employed to act as "polishing treatments" in the maintenance program) also may prove beneficial in further strengthening the passive film.

In boilers in which **tannin blends** are employed both as oxygen scavengers and as sludge dispersants, the magnetite film may also incorporate **iron tannates**.

Quebracho and certain other tannins may be very useful where reducing conditions are not always consistently maintained because they help to sustain the magnetite film intact during periods of BW instability (as may occur under low FW temperature and high oxygen content conditions). Despite the fact that tannins are often regarded as old technology, they work well and can be successfully used in boilers operating at up to 650 to 800 psig, not merely in HW and LP steam plants.

When boiler cleaning takes place, it often is followed by the circulation of a hot **alkaline phosphate** solution to provide adequate passivation of metal surfaces. (A typical formulation may also include *sodium gluconate*, *antifoam*, and *dispersants*.)

Temperatures reached during phosphate-based cleaning programs are only modest, and under these lower temperature conditions the passivated film consists of **gamma iron oxide** (γFe_2O_3) together with **primary ferrous phosphate** [$Fe_2H_2(PO_4)_2$] and **tertiary ferrous phosphate** [$Fe_3(PO_4)_2$].

5

WATERSIDE AND STEAMSIDE PROBLEMS: HOT WATER HEATING AND LOW-PRESSURE STEAM BOILER SPECIFICS

It is not possible to describe and provide fine-tuned controls for every potential waterside or steamside problem that may arise, in view of the countless permutations of boiler plants and specific operating conditions that exist around the world. But many problems are inevitably more common than others, and some of these are described in the various sections of the next four chapters, together with some practical notes on their control. Although many of the issues described have been neatly compartmentalized for the sake of simplicity, this generally is not the case in practice and waterside or steamside problems should always be investigated in the context of the overall boiler plant.

As a preamble to looking at some of these specific problems, it is worth reiterating effective control strategies are achieved through the **planned avoidance of problems** and understanding **cause-and-effect relationships**.

The planned avoidance of boiler waterside or steamside dilemmas is more likely to be achieved under the following circumstances:

- When the overall boiler system layout and key equipment functions and interdependence are clearly understood (systems surveys are

essential; schematic drawings of equipment layout and flow diagrams make it easier to understand how the system functions)

- When the most common waterside or steamside interactions and resulting cause-and-effect problems that may develop have been anticipated and suitable water treatment "risk aversion" protocols proposed
- When the individual water treatment equipment, products, and service components that are required to minimize risk have been integrated into a cohesive program

With regard to cause-and-effect relationships, in practice, a problem originating from a single-source cause may have a lead-on effect that gives rise to multiple localized problems or becomes evident in several different areas of the boiler plant. Conversely, what appears to be a single localized problem may in fact be the combined effect of a number of smaller separate causes.

Consider the frequent issue of **oxygen corrosion** that may affect a (pre-boiler section) *economizer* and also various downstream (boiler section) *boiler surfaces*. In most cases, the basic cause, common to both resulting problems, is inadequate or inefficient FW deaeration.

To further complicate the matter, some waterside chemistry dysfunctions or mechanical–operational problems may give rise to the same noticeable effect; thus, systematic causal investigations must be conducted to avoid being drawn to wrong conclusions. In addition, there often is a tangible link between certain operational and water chemistry–water treatment problems. For example, the development of a simple mechanical problem such as a maladjusted burner may result in **flame impingement** on a heat transfer surface. The resulting high localized temperatures may induce a change in the waterside chemistry through **localized mineral supersaturation** and the subsequent **precipitation of dissolved salts** that, in turn, leads to both **waterside deposition** and **corrosion**. (Further effects may then take place, and tube failure is ultimately likely.)

The opposite scenario also may occur, whereby a localized pre-boiler water chemistry problem can affect the downstream, mechanical operation of a boiler. As an example, difficulties in the control of pretreatment equipment may lead to **treated MU water instability**, causing downstream **after-precipitation**, leading to **FW line blockages**, and finally resulting in boiler cutout as a result of low water.

Sometimes the chain of cause and effect completes a circle and a "catch 22" situation develops.

Waterside problems also may be the result of other problems that are not directly obvious. Thus, for example, issues of **high-temperature waterside corrosion** are sometimes associated with **weld defect problems**, which include:

- Burnthrough
- Inclusions
- Porosity
- Cracking
- Incomplete fusion.

Finally, it should be remembered that effectively controlling specific boiler plant system waterside problems requires diligent monitoring of waterside chemistry. This in turn requires the collection of truly representative steam and water samples and the use of appropriate methods of analysis and sensitivities.

5.1 PROBLEMS WITH HEATING COILS

Low-temperature hot water (LTHW) and **low-pressure hot water (LPHW) systems** operate below 250 °F/121.1 °C (equivalent to 29.8 psia/15.1 psig). This is approximately the same as **LP steam systems**, which operate below an MAWP of 15 psig/29.7 psia, equivalent to 249.8 °F/ 121 °C.

Many LTHW and LP steam systems run only on a seasonal basis, providing HW or steam for space heating in winter.

Both types of boiler systems may incorporate **finned copper heating coils**, which are located above the furnace and gas-pass tubes (*smoke tubes* or *fire tubes*) and provide for *indirect* heating of domestic HW. Where coils are fitted and the boilers are only fired during winter months, domestic HW heating usually is provided via gas heaters for the summer.

These coils are subject to a variety of aggravating problems that may develop over time and ultimately lead to coil replacement. The frequency of replacement may be as often as every 2 to 3 years in some cases but perhaps only every 7 to 10 years in others. The timespan depends primarily on the particular source of water used for boiler MU and domestic supply and any pretreatment provided. Usually the first time that developing problems may be seriously investigated is when users complain of an inadequate HW flow, reduced pressure, or low temperatures.

Problems associated with domestic coil systems include:

1. **Domestic heating coil internal corrosion.** Where naturally soft or lean city water is supplied and the Langelier Saturation Index (LSI) is below –1.0, **acid corrosion** takes place as a result of the acidic nature of the water. This water often has a high dissolved gas content, which additionally leads to **pinhole corrosion**. Where water velocities are too high (say, over 6 ft/s 1.8 m/s) the protective oxide layer is stripped off and **erosion corrosion** takes place.

   Typically the internals of the coil show pits and pinholes and may even perforate. Corrosion debris is evident, usually containing *green* **hydrated copper carbonate** ($CuCO_3 \cdot nH_2O$) and *red* **cuprous oxide** (Cu_2O).
2. **Domestic heating coil internal deposition.** Where hard water MU is supplied, the rapid deposition of *white*, *gray*, or *brown* **calcium carbonate** scale ($CaCO_3$) takes place. Where soft or lean water is supplied, it may contain *phosphate* as a **threshold agent** (employed to stabilize the water supply, thus preventing **aftertreatment deposition** in the mains and minimizing the corrosion of mains piping). The result of the presence of phosphate typically is *blue-green* to *black* **copper phosphate trihydrate** ($Cu_3[PO_4]_2 \cdot 3H_2O$) depositing out in the coil.

   A further problem is that heating coils generally are located at the lowest point of the domestic HW heating system and act as **dirt pockets** for the accumulation of general dirt and debris, as well as corrosion products resulting from the various points of **galvanic corrosion** that inevitably takes place.
3. **Miscellaneous heating coil problems.** These vary from system to system. They are relatively common in HW boilers, where little or no blowdown (BD) is ever provided for **BW sludge** to accumulate on the *external fins* of the copper coils, thus preventing effective heat transfer. When *coil gaskets* at the installation points on the top front of the boiler weep, and where the water treatment product contains a dye, **color stains** surround the gasket area.

In the long term (20–40 years), the overall domestic HW system is subject to pinhole leaks stemming from the galvanic corrosion of steel riser pipes (usually located in inaccessible areas), with resultant flooding within the building. Galvanic corrosion develops because these systems typically contain a wide range of mixed metals such as *black*

iron, *carbon steel*, *galvanized steel*, *copper*, and *copper alloys*, all generally installed without benefit of dielectric insulators.

5.2 PROBLEMS ASSOCIATED WITH THE USE OF GLYCOLS

The operational duties of these smaller boiler systems vary widely, and for HW closed-loop heating systems, where the boiler is periodically offline, or in *indirect heating systems* where pipework, valves, or final heating units are exposed to chilly winds or icy conditions, some **boiler winterization** may be necessary. This is usually provided by replacing some of the water with **glycols** or other *heat transfer fluids*.

Typically, the level of glycol required in a HW heating system is only 15 to 25% v/v or so (less than the 35–45% usually employed in cold and chilled-water closed-loop systems). Where glycols are added, the system must be cleaned and flushed first. The system can be partly drained to accommodate the volume of 100% glycol required or alternatively filled with a prediluted mix. If a 20% v/v strength is required, 25% v/v should be specified to allow for inaccuracies in mixing.

Correct glycol selection and regular monitoring of the *in-use concentration* and *stability* is necessary to ensure adequate long-term **freeze protection** and also freedom from the effects of **glycol-derived corrosion** resulting from glycol degradation.

Typically, **ethylene glycol** is employed as a *freeze-point depressant*, but other (normally higher cost) alternatives exist. However, glycols tend to oxidize over time in the presence of air or oxygen, *particularly when heated*, and give rise to *aldehydes*, *acids*, and other oxidation products. Where inadequate levels of water treatment buffers and corrosion inhibitors are employed (phosphate-based inhibitors are often employed), the resulting water–glycol mixture pH may reduce to below 7.0 (often reaching $\cong$ 5.5) and **acid corrosion** results.

NOTE: Glycol selection should also take into account the risk of leaks to the environment and the ultimate safe disposal of the material. Propylene glycol is a safer alternative to ethylene glycol because of its very low mammalian toxicity.

Where pH levels have dropped below 7.0 due to glycol degradation, there is usually little alternative but to drain, flush, repassivate, and refill with a new inhibited glycol solution.

5.3 PROBLEMS OF CORROSION IN HOT WATER AND LOW-PR5ESSURE STEAM HEATING SYSTEMS

In all space heating boiler systems there is a tendency to keep water treatment programs as simple as possible. Ideally, chemical inhibitors should be added in proportion to *MU demands*, *metered water consumption*, *oxygen content*, or other preemptive measurement. More typically, the "standard" process is to periodically (weekly to monthly) analyze the BW for a few basic control parameters, including measuring the **multimetal corrosion inhibitor reserve**, and then to merely top-up the inhibitor when the reserve is below the minimum specification. Chemical treatment often is added directly to the BW by handpump via a *hose cock* (bib cock) connection.

This simple approach means that HW heating and LP steam heating systems generally are treated in like manner, and often no specific **oxygen scavenger** is employed. Thus, the potential for significant oxygen corrosion commonly exists.

Also, no specific **amine-based inhibitor** is generally provided to protect LP steam condensate pipework against the ravages of *carbonic acid* (H_2CO_3)-induced condensate line corrosion.

The rationale for these simple approaches to water treatment is the argument that these kinds of systems have minimal requirements for MU water and are therefore subject to a reduced level of risk. In practice, the validity of this argument is suspect but is difficult to prove because totalizing water meters are seldom installed on the MU water line.

5.3.1 Oxygen Corrosion

In all probability the most common operational problem associated with most LTHW heating and LP steam systems is that of maintaining control over oxygen corrosion of the boiler, especially in the tubes, tube sheets, and at the waterline.

Oxygen corrosion usually takes the form of *deep pitting* and involves both **tuberculation** and **differential aeration corrosion** mechanisms. The BW commonly is brown and murky, and chemical treatment reserves usually are very low or absent. The source of the oxygen is either **MU water dissolved oxygen** (DO) or **air in-leakage**.

Sludge in the boiler is typically red to brown (**hematite**) but becomes black with age (**coarse magnetite**).

A wide range of cause-and-effect relationship alternatives may arise, depending on the particular circumstances, especially in smaller residential and commercial properties. But combinations of *poor system design*,

very variable waterside chemistry, and *less than ideal operating procedures* (including lack of internal washouts and too much or too little BD) result in corrosion. This situation is far more prevalent than many boiler users and operators and water treatment professionals wish to believe.

Basic causes of oxygen corrosion of boiler vessels include:

1. When LP steam boilers are operated in a daily/periodic on–off mode, the repeated cycles of steam condensation result in partial vacuum conditions that provide the impetus for regular ingress of air into the system.
2. When systems are poorly designed, with unlagged condensate receiver and FW tanks open to the atmosphere, thus permitting loss of heat (colder water holds more oxygen) and *permanent* contact with air. (This vent point is commonly employed for the addition of chemical treatment.)
3. When systems are old and have had limited maintenance over the years. They leak water out and air in.
4. When operators believe that their HW systems do not lose water through pump mechanical seals or other places. They also commonly state that their LP steam heating systems return 100% condensate, so that no additional corrosion protection precautions need be taken above or beyond the initial fill of chemical treatment and an occasional top-up dose.

   (This scenario is sometimes aided and abetted by water treatment professionals who also operate in a "there are no losses" mode. As discussed earlier, typically no **water meters** are installed to measure MU usage, and it is difficult to either confirm or deny water losses. **Tracer dyes** are sometimes used, but they are not always effective. There is no substitute for a water meter on the MU line.)
5. When chemical treatment for both HW heating and LP steam heating systems is generally some combination of a *nitrite/borate/silicate/molybdate* formulation, usually with TTA/polymer or phosphate but having no specific **oxygen-scavenging** capability.

Where the systems are tight and almost no losses occur, treatment programs based on these inhibitors can work very effectively (as long as the systems have been properly cleaned and passivated beforehand). For HW heating systems where significant water losses occur, however, (as when MU requirements exceeds, say, 5–10% of the system volume per month), the loss of treatment permits significant oxygen corrosion to occur.

Similar problems develop with LP steam heating systems, where returned condensate is only, say, 95% of steam output because the compensating MU brings more DO with it to stimulate the continuing corrosion processes.

5.3.2 Galvanic, Acid, and Under-Deposit Corrosion

Apart from oxygen corrosion, HW space heating boiler systems suffer from medium- to long-term **galvanic corrosion**. In common with HW domestic coil heating systems, these closed-loop systems contain a variety of mixed metals such as *black iron*, *carbon steel*, *galvanized steel*, *copper*, and *copper alloys* that may interact. Again, these are generally coupled together without benefit of *dielectric insulators*.

In LP boilers with little returning condensate the requirement for MU is correspondingly high and may be relatively "cool" and partially oxygenated. Here it is not uncommon to observe the transport of **ferrous bicarbonate** [$Fe(HCO_3)_2$] into the boiler (especially where no neutralizing amine is supplied) and the subsequent development of **iron sludge**, which settles on the top of combustion tubes and to the bottom of the boiler.

Under the sludge considerable orange-red **tuberculation corrosion** deposits may develop. In cause-and-effect fashion, the tubercles grow cause fouling, permit **under-deposit corrosion** to persist, and generally act as a binding agent for carbonates, silicates, and other precipitates.

Acid corrosion developing through the breakdown of glycols is also very common, as discussed in section 5.2.

5.4 OTHER WATERSIDE PROBLEMS IN HOT WATER HEATING AND LOW-PRESSURE STEAM SYSTEMS

In practice, the process of periodically topping up the inhibitor formulation through a hose cock or via a timer-controlled pump works well when water losses are minimal and the boiler is clean. But as discussed previously, when excess water is lost from the system through various means and MU demands become significant, the practice becomes one of "chasing your own tail," and the various common forms of waterside corrosion, sludging, and deposition rapidly develop and flourish.

5.4.1 Excessive Water Loss

The second most common problem in HW heating systems after oxygen ingress probably is that of **uncontrolled** or **excessive water loss**.

This specific problem often goes hand-in-hand with the associated issues of:

- Failure to recognize or measure these water losses
- Failure to take proactive measures to prevent boiler system damage and loss of efficiency as a result of problems stemming from excessive water loss

In many systems where **oxygen pitting corrosion** has taken place, it often is difficult to decide whether the ingress of causative oxygen stemmed primarily from DO in the MU water required to compensate for *excessive water losses* or simply overall system *air-ingress*, especially because these conditions tend to go hand-in-hand.

In LP steam boiler systems, this problem of uncontrolled or excessive water or condensate return loss also occurs. It may be *uncontrolled* perhaps because of leaking steam traps or excessive as a result of too frequent or prolonged BD. Irrespective of the basic cause, it is necessary to obtain an accurate assessment of **materials balance** as a first step in understanding the magnitude of the problem and providing resolution.

NOTE: All boiler plant operators are urged to meter the MU water consumption as an aid to calculating a material balance. Steam generation rates can be reasonably accurately determined from the fuel consumption because records of fuel costs are always maintained. Daily and weekly BD rates usually can be estimated from the use of a measuring bucket or pipe velocity table. The difference between steam production and MU represents a combination of BD and loss of CR.

Apart from the oxygen corrosion that results in HW and LP steam heating systems where water losses occur as a result of leaking pump mechanical seals, excess BD, faulty steam traps, and other sources, a subsequent effect is the development of **fouling**. This effect stems from the production of *corrosion debris* and (high iron content) *sludge* that eventually settle out in the boiler. This corrosion debris, sludge, and other foulants must be periodically removed from the boiler by BD, which merely adds to the water loss, and the cycle perpetuates.

Under conditions of water loss and poor waterside control, it is fairly common for iron sludges and foulants formed elsewhere to settle in the boiler. Trying to identify the source of this problem is complicated when the transport of soluble iron salts such as **ferrous bicarbonate** $Fe(HCO_3)_2$ into the boiler takes place. A further complication occurs

when appreciable BW silica is present because, rather than this iron forming a sludge or even magnetite, insoluble deposits of **ferrous metasilicate** ($FeSiO_3$) preferentially form. This mineral is extremely hard and adherent, it causes a severe loss in heat transfer, and it is very difficult to remove.

Yet a further problem concerning excessive water loss is the increased risk of **carbonate scale deposition**. It is the usual case to propose that, because heating systems are closed loops with minimal losses, many operators believe that they do not require sophisticated chemical treatment programs, injection–feed methods, or monitoring and control processes. To further this view comes the added philosophy that, irrespective of hardness content, the MU water supply to these systems does not require any pretreatment such as *ion-exchange softening*.

Of course, this argument is perfectly true where it can be *positively* demonstrated that MU water requirements really are very low. Once again however, if this is not the case, then—most treatment programs are designed primarily for corrosion control and do not compensate for undue hardness entering the boiler—calcium carbonate scale can and does develop over time. This process takes place even where the MU water is relatively soft, and results in the formation of insulating **boiler tube deposits** or **boiler vessel sludge**.

5.4.2 Problems of Maintaining Inhibitor Levels and Controlling Blowdown and Surging

Where uncontrolled water loss is demonstrated to be minimal in heating boilers, logic dictates that potential problems also are likely reduced. Treatment programs can therefore be simple, boiler sludges will be low, and (boiler insurance or legal requirements apart) little or no BD is required during the operation of heating boilers.

As can be seen, the requirement for BD (in common with other control parameters) is fundamentally dependent on the level of MU required, reinforcing the need to establish some reasonably accurate assessment of water consumption. In practice, even with quite "tight" systems, some sludge does develop and a BD of 2 to 3 seconds' duration is periodically required. It is preferable to blow the boiler down more frequently than to open up the BD valve for a longer time of, say, 8 to 10 seconds.

NOTE: Practical BD schedules range from daily to weekly for LP steam boilers and from weekly to monthly for HW heating boilers. In HW systems where daily BD is required to control the development BW sludge this indicates significant water loss. Where the system is "tight," a daily BD of even

1 or 2 seconds is likely to be excessive and will lead to loss of inhibitor, probably to a point below the minimum protective reserve requirement.

In LP steam systems, where frequent BD is required to prevent a rapid escalation of TDS/chloride conductivity, this is an indication of solid-water loss rather than a steam loss.

Combinations of air ingress problems, water losses, or erratic boiler BD practices can easily lead to the development of out-of-balance BW chemistry and a **loss of corrosion inhibitor**.

Also, in severe cases in which lean or acid MU water is employed, or where glycol degradation occurs, the loss of inhibitor and associated pH buffer permits the BW pH to drop below 7.0 and **acid corrosion** occurs.

Under these conditions, the tendency is to try to compensate as quickly as possible for the loss of inhibitor and either add treatment directly to the condensate receiver, FW tank, or FW pump. This usually is *not* a good idea because in many cases the physically compact FT boiler design is insufficiently forgiving and problems of **surging** (**priming**) and **foaming** occur. This typically leads to **carryover** of BW and also the development of **water hammer**.

There are several causative problems here, and they tend to impact each other:

1. The primary types of corrosion inhibitor treatments employed are generally based on inorganic chemicals such as **sodium nitrite** (together with combinations of *borate*, *silicate*, *molybdate*, and *phosphate*) and the addition of even 2 to 3 pints (0.95–1.4 liters) to a boiler can immediately raise the TDS in the BW to a level at which priming can occur. Secondary problems include an associated rise in the level of BW suspended solids and sludge.
2. Where there has been no BD for a prolonged period but water losses occur, the *BW cycles of concentration* (COC) can build up to excessive levels, perhaps 50 to 100 times, and *alkalinity* also may rise significantly; both situations create high surface tension and the base conditions for **steam bubble surface-film stability**. Here, the sudden addition of almost any type of corrosion inhibitor contributes more TDS to the BW than operational circumstances can tolerate. Surging and priming take place, caused by the increase in surface tension imparted by high TDS water, which prevents the rapid and instant bursting of small steam bubbles at the steam–water interface. Bubbles tend to be fewer but larger, leading to the surging of the BW when the steam is finally released.

3. **Cast-iron sectional boilers** often suffer from initial surging or priming, spouting, foaming, and carryover under startup conditions or when changing from idle to online operation. The problem is aggravated where a "top-up" dose of inhibitor is added. These problems are especially prevalent with LP steam models, and it may thus appear that as a class of boiler, cast-iron plants generally are intolerant of even slight deviations in waterside chemistry or operational control. In reality, however, this in not the case. The fact is that the smallest LP steam boiler systems tend to be of cast-iron construction because of their relatively low cost and wide flexibility of sizing options. As a consequence of the very small volume of water typically involved, these boiler simply lack the tolerance for swings in TDS, BD, inhibitor levels, and other parameters that larger boilers possess.

   Where the MU water supply to cast-iron boilers does not precisely keep up with steam generation demands, the water level can quickly decrease and the problems become even more acute. Conversely, where MU does precisely keep up with steaming rates and is supplied to a common condensate receiver–FW tank via automatic level control, the tank can easily overfill when condensate finally drains back under on–off operating conditions. This gives rise to a loss of valuable hot, treated water from the system and the start of another chain of cause and effect problems.

Where smaller boilers are involved, careful control over water throughput and COC, as well as general waterside chemistry and mechanical operating practice is necessary (including BD schedules), to prevent surging, the loss of inhibitor, and the onset of cause and effect problems.

Here, the use of inhibitor formulations having a less dramatic effect on TDS (such as certain **tannins**) may be extremely beneficial. Formulations are available that are based on tannin chemistry and contain blends that act as oxygen scavengers and metal passivators, with additional sludge dispersant and antifoam properties.

5.4.3 Lead and Lag Boiler Operation

Another operational problem that may develop concerns multiple LP steam-heating system installations in which an imbalance in waterside chemistry results in low TDS/chemical inhibitor in one boiler and high TDS/chemical inhibitor in a second unit.

This situation typically is caused by a **poor boiler system design** (including inadequate valving of steam–condensate distribution and

collection lines, and deficient boiler balancing arrangements) often coupled with **lead and lag operation**.

As the *lead* boiler generates steam, the condensate falls back into an idle or offline boiler because of inadequate valving. Excessive MU is supplied to the lead boiler and the TDS quickly rises to exceed control parameters, while the *lag* boiler steam space (and possibly some of the steam header) fills up with condensate, diluting any chemical inhibitor present below the minimum protective inhibitor reserve level.

Because the lead boiler requires frequent BD (losing chemical inhibitor in the process) and the lag boiler inhibitor becomes excessively diluted because of condensate ingress, the result is that both boilers do not have appropriate waterside chemistry conditions and corrosion develops.

Clearly, this kind of problem requires more than a "quick-fix" solution if operational stability is to be attained.

5.5 WATERSIDE PROBLEMS IN MEDIUM-TEMPERATURE HOT WATER AND HIGH-TEMPERATURE HOT WATER SYSTEMS

Medium-temperature hot water and **medium-pressure hot water (MTHW/MPHW) systems** typically operate above 250 °F and below 350 °F/176.7 °C, whereas **high-temperature hot water** and **high-presssure hot water (HTHW/HPHW) systems** operate above 350 °F and below, say, 450 °F/232.2 °C.

In practice, it is sometimes hard to precisely define whether a particular system is MTHW or HTHW because the operating conditions may vary among designs, but both tend to be large-volume systems, with the boilers centrally located within a large hospital, college, housing complex, or similar facility. The central plant supplies HW to satellite buildings, where it is converted to LTHW or LP steam via **heat exchangers** or **converters**.

Problems associated with MTHW and HTHW systems resemble those of LTHW systems, although these are much less forgiving than LTHW systems when waterside conditions go awry, and they tend to receive more attention both at the design stage and in their daily operation.

Generally, chemical feed arrangements and TDS controls are more sophisticated than in LTHW systems and some form of **pretreatment** is almost always provided.

*NOTE: The term **pretreatment** is generally assumed to refer to some form of permanently installed equipment employed to treat MU water or FW. Such equipment provides physical or physicochemical water conditioning processes (such as ion-exchange softening) and is employed prior to the application of any internal FW or BW chemical treatments.*

*Similarly, **posttreatment** refers to similar process equipment after the boiler section (such as condensate polishing).*

The primary problems to be addressed are:

1. **Provision of pretreatment:** The initial fill volume and MU supply is almost always pretreated in some manner. Because of the large volume of water in these systems, even low-hardness waters can produce sufficient quantities of calcium carbonate scale to severely impede heat transfer; thus, for MTHW pretreatment, the use of **ion-exchange softeners** is the norm. For HTHW, some form of demineralization such as **reverse osmosis** (RO) or **deionization** by cation–anion exchange is typically preferred.
2. **Prevention of water loss and air ingress:** These problems generally are interrelated. Any water loss results in a physical loss of treatment and subsequently the requirement for some further consumption of treatment reserve, proportional to the MU entering the system.

   Where air-ingress takes place, the inhibitor reserve may be lost very quickly. Thus, a higher product reserve is preferred, and these chemical blends should incorporate a specific *oxygen scavenger.* (Although there is a slightly higher cost associated with this additional protection capability, it is infinitely preferable to pay the extra money than to deal with unplanned repairs at some later stage.)

   Where water softening is provided and there is no reduction in system water TDS, treatments are primarily based on *inorganic* corrosion inhibitor blends (nitrite, molybdate, etc.). Under these circumstances, there is no benefit in using an expensive *organic* oxygen scavenger to keep the TDS level low, and a common chemical such as **catalyzed sodium sulfite** may be used.

   Demineralized water is often employed for HTHW systems, and here it is preferable to employ an organic oxygen scavenger. **Hydrazine**, although a health hazard, is often used, although **diethylhydroxylamine** (DEHA) is preferred from an overall safety position or where there are high levels of nonferrous metals present. The pH typically is maintained at 8 to 10, depending on specific circumstances.

3. **Control of foulants and corrosion debris:** Because of the very large volume in these HW systems, there is an obvious reluctance to unnecessarily drain them down because of the development of waterside problems. Therefore, it is important to ensure that before regular operation they are provided with a proper precommission cleaning procedure. This process removes *silt*, *mill-scale*, *grease*, and other foulants, thus enabling passivation and subsequent maintenance inhibition to take place.

   Because of the duty requirements of these systems, pipework layouts are often tortuous and may contain stagnant areas where localized corrosion may develop or sludge may accumulate. The breakdown of glycols may also contribute to the development of foulants and corrosion debris. It is therefore good practice to incorporate both **general dispersants** (say, a 4,000–5,000 MW *polyacrylate*) and **iron dispersants** (say, a *terpolymer*) in the inhibitor formulations.

   Periodic testing for turbidity, iron, and sludge from several points in the system is also important.

   Finally, the use of side-stream filters is recommended. Bag filters generally are satisfactory, although for the removal of the finest iron particles, an in-series twin-bag system may be required; use 5 to 10μ bags followed by 1 to 2μ. Where only one bag filter is employed, use either conventional 5μ filters or high-quality depth filters.

A summary of waterside and steamside problems affecting LPHW heating and LP steam boiler plants is provided in Table 5.1, and problems affecting MPHW/HPHW are presented in Table 5.2.

Table 5.1 Summary of waterside/steamside problems affecting LPHW and LP steam heating boiler plants

Type of problem	*Notes*
1. Problems with heating coils	Acid corrosion from soft water.
Internal coil corrosion	Pinhole corrosion from O_2 and CO_2.
Note: corrosion debris is:	Erosion corrosion over 6 ft/s flow.
green hydrated copper carbonate $Cu^{[11]}CO_3 \cdot nH_2O$	
red cuprous oxide Cu_2O	
*I*nternal coil deposition	Hard water scale from hard water.
	White calcium carbonate $CaCO_3$
	Phosphate scale from threshold agents. *Blue/green/black* copper phosphate trihydrate $Cu_3(PO_4)_2 \cdot 3H_2O$
	Dirt pockets due to low level of coil.
External coil problems	BW sludgei settles on external fins.
	Gasket weeping from inhibitor.
	Color stains from inhibitor dyes.
2. Problems with glycols	Reduced freeze protection from
Loss of glycol strength	water leaks and glycol oxidation.
Glycol degradation	Acid corrosion (system pH < 7) from extreme degradation of glycols.
3. Problems of corrosion	Tuberculation and pitting due to
Oxygen corrosion	DO, air in-leakage, loss of nitrite and
Note: corrosion debris is:	lack of specific oxygen scavengers.
red/brown hematite sludge	
black coarse magnetite	
Galvanic and under-deposit corrosion (UDC)	Mixed metal corrosion Cu/Fe/Zn
	Iron transport –iron sludges, esp. ferrous bicarbonate $Fe(HCO_3)_2$
	UDC from fouling and binders.
4. Other system problems	Pump, valve, steam trap losses and
Uncontrolled and excessive water losses	no water meter leads to O_2 pitting, Fe fouling and deposits of carbonate scale and ferrous metasilicate $FeSiO_3$
Lack of BD control	Water losses, low inhibitor levels
High treatment/small boiler	Surging/carryover from high TDS.
Poor design, lead and lag boiler operation	Excessive TDS in lead boiler.
	Lack of treatment in lag boiler.

Table 5.2 Specific waterside/steamside problems affecting MPHW/MPHW and HPHW/HPHW boiler plants

Type of problem	*Notes*
Lack of adequate pretreatment	Higher temperatures/pressures demands better pretreatment, feed and control. – Use softeners and/or dealkalization for MPHW. – Use demin/RO for HTHW.
Prevention of water loss and air ingress	Good control over water losses and DO ingress is needed to prevent loss of inhibitor and reduced waterside protection. – Use catalyzed sulfite with MPHW. – Use DEHA for HTHW.
Control of foulants and corrosion debris	Thorough pre-cleaning needed to prevent initial fouling in large tortuous systems. Prevent stagnation and glycol degradation. – Use both general and iron dispersants. – Test for sludge/iron pH. – Side-stream filters very useful.

6

WATERSIDE AND STEAMSIDE PROBLEMS: PRE-BOILER SECTION SPECIFICS

This chapter and the two chapters that follow consider the waterside and steamside problems associated with high-pressure (HP) boilers and divide the issues into pre-boiler, boiler, and post-boiler sections. This division has been undertaken primarily to maintain each chapter at a reasonable length; it should be remembered that waterside chemistry knows no such division. Of course, many of the basic problems that affect hot water (HW) heating and low-pressure (LP) steam boilers, which were discussed in Chapter 5, also affect HP boilers. In HP plants, however, these problems, their various interactions, causes, and effects can be more far-reaching and severely disrupt industrial manufacturing processes or the generation of electricity. High-pressure boiler plants also tend to be larger and encompass more associated equipment and subsystems so that there is always more to go wrong!

A HP boiler is typically defined as operating at a **maximum allowable working pressure** (MAWP) of 15 psig or higher and possessing over 6 boiler horsepower (207 lb/hr), although the vast majority of HP boilers operate at significantly higher pressures than this and are rated in the thousands of pounds per hour of steam-generating capacity.

There are a variety of waterside operational problems that may potentially develop in HP plants. Some of these occur in the **pre-boiler section** and mostly concern the boiler feedwater (FW) system. For any particular boiler plant, the *steam output*, *operating pressure*, *types of pretreatment*, and *daily operating procedures* are all considerations that factor into the scope and severity of these problems.

Pretreatment (and internal treatment) is often limited for smaller HP FT boiler steam systems but gradually becomes more extensive with larger and higher output FT and WT plants.

Although *all* HP FT boilers operate above a MAWP of 15 psig, for commercial space heating applications they are seldom designed to provide steam above 30 psig/44.7 psia.

Pretreatment for FT boilers designed for industrial duty becomes slightly more exacting because these typically operate at about 85 to 100 psig/114.7 psia (338 °F/169.9 °C) perhaps up to, say, 250 to 300 psig (264.7–314.7 psia).

Water tube (WT) boilers tend to be used in larger facilities and, although they also may typically operate at only 100 psig, they cover a much wider pressure (and output) range, with some designs rising to over 2,000 or 3,000 psig, thus necessitating extensive pretreatment.

6.1 OVERVIEW OF PRE-BOILER SECTION WATERSIDE PROBLEMS

Problems that originate in the pre-boiler section of HP boiler plants are often the cause of operational problems further downstream in the system; these problems must be controlled with appropriate internal treatments. Although programs can be devised to deal with almost all types and qualities of FW, it is a *fundamental* requirement that the water quality be as *consistent* as practically possible.

Trying to routinely compensate for variable FW quality is a futile exercise; wide swings in water chemistry inevitably occur, and severe boiler waterside problems will likely result under these operating conditions.

There are three primary factors whereby FW system problems may either originate or manifest themselves:

- FW contamination from makeup (MU) water
- FW contamination from returning condensate
- Problems associated with the final blended FW

Each of these problem sources requires effective operational control and is discussed in the following sections.

6.2 FEEDWATER CONTAMINATION FROM MAKEUP WATER

Many different types of external treatment processes are available to deal with typical MU water contaminants such as *undesirable dissolved solids*, *colloidal particles*, or *noncondensable gases*.

If, in any boiler plant, the installed treatment processes are unsuitable or inadequate for the needs or if operational problems persist, downstream operational problems certainly will develop in a short time. The extent of these problems and their associated costs are likely to be serious if the external treatment problem is not rectified at the source. In almost all cases, internal chemical treatment cannot totally and economically compensate for lack of pretreatment.

Where downstream boiler plant problems do result, these may often be traced back to inappropriate FW quality. This does not mean that the FW is necessarily contaminated in some way, but rather that the most suitable or necessary type or capacity of pretreatment equipment (such as a *water softener*, *dealkalization plant*, or *deaerator*) has most probably not been installed.

There may be several reasons for this, including perhaps a policy of limiting the available capital expenditure, or reluctance to embrace the appropriate technology, or insufficient knowledge to recognize the genuine need and the benefits that would accrue. In those facilities where the installation of additional external treatment has not kept pace with the growth in steam generation capability, downstream operational waterside problems can be expected.

6.2.1 Lack of Softening or Dealkalization Capability

A lack of much-needed MU water softening, dealkalization, or similar external treatment capability is quite common in many small to mid-sized industrial facilities. It seldom produces a complete boiler failure or anything quite so dramatic, but it is nonetheless very costly in terms of additional fuel costs and maintenance. Personnel may learn to live with the resultant poor quality of FW for many years, accepting the position as "normal" until the facts are pointed out and alternative proposals are considered.

The use of FW that has been inadequately pretreated makes the mechanical operation of a boiler and the control of boiler water conditions innecessarily difficult. Additional quantities of internal treatment chemicals and higher rates of blowdown (BD) are usually required, which reduces boiler plant efficiency and raises the cost of generating steam.

Higher rates of sludging also take place in the boiler vessel. In turn, this potential **fouling** problem requires additional maintenance time because more frequent internal surface cleaning, wash-down, and boiler vessel sludge removal usually is required. **Carryover** of contaminants into the steam also is more likely.

Two examples of the results of using a FW of inappropriate quality follow. External pretreatment is needed.

1. Example of a **softening need**. Where a lean water of very low *total hardness* is used as a source of MU water, some facility engineers may argue that there is no benefit in providing an ion-exchange softener. Although the water is lean, a higher feed rate of internal chemical treatment nevertheless is necessary (to control the small additional *calcium* and *magnesium hardness* loading) than would otherwise be required if a softener had been installed.

   Cycles of concentration (COCs) usually will be high because of the lean nature of the MU water (perhaps 30–50 × COC). Where a phosphate precipitant program is employed, which is quite typical, the higher concentration of hardness salts results in a higher than tolerable level of flocculated sludge in the boiler. The potential for **waterside fouling** and **baked-on sludge** to occur is very real. The fact is that boilers are not designed to act as precipitation and flocculation vessels, and any actions that can be taken to limit the sludge produced therefore should be implemented.

   A sodium ion-exchange water softener is required for *all* boiler plants operating at an MAWP of over 15 psig.

2. Example of a **dealkalizer need**. Many sources of MU water contain naturally high levels of alkalinity (say, greater than 200–250 ppm total alkalinity as $CaCO_3$) yet must be used because no other suitable supply source exists. Typically, the hardness is also high, and under these circumstances, a water softener is always provided. It is much less common, however, to find that a dealkalization plant (DA) has been installed, with the consequence that although the treated water contains practically no *calcium* or *magnesium*, the levels of *alkalinity* and *total dissolved solids* (TDS) remain high.

   These factors severely enhance the risks of **condensate system corrosion** by *carbonic acid* (resulting from a breakdown of the alkalinity in the boiler water and carbon dioxide [CO_2] carryover into the steam) and **BW carryover**. In addition, boiler operation is more difficult because the possible COC is severely limited, there-

by increasing the requirement for BD and consequently raising the cost of steam generation.

Where water containing high alkalinity is used as boiler FW, the costs and problems associated with efficiently operating the boiler and controlling waterside conditions are needlessly high. A dealkalization plant is required—ideally a **strong acid cation DA** type.

Where in practice a DA plant is required, by careful selection, equipment can be provided that will not only remove the excess alkalinity but also *reduce* the TDS to the extent of the alkalinity removed, thereby raising the potential for high COC and lowering BD and fuel costs. The savings in fuel and treated HW provides the necessary impetus for capital expenditure. The payback period typically is under two years, and often much shorter.

Depending on the proportions of hardness alkalinity and nonhardness alkalinity present in the MU water source, there are several options for dealkalization by ion-exchange:

- **Strong acid cation** (hydrogen form), followed by deaeration/degassing and neutralization
- **Weak acid cation** (hydrogen form), followed by deaeration, neutralization, and water softening
- **Split-stream strong acid cation**, employing resins in both hydrogen and sodium form, followed by blending and deaeration
- **Anion exchange** (chloride form)

This last design (chloride anion exchange) is very often specified when some form of dealkalization plant is under consideration. Selection usually is made on the grounds of operator safety and reduced risk of boiler corrosion. Although it may have the attraction of not creating any potential for acid handling or acid introduction into the FW line or not requiring a deaerator, these are mere diversions.

The fact is that, although safety is an important issue, it can be overstated—a responsible boilerhouse facility will already have appropriate safety training programs and safe-handling rules in place.

A chloride-based DA will *not* reduce the TDS of the water, and therefore the tangible benefit of continuous cost savings through lower boiler BD rates is never realized. Also, the introduction of additional chlorides into a boiler may provide the potential for **pitting corrosion** to take place.

Dealkalization by some form of cation exchange is relatively simple, can be completely automated, and, in view of the significant returns in fuel and treated HW savings, is almost always preferred.

6.2.2 Hardness Breakthrough

A common FW contaminant is *calcium* and *magnesium hardness* resulting from periodic **hardness breakthrough** when operating a *sodium cycle, cation exchange softener.* When hardness breakthrough occurs, treated MU water hardness levels rise quickly from a typical total hardness leakage of 1 to 2 ppm (as $CaCO_3$) to perhaps 30 to 40 ppm or more. This problem usually does not affect larger boiler plants, where duty and standby softening capacity is available and often some form of continuous hardness monitoring is installed, but it is a relatively common problem at some smaller boiler plants.

Hardness breakthrough can be particularly troublesome at those small, hard-working facilities that employ just one *automatic* softener. The problem may develop gradually and go unnoticed for some time. This may be because the softened water is not tested daily or, more usually, because the soft water is tested soon after resin regeneration rather than immediately before the point of exhaustion (which may be many hours later, but perhaps still 2 or 3 hours before the end of a working shift or plant shutdown).

Where smaller plants use *manually* operated softening plants, the incidence of hardness breakthrough occurs less frequently. Typically, the operator performs a hardness check just before resin exhaustion is anticipated to confirm the validity of regeneration.

Poor control of the softened MU water leads to excessive **boiler sludging** and **scale deposition** on heat transfer surfaces.

Hardness breakthrough problems generally manifest as a periodic but sudden drop in **alkalinity** and a loss of **phosphate reserve** in the boiler. Reasons for hardness breakthrough include:

- **Increased demand for softened MU**, perhaps caused by an increase in plant capacity without increasing softener capacity installed, or the use of additional steam for processing so that the return of condensate is diminished. Here a larger plant is required. If the existing plant is not too old, a second identical unit usually is installed and the equipment is operated as duty/standby, with water-meter countdown crossover and immediate regeneration of the out-of-service unit.
- **Reduced operating capacity** due to **iron fouling** of the resin, which occurs because soluble iron (in the form of ferrous bicarbon-

ate [$Fe(HCO_3)_2$]) is often present in groundwater up to perhaps 0.5 to 1.0 ppm Fe. **Manganese fouling** also may occur. The resin will require either cleaning or replacement to restore exchange capacity.

NOTE: Periodic cleaning of softener resin with an iron stripping formulation based on phosphonate or a terpolymer is useful. The cleaner is introduced into the resin bed, perhaps via the brine draw during resin regeneration, at a level of, say, 1 to 2 U.S. pints/cu ft (16–32 ml/l) of resin. The regeneration process is temporarily halted for several hours and the resin is allowed to soak; the process is then restarted and the stripped iron goes to drain.

- **Reduced operating capacity** due to physical **resin breakdown**. Most types of ion-exchange resin suffer some breakdown and volume loss over time because of *attrition*, *excessive heat*, or other factors. Water softeners should be inspected annually, and a *double backwash* procedure should be provided. This generally lifts the broken resin ("fines") to the top of the bed, where it can be removed and replaced to restore capacity. Allow for 5 to 10% resin operating capacity loss per year because of physical breakdown. At many sites the resin is unfortunately not inspected regularly but merely replaced when a serious decline in operating capacity is noticed. Here a resin life expectancy of, say, 6 to 8 years probably is the norm.
- **Loss of resin from the softener** due to poor regeneration procedures or excessive water pressure. The resin may either be lost down the drain or it may enter the FW system, whereupon it melts or disintegrates and causes fouling of waterside surfaces.
- **Inadequate brine regenerant** as a result of insufficient regeneration cycle time allocated for the *brine-draw* stage or a reduced strength of available brine. Softener brine strength typically varies between 10 and 25% sodium chloride (NaCl) on a weight–volume basis, depending on the brine tank design, the regeneration resin capacity/salting rate required, and the time allocated for dissolving salt. The *minimum* recommended time required to provide for an adequate strength of brine solution is 8 hours.

6.2.3 Chloride Leakage

A common problem associated with the operation of ion-exchange water softeners is due to **chloride leakage** contamination into the FW following regeneration. This is an operational problem caused by inadequate rinsing and usually is detected in the boiler by a periodic and sudden rapid rise in the boiler water's electrical conductivity and a call

for increased BD. High chlorides cause **depassivation** and **depolarization** problems.

6.2.4 Acid Breakthrough of Ion-Exchange Plant

Feedwater contamination problems may also occur where ion-exchange plants are employed for **dealkalization** or **demineralization/deionization** (DI) processes. Where such equipment is used, however, it is common for some form of continuous monitoring to be provided, perhaps in association with an audible alarm to provide a warning of out-of-specification FW.

Where dealkalization by *acid cation exchange resin* is employed, a small risk exists of contamination from **acid breakthrough**. A failure in the neutralization process may lead to acidic treated water entering the FW system, which reduces the FW pH and results in localized **acid corrosion**.

Where dealkalization by **hydrogen cycle, weak acid cation exchange resin** is employed, it is common to regenerate at 120% of theory (i.e., 1.2 *equivalents* of acid per *equivalent* of cations exchanged). Under these conditions, some mineral acidity can be expected during the early portion of the run and neutralization is therefore required. By reducing the regeneration to only 100% of theory, the leakage of mineral acidity can be eliminated with only a slight loss in operating capacity and some marginal increase in alkalinity leakage.

Where-high purity MU is provided for higher pressure WT boiler plant FW, some form of continuous analyzers for measuring **treated water pH** and **conductivity** are almost always installed, as are **sodium** (Na) **ion-selective electrodes** for detection of sodium leakage. Automatic online **silica analyzers** also may be installed, but they measure only *reactive* (ionizable) *silica* (SiO_2), not *colloidal* or *total silica*, so caution is required where unforeseen silica leakage may present a problem.

6.2.5 Sodium and Silica Leakage

Where MU is intended for power boiler FW, particularly strict limits are imposed on **sodium leakage** (*breakthrough*) and **silica leakage** to prevent FW contamination and subsequent downstream **caustic gouging corrosion, caustic cracking corrosion**, or **silica deposition**.

Control also is required to prevent contamination from **chloride** and **sulfate leakage**.

Because of their lower charge densities, *monovalent ions* are exchanged less efficiently, so *chloride* and *sodium ions* in particular tend to slip through the resin beds. Where twin-bed DI is employed,

under normal conditions the pH of the cation exchanger effluent is 2.0 to 3.0, while that of the anion exchanger is close to 8.0. The effluent from the cation bed will always contain some low level of *sodium*, which creates *sodium hydroxide* in the strongly basic anion bed. Should the anion pH rise to 9.0 or higher, however, excessive **sodium ion leakage** from the cation exchanger is indicated.

As the DI plant becomes exhausted, **silica leakage** occurs in the treated MU water and the pH falls abruptly. Furthermore, where *sodium ion leakage* occurs from the cation bed, it produces a regenerative effect on the anion bed, which may also lead to *silica leakage*. To differentiate between the two phenomena, sodium ion leakage from the cation bed should be assessed directly using *selective sodium-ion electrodes*, *flame photometric analysis*, or other appropriate test methods.

Ionic silica is not totally removable by DI. **Colloidal silica** is difficult to remove by both DI and **reverse osmosis** (RO); it may cause some resin fouling as well as leaking into the treated water. Where the cation effluent is maintained at a pH of 2.0 to 3.0, however, silica tends to both *depolymerize* and *ionize* thus enabling its effective removal in strongly basic, anion resin beds.

Reverse osmosis plants also are not immune from silica fouling, and where the raw water source naturally contains relatively high levels of silica, good pretreatment of the RO FW is a prerequisite. To reduce fouling of RO membranes by silica, pretreatment by *acid adjustment*, *alum coagulation*, and *filtration* usually is provided.

Twin-bed DI plants in good operating condition typically produce a slightly alkaline treated water with a sodium leakage level of perhaps 1 to 3 ppm, a silica leakage of 0.05 to 1.0 ppm, and a resistivity of typically 0.1 to 0.5 megaohm per cm (MΩ/cm).

Ion leakage can be reduced by several methods, including:

- Reducing water throughput velocity rates to extend the reaction time
- Increasing the bed depth; usually a minimum bed depth of 24 in (61 cm) is required
- Increasing the number of ion-exchange sites by the use of countercurrent (counterflow) regeneration
- Following the twin-bed with a third cation exchange bed or a mixed-bed (MB) polisher. Processes such as RO followed by twin-bed DI, plus twin MB polishers may yield treated water with silica leakage down to 0.5 ppb SiO_2. An alternative arrangement for the minimization of silica is the use of a double-pass RO followed by MB polishers.

6.2.6 Organic Fouling

A further problem that may cause contamination of the treated MU water is *anion leakage* as a result of **organic fouling**. This significantly affects anion resins, preventing ion removal by ion exchange and thus reducing bed capacity.

Organic fouling also affects cation resins, albeit to a lesser degree. The fouling primarily stems from the attachment to the anion exchange site of a variety of low-level **organic matter** of variable molecular weight that is present in the raw water source.

These organics include *trihalomethanes, tannic, humic acids,* and *fulvic acids* (as well as *organic process contaminants* and *microbiological breakdown products*). Their presence in FW may lead to problems of BW **foaming** and **carryover**. Where this problem occurs, special resin cleaning procedures can be implemented; however, the best course of action is to change standard **gel-type ion exchange resins** to **isoporous** or **macroporous** resins, or to install an **organic trap** or **activated carbon filter**.

- *Gel-type resins* have a high capacity but a nonuniform cross-linking structure, whereas *isoporous resins* possess a uniform cross-linking structure, and *macroporous resins* have a spongelike, open-pore structure. Both isoporous resins and macroporous resins exhibit good reversibility toward organic anions, permitting regeneration without loss of capacity, although the overall exchange capacity is reduced.
- *Organic traps* contain isoporous, macroporous, or other specifically designed resins (such as *reticulated, cross-linked polystyrene resins* devoid of ionic function) and take up organics by a combination of ion exchange, adsorption, and other mechanisms. They typically are installed to precede the DI plant.
- *Activated carbon filters* remove a wide range of organic matter by adsorption onto the carbon bed. The bed may be derived from a number of different carbon sources, and the correct selection of bed type, capacity, and porosity is a specialized function. Activated carbon may be usefully employed in organic traps, complementing the resin bed, but its capacity and organic removal rate characteristics are *flow-dependent*. Excessive flows may compromise the rate of adsorption of organic matter.

6.2.7 External Treatment Carryover and After-Precipitation

Additional problems that may cause serious contamination of the treated MU water are those related to **carryover** and **after-precipitation** from external treatment processes. Both of these processes may result in the presence of insoluble solids in the various lines, tanks, and valve areas of the pre-boiler section. Some solids may even pass through to the boiler.

The effect of carryover and after-precipitation is that solids settle out and cause **pre-boiler system fouling** and result in *reduced flow* and *equipment waterway blockages*. **Check valves** are especially prone to blockage.

Hard **crystalline scale** and **deposition** also may result from the interaction of *silica*, *residual hardness*, and *inorganic coagulants* carried over into the treated water. Also, pre-boiler system damage by **erosion** may occur.

- **External treatment carryover** often consists of *sand*, *grit*, or *destabilized colloidal particles* together with *aluminum and iron salts* (typically present as finely suspended precipitate). Carryover results from inadequate flocculation following coagulation processes or from employing filters that may be overloaded or subject to poor backwashing procedures. This form of contamination must be eliminated either by accelerating the precipitation–settling process or by improving the filtration–separation process. Methods for reducing risk of carryover include using a *hot lime process* (faster precipitation than using *cold lime*), *clarifier sludge recirculation*, and *upward-flow sludge blanket* techniques, and the use of *cationic*, *organic polyelectrolytes*.
- **External treatment after-precipitation** occurs when treated MU water becomes unstable and supersaturated with *calcium carbonate* or *magnesium hydroxide*, following a precipitation softening process. The time required for complete precipitation varies considerably, depending on the source of the water, plant design, operating conditions, and the presence of substances that can interfere with the process, such as *ammonium* or *polyphosphate salts* (originating from fertilizers, farm run-off, etc.).

If inadequate precipitation time is available or if interference occurs, **unstable treated water** results and *salt deposition* continues to occur in the pre-boiler section.

Traditionally, **stabilization** of unstable treated water generally is provided by simply *lowering* the treated water pH slightly or by using a **threshold phosphate** technique. Neither of these techniques is particularly suitable for boiler FW makeup because an *alkaline* FW is required and rapid reversion of the polyphosphate will take place under hot FW conditions, thus leading to **phosphate deposits** in the pre-boil-

Table 6.1 Summary of FW contamination from MU water

Type of problem	*Likely results or increased risks*
Lack of ion-exchange softener with low hardness MU water source	Extra chemical treatment need Waterside fouling Baked on sludge Increased BD and higher costs
Lack of dealkalization with high alkalinity MU water *NOTE: Anion dealkalizers do not use acid, but also do not reduce MU water TDS and introduce additional chlorides (risk of pitting).*	Excessive CR line corrosion BW carryover Low cycles of concentration higher operating costs
Hardness breakthrough with ion-exchange (base exchange, BX) softening *NOTE: Caused by Fe/Mn fouling, resin breakdown/loss, or inadequate regeneration.*	Increased risk of carbonate scale or phosphate sludge Loss of alkalinity and hence an increased silica deposition risk
Chloride leakage with BX softening *NOTE: Caused by inadequate rinsing.*	BW carryover Increased BD Temporary loss of control Depassivation
Acid breakthrough (split-stream softening, dealk/DI).	Failure to neutralize results in acid corrosion of feed system
Na leakage (DI). *NOTE: Deposits may develop containing high concentration of NaOH, resulting in:*	Caustic gouging Caustic induced SCC (where stressed)
Silica leakage (DI).	Silica volatilization Deposition on boiler surfaces, superheaters, and turbine blades
Cl^- and SO_4^{2+} leakage (DI).	Anodic depolarization, leading to depassivation and corrosion
Organic fouling of DI resins.	Loss of treated water capacity Anion leakage
External treatment carryover, and after-precipitation	Fouling and blocked check valves Erosion/corrosion

er section. Additional treatment processes such as *filtration* and *ion-exchange softening* are also likely to be required.

6.3 FW CONTAMINATION FROM RETURNING CONDENSATE

In most boiler plants, a high percentage of the generated steam is condensed after use and returned to the pre-boiler section, where it is supplemented with sufficient MU to meet the current total FW demand at any particular time. Because this returned condensate or condensate return (CR) generally comprises the greater part of the FW supplied to the boiler, any contamination of the condensate may result in contamination of the FW system that is ultimately transported into the boiler section itself.

Condensate contamination originates from several sources, including **BW carryover** into the generated steam, **corrosion debris pickup** within the steam and condensate distribution systems, and **process leaks**. It is very important, therefore, to regularly monitor steam and condensate quality. This can be achieved by means of periodic sampling using sample coolers and (typically) stainless steel water sampling containers, and appropriate analytical testing programs perhaps supported by an automatic, real-time conductivity measuring and alarm facilities.

6.3.1 Transport of Boiler Water Solids

Although much of the solids resulting from BW carryover are deposited somewhere within the condensate system, the balance is transported back to the FW system to begin another cycle. Boiler water is always alkaline (often strongly caustic), and the carryover of BW solids produces a highly alkaline condensate that has a detrimental effect where high steam purity is required. Strongly alkaline condensate can have a scouring effect on condensate lines, sweeping up old corrosion debris, which is then carried through with the alkaline condensate to the FW system. Sufficient slugs of dirty, alkaline condensate can cause **pre-boiler metal damage** and throw any **FW pH control system out of balance**.

In addition, the solids may cause **fouling** problems such as *reduced deaerator venting*, *sticking check valves*, and *blocked feed pump*.

6.3.2 Oxygen Loading

The contamination of returned condensate may develop in several ways. Where the steam–condensate system is subject to air infiltration, the result-

ing **oxygen loading** of the condensate leads to a *high deaeration demand* being imposed on FW deaerating heaters and DO chemical scavengers.

Where problems develop, there is always a cause-and-effect process. In this case, as oxygen infiltrates the CR system, **enhanced condensate line corrosion** results (i.e., corrosion over and above the level that may be caused by the **carbonic acid** formed during steam condensation). This enhanced corrosion, in turn, creates the potential for further downstream *corrosion debris pickup* by the returning condensate and transporting this material back to the FW system.

6.3.3 Corrosion Debris Pickup, Transport, and Redeposition

The problem of corrosion debris and deposit pickup may happen anywhere in the steam distribution or CR systems (such as from a *superheater*, *steam trap*, *surface condenser*, *FW preheater*, or *condensate line*).

Corrosion debris that may be picked up and transported by returning condensate includes *oxides of iron*, *copper*, *nickel*, *zinc*, and *chromium*. Redeposition may then occur in the FW line, causing **feedline blockages**. The transport of corrosion debris also brings with it further problems of **impingement** or **erosion-corrosion**, which can occur anywhere in the pre-boiler system. In old and corroded plants, the use of filters, strainers, condensate polishers, or (for smaller plants) high temperature–resistant bag filters is highly recommended to prevent the corrosion debris from entering the FW system.

6.3.4 Oil and Process Contamination

A wide range of **process contaminants** may be inadvertently transported back with returning condensate following the purposeful injection of live steam into a manufacturing process and its subsequent contamination by the process. Contaminants also may infiltrate the CR system through a leaking heating coil, an open surge tank, or similar access point.

Process contamination may, unfortunately, occur regularly in certain industries, and these process materials inevitably find their way into the FW system, and from there to the boiler, unless adequate precautions are taken. The result is severe fouling of the boiler, contamination of the steam generation process, and the potential for damage and boiler failure caused by overheating.

Boilers may need to be taken offline immediately and boiled out, or at the least blown down very heavily for some period to remove the contaminants.

Condensate contaminated by process leaks is unsuitable for reuse as boiler FW and must be dumped or otherwise disposed of.

- Process leaks from *phenols*, *glycols*, and various other organics badly contaminate the FW system and lay down **sticky films** in lower pressure boilers and **varnish** in higher pressure systems.
- Process leaks of *sugars*, *fats*, *colloidal materials*, *pectins*, *emulsions*, and *proteins* cause **stable foams** in the boiler, leading to **carryover** and a further contamination cycle.
- Where contamination from *edible oils*, *fats*, *solvents*, and the like occurs, the development of **stable foams** or **colloids**, *saponification* of fatty materials into crude **soaps**, and a very serious risk to heat transfer surfaces may result.
- *Dyes* can produce **FW discoloration**.
- *Acid leaks* cause problems of **fluctuating feedwater pH levels** and **acid corrosion**.

Table 6.2 Summary of FW contamination from returned condensate

Type of problem	*Likely results or increased risks*
Carrythrough of BW solids with the condensate.	Highly alkaline condensate Pre-boiler metal damage pH control out of balance Fouling to DA vent, check valves and FW pump
High O_2 loading of returning condensate.	High deaeration demand that may exceed DA capacity.
Steam/CR system corrosion debris pickup, tranport, and re-deposition.	Wide ranging FW line blockages and impingement/erosion Enhances risk of pre-boiler corrosion
Process contamination.	Sticky films (LP boilers) Varnish (HP boilers) Steam discoloration FW pH fluctuations Acid corrosion Stable foams leading to carryover
Oil and hydrocarbon leaks.	FW system fouling and deposit binding Non-wettable boiler surfaces.
Condenser leaks.	Fouling, deposition Chloride depassivation and pitting corrosion of FW lines and boiler

- *Oil* and *hydrocarbon leaks* that return with the condensate coat heat-exchange surfaces and cause **FW system fouling** and **deposit binding**. These materials must be removed or they will reenter the boiler to produce **nonwettable boiler surfaces**, and create serious problems. Oil in condensate should be removed by the use of an inline *pre-coat filter*. The pre-coating should be either *aluminum hydroxide* or *ferric hydroxide* becaue both these hydrous oxide gels have an affinity for oil.
- Condenser leaks permit dissolved solids, oxygen, organics, and suspended solids to enter the CR system and from there to enter the FW system. This is a very serious problem and leads to **feed system fouling** and **deposition** and the **depassivation of metal surfaces**, which in turn induces **pitting corrosion** to occur.

6.4 PROBLEMS ASSOCIATED WITH THE FINAL FEEDWATER BLEND

Boiler FW is comprised of variable ratios of returned condensate and a MU water source. The MU requirement is proportional to the sum of nonrecoverable steam and BW blowdown that is lost from the plant.

Apart from the waterside problems discussed earlier, which are due to impurities introduced with either the MU or the returned condensate, additional problems may develop both in the pre-boiler system and further downstream. These problems are associated with the final blended FW and are primarily related to *oxygen corrosion* of various items of pre-boiler equipment or the deposition of *scales* and *metal oxides* on waterside surfaces.

Some additional very specific types of corrosion may also occur in the economizer, feed pumps, and other items of pre-boiler equipment, the mechanisms of which must be firmly understood if they are to be properly controlled. Some of the waterside problems affecting these items of equipment are discussed in the following sections.

6.4.1 Problems of Inadequate Feedwater Deaeration

Inadequate FW deaeration is a common cause of serious corrosion problems that affect many hundreds (if not thousands) of boiler plants of all sizes around the world. Despite the abundance of available literature advising the need to eliminate oxygen from boiler FW, inadequate deaeration continues to cause permanent waterside damage.

The dissolved oxygen (DO) passes through the pre-boiler section

and enters the boiler section, where it is particularly damaging to passivated metal surfaces. Dissolved oxygen causes serious **pre-boiler oxygen corrosion** and **boiler section pitting corrosion**.

Additionally, when internal chemical treatment programs containing chelants are employed *and* DO is present, the risk of boiler metal damage is significantly increased because of **oxygen-induced chelant corrosion** attack.

NOTE: The use of chelants is sometimes unnecessarily barred because of fears of chelant corrosion. Chelant programs do not sequester iron oxides (such as an adherent magnetite film), however, and, when correctly used under constant reducing conditions, are very useful. They can sweep out old alkaline earth deposits and provide particularly clean boilers.

Where inadequate FW deaeration takes place and **oxygen corrosion** occurs, the descriptive terminology employed often relates to the particular components involved:

- **Deaerator corrosion**
- **Economizer corrosion**
- **Feed tank corrosion**
- **Feedline corrosion**
- **Tube pitting corrosion** (FT boilers)
- **Shell boiler corrosion** (FT boilers)
- **Top drum corrosion** (WT boilers)

Apart from the usual classifications of boiler plants (FT, WT, pressure rating, steam output, etc.), they also may be grouped according to whether a **deaerating FW heater** (*deaerator*) is provided, and this is a useful consideration in view of a common need to provide adequate deaeration.

All large industrial WT and power boiler plants utilize deaerators and supplement the DO removal process by means of a suitable chemical *oxygen scavenger*. Many midsize factories operating FT boilers or FT–WT boiler combinations also employ mechanical deaeration. This is especially common in the United States, Germany, and several other industrialized countries where boiler design custom and practice virtually dictate that a deaerator be included in almost every midsize and larger boiler plant facility.

For these medium to large operations, apart from taking measures to ensure the continuous efficiency of deaeration and oxygen scavenging, little more can be said because all that can be done practically to remove DO is being done. The problems of inadequate FW deaeration, the resultant corrosion risks entailed, and the consequent need for constant vigilance primarily affects those owners and operators of small to midsize steam-raising boiler plants where mechanical deaeration is not available.

These deaerator-less plants include countless HVAC systems around the world located in hotels, apartment complexes, office blocks, skyscraper towers, prisons, medical and educational establishments and other such institutions, as well as smaller laundries, dye-houses, food and beverage plants, factories, and other general manufacturing facilities. It is no coincidence that the most common water treatment concern at many of these locations is avoiding boiler pitting corrosion through the effective removal of DO and the maintenance of adequate BW chemical oxygen scavenger or inhibitor reserves.

Although the need to properly soften the FW; control BW variables such as alkalinity, TDS, and sludge; and limit carbonic acid corrosion remains vital, these other problems generally are secondary to effective control over DO. If severe boiler plant damage and system failure are to be avoided, it is necessary to continuously maintain waterside reducing conditions and properly passivated boiler surfaces.

Actions to achieve this objective include:

1. Add chemical oxygen scavengers as far back in the FW system as possible.
2. Where *sulfite* or *bisulfite* oxygen scavengers are employed, a catalyst (such as a **cobalt salt** or an **ethorbate**) is vital to speed up the rate of deaeration.
3. Raise the FW temperature to as high a level as practically possible using returned condensate, live steam injection, or FW heaters.
4. Keep injection points for *catalyzed sulfite* and *chelant*-containing programs as far apart from each other as possible to avoid inactivation of the cobalt salt catalyst through chelation.
5. Where risks of inadequate FW deaeration remain high because of fluctuating FW conditions or other reasons, consider supplementing or replacing catalyzed sulfite with blended natural **tannin** formulations. Although **gallotannins** are also effective oxygen scavengers, the main benefit is derived from the fact that certain tannin blends produce a very stable, passive **iron tannate–magentite** film, which

provides temporary protection against pitting corrosion during periods when reducing conditions are not properly maintained in the boiler. (Tannins are suitable for boilers operating up to, say, 650–750 psig). For very small boilers where chemical costs are relatively minor and there is little MU water demand, **nitrite** provides a further alternative to the use of sulfite for the removal of oxygen. Nitrite is also an anodic inhibitor and stimulates the passivation process.

NOTE: Never use nitrite and sulfite in the same boiler. They are incompatible.

Although deaerators provide the primary means of mechanical deaeration, they are not of themselves immune from corrosive attack. Acid condensate (or MU water that has been subjected to *split-stream softening* or *dealkalization* and remains acid due to a lack of pH adjustment) can damage the deaerator.

Deaerator acid attack can occur at several points in a deaerator, including:

- The supply line to the deaerator, especially after the point at which hot condensate enters
- The gas scrubbing section
- Vent condenser, especially the condenser tubing
- Storage section, especially above the waterline

Economizers are always subject to a risk of very severe pitting corrosion as a result of the release of DO with rapid increase of water temperature. Therefore, they should be inspected at every available opportunity.

In smaller boiler systems, the FW tank often acts as a common condensate receiver, MU water heater, and deaerating vessel. As such, the tank is subject to the same corrosion problem risks that befall deaerators, economizers, and FW lines. Smaller systems often are inadequately designed and constructed, with the result that they may suffer serious oxygen corrosion in a particularly short time. (It is not unknown for tank wall perforation to occur within 3 to 6 months of the installation of a new FW tank as a result of pitting corrosion.)

6.4.2 Selective Corrosion Problems Affecting Pre-Boiler Section Equipment

Several items of pre-boiler equipment (and post-boiler equipment) may suffer from selective forms of **galvanic corrosion**. One fairly common

form of galvanic corrosion is **dealloying** (**selective leaching**). This is a general term that covers the preferential leaching of alloying components from a wide range of *copper alloys*. Dealloying also includes the selective corrosion of *iron* in *cast irons* (**graphitic corrosion**).

These galvanic corrosion processes take place when one or more elemental constituents of an alloy is leached, often leaving a weak, porous structure, although the component dimensions often are unchanged. Dealloying particularly affects equipment constructed of *cupronickels*, *bronzes*, *brasses*, and *gunmetal*, such as FW heaters, strainers, valves, and pump impellers.

The corrosion of copper alloys is accelerated by:

1. Soft waters
2. Deposition on component surfaces
3. Idle or stagnant FW
4. High chloride water
5. Excessive velocities (erosion–corrosion)

Examples of the dealloying of cuprous alloys include:

- **Dezincification:** As either **plug dezincification** (localized corrosion) or **layer dezincification** (general corrosion) and refers to **zinc** (Zn) being selectively leached out of *brass*. It can be prevented either by reducing the Zn content to below 15% or by the addition of trace amounts of inhibiting elements such as **arsenic** (As)
- **Denickelification: Nickel** (Ni) leached from *cupronickels*
- **Destannification: Tin** (Sn) leached from *gunmetal*
- **Dealuminification: Aluminum** (Al) leached from *aluminum-bronzes*

Certain pre-boiler *cupronickels*, such as 70:30 alloy tubes, subjected to high temperature, stress, and stop–start operation may suffer **oxygen corrosion–induced dealloying** followed by **exfoliation corrosion**, in which oxidized sheets peel away from the solid metal.

As noted previously, dealloying also affects pre-boiler components manufactured of cast iron, such as FW pumps and valves. These components may, under certain (long-term) circumstances, suffer a selective form of preferential leaching galvanic corrosion. Specifically, **graphitic corrosion** may take place when the (*anodic*) iron matrix con-

verts to *iron oxide* while the (*cathodic*) graphite in the cast iron remains intact. The casting retains its shape but eventually loses all strength and can be cut with a knife. This problem primarily affects **gray cast iron**, but it less commonly affects **nodular cast iron**. The rate of graphitic corrosion increases with low pH in water, with high sulfate content, and under idle operational conditions.

A further pre-boiler corrosion problem is the **erosion–corrosion** of FW pump impellers, housings fittings, and pipes or tubes. It may be caused by *impingement* by high-velocity steam, metal oxide particles, or high-speed turbulent FW striking the surface of the component. Erosion–corrosion causes metal wastage through mechanical abrasion, and the resulting flow-oriented thinning of components may quickly cause impeller failure or tube rupture.

NOTE: Problems of erosion–corrosion by particulate matter or water droplets in steam also affect post-boiler components such as turbine blades.

Where air bubbles and other gases are entrained in turbulent FW and an abrupt *reduction* in pressure takes place, **cavitation** may occur. The result of the extremely rapid formation and collapse of steam bubbles on the *suction side* of feed pumps or the *discharge side* of valves produces erosive **microjets** that over time may promote severe cavitational metal wastage.

6.4.3 The Deposition of Scale and Corrosion Debris in Pre-Boiler Sections

As discussed previously, serious fouling, deposition, and corrosion problems may occur in the FW line as a result of the entry of *carryover*, *after-precipitation*, *corrosion debris pickup*, or *oxygen* and other contaminants, from either the MU or returning condensate.

Where deposits occur in the final FW system, analyses often show that these deposits are composed of both ***new* localized scale and corrosion products**, plus ***old* redeposited debris** transported from other parts of the boiler plant system.

Additionally, as a result of the turbulent nature of the flow of FW as it passes through the system, both new and old debris also may continue to pass through and eventually lodge in the boiler. As a consequence, the **transport of corrosion products** and **debris** from various parts of the overall boiler plant system through the pre-boiler section (where additional debris may originate) and on to the boiler continues to be a

major cause of tube failure in HP WT boilers. This transport mechanism has been a significant cause of boiler failure since records began.

The transport of pre-boiler corrosion debris to the boiler section includes the **oxides** of **iron**, **copper**, **nickel**, **zinc**, and **chromium** and results from the corrosion of pre-heaters and condensers, and the like. Specifically, equipment components variously fabricated from *admiralty brass*, *aluminum brass*, *cupronickels*, and *stainless steels* are most affected.

In higher pressure boilers, along with metal oxides, transported debris also commonly includes various minerals:

- **Malachite** [$CuCO_3 \cdot Cu(OH)_2$]
- **Ammonium carbamate** [NH_2COONH_4]
- **Hydrated basic ferric ammonium carbonate** [$(NH_4)_2Fe_2(OH)_4(CO_3)_2 \cdot H_2O$]

NOTE: Apart from debris transport, a further major cause of HP boiler tube failure is the gradual and inevitable buildup of metal oxides and deposits resulting from physicochemical reactions occurring solely within the boiler itself, which is why scheduled, periodic cleanings are programmed into all power boiler operational schedules around the world. Nevertheless, power boiler operators and associated research organizations continually strive to develop new designs and procedures to reduce the frequency of such cleanings and their turnaround times.

Apart from the redeposition of foreign sources of debris, localized FW line deposition of insoluble salts also may occur. This simply may be due to precipitation reactions resulting from the addition of treatment chemicals.

In particular, where *polyphosphate* is added either to the MU waterline (say, as a stabilizer against the risks of after-precipitation) or to the FW line or FW tank (as a precipitating treatment for residual hardness), there is some risk of **FW line phosphate deposits** developing. Such deposits are likely to be primarily composed of hard, intractable **calcium phosphate** [*tricalcium phosphate* $Ca_3(PO_4)_2$] scale, but they may include **magnesium phosphate** [$Mg_3(PO_4)_2$] and other insoluble phosphates and hydroxides. The risk of precipitation and subsequent deposition is increased where the pH is below 8.3, if the FW line is particularly long, or when the FW temperature is high.

NOTE: Precipitation and deposition risks associated with high FW temperatures are unavoidable because FW temperatures should be as high as practically possible for any particular boiler system design. The obvious solution is to remove the source of deposition, not to reduce the FW temperature.

In considering these risk factors, there generally is little that can be done to shorten a FW line, and a long line may in fact be desirable where an oxygen scavenger is fed directly to the line because it will increase the DO contact time. To improve operating efficiency, however:

1. The FW temperature should be as high as possible. Depending on the particular circumstances, FW pH typically should be 8.5 to 8.7 or slightly higher.
2. To minimize the risk of phosphate deposits, all efforts should be made to keep residual FW hardness levels to an *absolute minimum* (good softening!).
3. Phosphate precipitant treatments should almost always be added directly to the boiler shell or drum, or to the FW line as close as possible to the boiler. (The phosphate dosing pump should be interlocked with the FW pump when dosing to the FW line.)

A further problem is **FW line iron deposits**, which may be produced where **soluble iron** is present. The iron precipitates as a result of heat and the presence of trace amounts of oxygen. The reactions under these circumstances include the following:

$4Fe(HCO_3)_2$	+	O_2	+	$2H_2O$	→	$4Fe(OH)_3\downarrow$	+	$8CO_2\uparrow$
ferrous carbonate		oxygen		water		ferric hydroxide		carbon dioxide

$Fe(HCO_3)_2$	→	$Fe(OH)_2\downarrow$	+	$2CO_2\uparrow$	
ferrous carbonate	*heat*	ferrous hydroxide		carbon dioxide	

$4Fe(OH)_2$	+	O_2	+	$2H_2O$	→	$4Fe(OH)_3\downarrow$
ferrous hydroxide		oxygen		water		ferric hydroxide

$2Fe(OH)_3$	→	$Fe_2O_3\downarrow$	+	$3H_2O$
ferric hydroxide		ferric oxide		water

The reaction products cause *fouling* and *deposition* in FW lines, the FW tanks of small boilers, and the economizers of large systems.

Precipitated iron also acts as a **binder** and forms deposits with other materials. The source of iron originates either from contaminated condensate or from MU water, where it is present in the form of **ferrous bicarbonate** [$Fe(HCO_3)_2$].

Where soluble iron is present in condensate, it often is associated with **copper**. When the problem is considered serious, it usually is removed by a condensate polisher. Soluble iron in MU often is associated with **manganese** and usually (but not totally) is removed either by *ion-exchange resins* (often inadvertently) or in an *aeration tower*, where the process employs a combination of air or chlorine oxidation, followed by precipitation and filtration.

No specific action usually is taken to remove **silica** (SiO_2) from MU water sources where the boiler plant operates at below 250 to 300 psig. Nevertheless, particularly undesirable FW line **silica deposits** may occur, and when this happens, often there is no simple, low-cost, practical way to remove them.

It thus becomes necessary to preempt the problem by tightly controlling the FW *pH*, *temperature*, and *residual hardness* levels where MU water source contains a high silica level (say, over 20–30 ppm SiO_2). The location of FW line chemical injection points and the type of chemicals dosed also may influence the risk of silicate sludges and scales developing, and these factors may also need to be considered.

Consider that as pH and temperature increase (normally desirable FW conditions), silica increasingly forms a soluble *silicate anion* that can react with any residual hardness (especially *magnesium hardness*) in the FW line to produce various forms of *magnesium silicate*. The glassy silicate scales become increasingly insoluble at higher pH and deposit in high heat flux areas, severely restricting heat transfer.

The most common deposits are:

- **Serpentine** [$(3MgO{\cdot}SiO_2{\cdot}2H_2O)$]
- **Hydrated magnesium orthodisilicate** [$(Mg_3Si_2O_7{\cdot}2H_2O)$]

When soluble iron is present in FW that also contains silica, the iron may be transported through to the boiler, where insoluble **ferrous metasilicate** ($FeSiO_3$) preferentially forms instead of magnetite.

Table 6.3 Summary of problems associated with the final FW blend

Type of problem	*Likely results or increased risks*
Inadequate FW deaeration.	Oxygen pitting corrosion to deaerator, economizer, FW tank, FW line Pitting in tubes and shell (FT) Pitting to top drum (WT)
Dealloying, selective leaching and graphitic corrosion forms of galvanic corrosion *NOTE: Corrosion is especially common in soft waters with high chlorides and under idle conditions.*	Selective corrosion of cuprous alloys, such as FW heaters and bronze pump impellers, producing: Dezincification Denickelification Destannification Dealuminumification Graphitic corrosion of cast iron FW pumps and valves
High temperature/stress and stop/start operation effects on 70:30 cupronickel tubes (as found in some FW heaters).	A chain of cause and effect including: Oxygen corrosion Dealloying Exfoliation corrosion
Impingement by high speed, turbulent water, and particles.	Erosion-corrosion of pumps, impellers, and fittings
Air bubble entrainment in FW.	FW pump cavitation
Localized pre-boiler scale and corrosion debris deposits.	Combination of: *New* phosphate, iron, copper, and silica deposition *Old* re-deposited debris Transport of Fe, Cu, Ni, Zn, Cr oxides to HP boiler section, leading to deposition, fouling, and possible tube failures Transport of minerals and debris including malachite, ammonium carbamate, basic ferric ammonium carbonate Precipitation in FW line of phosphates, iron, and silicates

7

WATERSIDE AND STEAMSIDE PROBLEMS: BOILER SECTION SPECIFICS

In any boiler plant system, the boiler itself typically is the single most expensive item of equipment and the source of generated steam. Thus, it tends to receive the highest percentage of whatever time, money, and human resources are available. This is understandable because any loss of heat transfer efficiency through deposition or other physicochemical waterside problems has the greatest impact here.

Almost all boiler section scale, fouling, deposit, or corrosion problems, however, tend to be associated with additional (and often very similar) problems both *upstream* and *downstream* of the boiler itself. Therefore, the presence of, for example, boiler deposits or localized corrosion issues should never be viewed in isolation. Rather, they should be investigated in the light of a likely chain of *cause* and *effect*, and the basic causes of the problems should be eliminated wherever possible, rather than simply the noticeable effects.

Thus, merely cleaning boiler internals of carbonate deposits, say, by the use of an acid wash will not prevent a recurrence. Does the boiler require the installation of a water softener, an improved chemical treatment program, or better testing and monitoring?

7.1 BOILER SCALING, FOULING, AND DEPOSITION

We typically use scaling, fouling, deposition, and several other terms in the same context and fairly indiscriminately because there is no universal definition. In general, these physicochemical processes may take

place at the same time in the same region of the boiler. Each term has a specific definition, however:

- **Scale** is a layer or layers of minerals *deposited* onto a heat transfer surface, which reduces the **heat transfer coefficient** (*U value*, stated in Btu/hr/sq ft/°F). In everyday parlance, scale also refers to thick layers of **corrosion product** built up onto a metal surface (often present in association with deposits) that may occur at high temperature as a result of a variety of *boiler surface* corrosion mechanisms.

  Mineral scales typically result from the effects of localized concentration of salts within the watersides of a boiler and the inverse solubility of many such salts at elevated temperatures. Scales often are hard, dense, and difficult to remove. They can be either **crystalline** or **amorphous** (lacking any characteristic crystalline shape).
- **Fouling** is caused by the *flocculation* or *deposition* of insoluble matter such as **sludge**, **amorphous scales**, **process contaminant**, or **corrosion debris**, and it relates to any *impediment to the flow of water* in a boiler system. Sludge often is one result of localized mineral *supersaturation* but is not always deposited at the point of origin. It may be transported from elsewhere before settling and causing fouling and may additionally bake onto heat transfer surfaces (**baked-on sludge**), giving the impression of being a mineral scale.
- **Deposition** commonly reflects a combination of physicochemical processes and localized effects. It may occur through fouling as a result of *contamination* by process materials, perhaps plus scaling from the *supersaturation of dissolved salts*, and coupled with some active *under-deposit corrosion*. As a consequence, deposits forming within a boiler are almost never single mineral scales but typically consist of a variable mix of scale and corrosion debris, chemical treatment residuals, process contaminants, and the like.

Silica and many of the metals commonly found in scales and deposits can form various permutations of oxides and salts, depending on the specific boiler area location and operating circumstances. Each mineral possesses distinct characteristics and may exert different effects.

Thus, although the analysis of scales and deposits typically is carried out by a combination of *wet chemistry* techniques and *atomic absorption spectroscopy*, an identification of the specific nature of the crys-

talline minerals requires additional and expensive resources. Equipment employed for this work includes *x-ray diffraction and fluorescence* and *polarizing microscopy*.

Although the risk of scale deposition and fouling in the boiler section is related to several factors such as the **FW volume demands**, **boiler pressure**, and **heat flux density** at various *boiler surfaces*, it is equally a function of the level of **FW contaminants** such as *residual hardness*, *sulfates*, *silica*, and *iron*. Thus, as a generality, the higher the quality of FW (reduced levels of contaminants), the lower the risk of deposition on *boiler surfaces*.

Also, basic factors such as the *transport of materials*, *residual hardness*, *ion leakage*, *soluble iron*, *colloidal silica and clays*, and other contaminants, which can produce scales and deposits in the FW lines and other parts of the pre-boiler section, may also produce similar detrimental effects in the boiler section. In the boiler itself, however, the buildup rate may be quicker and the results may be more devastating.

Commonly, **phosphate** or **carbonate** may be purposefully present in many boilers as a result of the application of certain internal precipitating treatment programs. Rather than providing a benefit, they can add further to the risk of deposition if the correct operational conditions are not maintained because adherent *scales* are produced rather than free-flowing *sludges* that are amenable to boiler blowdown (BD).

Also, gross **organic chemical treatment overdosing** or **thermal breakdown** further adds to deposition risks. For example, many common polymeric *dispersants* act as *flocculants* if significantly overdosed.

NOTE: Many common polymeric dispersants typically produce a flocculating effect in a boiler when they are present at levels exceeding 100 to 120 ppm or so of "active" polymer. BW actives should not exceed 40 to 50 ppm.

Where fouling and scale deposition occurs in a boiler, it sometimes is perceived as the result of the development of a *specific* boiler waterside problem and, as such, one that can be rectified by a slight change in either the chemical treatment program or the operating control parameters. Under these circumstances, such a treatment may thus be viewed or even promoted as a simple "cure-all" solution to the problem. This is seldom the case in practice. Rather, deposition is an early warning sign of inadequate control over *general* boiler waterside conditions. This warning may reflect a root cause problem, either with the day-to-day operation of the boiler or with the interrelationship of FW quality, external pretreatment processes, or internal treatment programs.

NOTE: The view that deposition is an indicator of more widespread problems is also common to cooling water systems. As a result of the complex nature of deposits, their removal by acid or mechanical cleaning of boiler or cooling systems is not always as simple a process as may be portrayed.

Different sequences of solvent addition or cleaning techniques may be required for each of the two or three most abundant minerals present. Passivation is always an essential element and mechanical repairs also may be required.

Most commonly employed sources of water contain readily measurable quantities of most or all of the minerals shown in Table 7.1. Under appropriate conditions, such as the application of heat or increase in concentration, most of these minerals produce scales, foulants, and deposits on the waterside of *boiler surfaces*.

7.1.1 Deposition by Alkaline Earth Metal Salts

The development of today's global boiler water (BW) treatment products and services market has stemmed from the requirement to manage two fundamental waterside problems:

Table 7.1 Commonly occurring minerals in natural MU water sources

Calcium bicarbonate	$Ca(HCO_3)_2$
Calcium chloride	$CaCl_2$
Calcium sulfate	$CaSO_4$
Ferrous bicarbonate	$Fe(HCO_3)_2$
Magnesium bicarbonate	$Mg(HCO_3)_2$
Magnesium chloride	$MgCl_2$
Magnesium sulfate	$MgSO_4$
Manganous bicarbonate	$Mn(HCO_3)_2$
Silica	SiO_2
Silicic acid	H_2SiO_3
Sodium silicate	Na_2SiO_3
Sodium bicarbonate	$NaHCO_3$
Sodium chloride	NaCl
Sodium sulfate	Na_2SO_4

- The need to limit and control boiler *metal corrosion* (resulting primarily from the action of dissolved oxygen)
- The need to prevent *deposition* on *boiler surfaces* (resulting principally from **hardness salt scaling** by **calcium carbonate** and other **alkaline earth metals**)

Although any given source of water typically has a wide range of dissolved minerals present, and each of these has a potential for causing difficulties to a greater or lesser extent, it is the *alkaline earth salts* (*hardness salts*) that are always present to some degree and generally are the most troublesome in a boiler. This section discusses these salts, their presence in natural makeup (MU) water sources, and their contribution to hardness scales and deposition in boiler plants.

Hardness is due primarily to the presence of **calcium** (Ca) salts but also to those of **magnesium** (Mg) and to a much lesser extent to those of **strontium** (Sr) and **barium** (Ba).

Trace amounts of other metals such as **iron** (Fe), **aluminum** (Al), and **manganese** (Mn) further contribute to the *total hardness*, although these are not *alkaline earth metals*. These metals may be present in natural water supplies as:

- **Bicarbonates**
- **Carbonates**
- **Sulfates**
- **Chlorides**
- **Nitrates** (normally quite low)
- **Phosphates** (sometimes)

Additionally, various nonhardness minerals such as **silica** are always present in MU water sources, normally at low levels (say, 3–15 ppm SiO_2, although this may rise to 50–70 ppm in certain well water or arid area supplies). Silica may cause serious problems of deposition and loss of heat transfer.

The amount of hardness present in natural surface and groundwaters depends to a large extent on the action of dissolved **carbon dioxide** in rainwater on the watershed's geological formations (such as *limestone*, *dolomite*, *gypsum*, or *magnesite*). The dissolved hardness levels remain relatively low because of the sparingly soluble nature of the salts formed. Typically, MU water sources initially contain anywhere from 5

to 500 ppm (mg/l) of total hardness (TH) reported as calcium carbonate ($CaCO_3$). Some well water supplies and arid area sources may be much higher than 500 ppm TH as $CaCO_3$.

An "instant" hardness guide to describe waters is:

- **Soft water:** TH = below, say, 40 to 50 ppm as $CaCO_3$
- **Medium hardness water:** TH = say, 50 to 150 ppm $CaCO_3$
- **Hard water:** TH = above, say, 150 to 200 ppm $CaCO_3$

NOTE: The reporting of calcium hardness, total hardness, and alkalinity as $CaCO_3$ is simply a convenience because the molecular weight for this compound is an easy-to-use 100!

$$(Ca = 40) + (C = 12) + (O_3 = 16 + 16 + 16) = 100.$$

Although the presence of hardness is reported as calcium carbonate, in reality, for most water supplies the most common major contributors to total dissolved solids are **calcium** and **magnesium bicarbonates**. These dissolved solids most readily produce crystalline scales and thus predominantly contribute to boiler system deposits unless removed by some form of pre-boiler, external treatment process.

It should be noted that calcium bicarbonate does not exist in the solid state; rather, it exists as an unstable salt in water, provided that an excess of free **carbon dioxide** is available to maintain equilibrium.

The reaction is shown below.

$CaCO_3$	+	CO_2	+	H_2O	$\rightarrow$	$Ca(HCO_3)_2$
calcium carbonate		carbon dioxide		water		calcium bicarbonate

The solubility of calcium carbonate in cold water is approximately 15 to 20 ppm, dependent on temperature and other factors, and is rarely present in MU water supplies. Where it is present, there is a phenolphthalein or P alkalinity.

- Carbonate = 2 × P alkalinity
- Bicarbonate = M alkalinity − Carbonate

Some natural water sources are slightly acid, having a pH perhaps as low as 5.6 to 6.0, although most supplies are slightly alkaline. The pri-

mary source of alkalinity, as noted previously, is **calcium bicarbonate alkalinity**, and (lime-treated MU waters apart), these waters tend to have a pH below 8.2 and contain some measurable quantity of free **carbon dioxide** (CO_2).

When the pH rises to above 8.2 to 8.4, the free CO_2 disappears and the bicarbonate converts to carbonate with both ions coexisting up to a pH level of 9.6 (see the equation below). No bicarbonate alkalinity exists above this pH level.

HCO_3^{2-}	⟷	CO_3^{2-}	+	H^+
bicarbonate ion	*pH change*	carbonate ion		hydrogen ion

Bicarbonates and carbonates provide the *total alkalinity* in most MU waters. Normally, there is no free *hydroxide alkalinity*.

- **Total hardness** is equal to the sum of the calcium hardness and the magnesium hardness.
- **Temporary hardness** or *carbonate hardness* is removed by heating water to precipitate the carbonate salt (e.g., bicarbonate hardness salts) and is equal to or less than the total alkalinity.
- **Permanent hardness** or *noncarbonate hardness* is that portion of the total hardness that cannot be removed by heating water (e.g., chloride or sulfate hardness) and is the difference between total hardness and total alkalinity.

7.1.1.1 Deposition of Calcium Salts

Most salts absorb heat when they go into solution, and their solubility increases with a rise in temperature; however, **calcium carbonate** ($CaCO_3$), in common with several other *anhydrous* salts such as calcium sulfate ($CaSO_4$) and calcium phosphate [$Ca_3(PO_4)_2$], has an *inverse* temperature solubility and thus readily precipitates to form deposits in hot water areas (FW tanks, FW lines, and boiler heat exchange surfaces).

Consequently, a loss of free carbon dioxide in the water, because of either a rise in temperature (as occurs in a FW heater or boiler) or an increase in pH (all boilers operate at an alkaline pH) leads to a change of equilibrium and the resultant rapid and troublesome precipitation of insoluble calcium **carbonate scale** on heat transfer surfaces. The reaction is as shown here:

$Ca(HCO_3)_2$	$\rightarrow$	$CaCO_3\downarrow$	+	H_2O	+	$CO_2\uparrow$
calcium bicarbonate	*heat or rise in pH*	calcium carbonate **scale**		water		carbon dioxide

The precipitation of calcium carbonate in the boiler involves a number of discrete processes, including **nucleation**, followed by the formation of **microcrystals** which compete to grow into larger crystals (**accretion**) that eventually form layers of dense, crystalline scale on the heat exchange surface.

In areas of the system where the heat gradient is less severe, calcium carbonate precipitates in both **crystalline** and **amorphous** forms. It may precipitate as a **calcite** or **aragonite** *sludge*, but more usually an aragonite *scale* is produced. Aragonite is hard and adherent, depositing in FW lines and various *boiler surface* components such as boiler tubes.

Where **precipitating phosphate programs** are used, residual calcium forms a sludge of the basic salt **hydroxyapatite** $[Ca_{10}(PO_4)_6(OH)_2]$.

7.1.1.2 Deposition of Magnesium Salts

Magnesium salts exhibit properties similar to those of calcium, except that they generally are slightly more soluble and normally are present in MU water sources at a lower level of concentration, so that the overall scaling and deposition effect of magnesium salts is lessened.

Under alkaline BW conditions, if magnesium bicarbonate is not removed by softening or other pretreatment processes, it forms **brucite**, an insoluble flocculant sludge of **magnesium hydroxide** $[Mg(OH)_2]$.

Where *phosphate* is added to the boiler, magnesium forms very insoluble basic salts similar to those of calcium. In the presence of *silica* (and despite the fact that silica becomes more soluble at higher pH levels), insoluble **magnesium silicate** is produced, commonly in the form of **serpentine** ($3MgO{\cdot}2SiO_2{\cdot}H_2O$) but also as **magnesium orthodisilicate** ($Mg_3Si_2O_7{\cdot}2H_2O$). Serpentine usually is found as a flocculant sludge or as a *binding component* of deposits.

7.1.1.3 Control over the Deposition of Calcium and Magnesium Salts

As a consequence of the rapid scaling potential of calcium and magnesium bicarbonates and related salts, it is not only cost-effective with regard to BD and internal chemical treatment savings but also opera-

tionally easier if these troublesome minerals are simply removed from the MU water at its source.

Therefore, to minimize the certainty of waterside carbonate deposition, essentially *all* types of steam generating boilers should be provided with a **water softener** or some other equally effective form of pretreatment equipment.

In practice, however, it is often the case that for small LP steam heating boiler systems with a very high percentage of CR, and in those regions of countries where "soft" water is supplied, no water softener is provided or deemed necessary. Instead there is merely a reliance on internal chemical treatments (or sometimes magnetic devices or other types of "gadget"). A good rule of thumb is:

- Where low-output LP steam boilers (i.e., those under 15 psig) genuinely receive back at least 95 to 97% of the steam generated as condensate and the MU water source is lean, a water softener is in all probability *not* required.
- Where no softener is installed merely because a boiler plant owner or operator assumes it to be an irrelevance in view of a "good quality" soft or lean water, the potential for scaling exists. Clearly, even when the MU water is quite soft (say, 15–20 ppm total hardness as $CaCO_3$), if the boiler has a low percentage of returned condensate and a correspondingly high MU water requirement, a scaling risk exists.

The demand for **alkali**, **phosphate**, and/or **polymer** internal chemical treatments becomes significant, and unless extremely good control over BW chemistry and boiler plant operations is provided, the result most likely will be a scaled boiler, higher fuel costs, and reduced efficiency. A softener is required under these circumstances.

NOTE: Under these low hardness but high MU demand circumstances, other risk factors also exist, especially in smaller boilers. Typically, the high MU water demand reduces the FW temperature, which permits the oxygen level to rise and thus requires additional sulfite scavenger to counter the increased risk of corrosion. Also, the requirement for BD is increased as TDS and SS levels also rise, so fuel and other operating costs increase accordingly.

Water softeners are relatively low-cost items and, irrespective of background rationale, a reluctance to provide such pretreatment equipment where deemed necessary generally is a false economy.

Where a softener has not been provided, a higher volume of sludge can be expected in the BW. Typically, the calcium precipitates either as insoluble **carbonate scale** or as **phosphate sludge** except where a **chelant-based** chemical treatment program is employed (which is unlikely in smaller boiler plants) or when an **all-polymer** program is employed.

Even where these organic polymer materials are employed, their ability to disperse sludge and transport hardness salts may be constrained by limited BD and other factors. Some sludge still develops. The fact remains that boilers simply are not designed to be settling and clarifying vessels.

NOTE: All-polymer programs employ various types of organic ***deposit control agents*** *(DCA) such as* ***phosphinocarboxylic acid*** *(PCA) products, which tend to be high temperature–stable sludge dispersants, crystal modifiers, and hardness transporters.*

Where hardness removal is required, the simplest pretreatment method for smaller, lower pressure boiler plants (below 200–300 psig) is to use a *cation-exchange softener*. This removes the calcium and magnesium at source and converts the bulk of temporary hardness salts into **sodium bicarbonate** ($NaHCO_3$), which decomposes to form **sodium carbonate** (soda ash) but does not scale under normal boiler operating conditions.

Rather, the sodium carbonate hydrolyzes in hot BW, producing **free caustic alkalinity** and a pH of approximately 11.0 to 11.7.

$2NaHCO_3$	$\rightarrow$	H_2O	+	$CO_2\uparrow$	+	Na_2CO_3
sodium bicarbonate	*heat*	water		carbon dioxide		sodium carbonate

Na_2CO_3	+	$2H_2O$	$\rightarrow$	$CO_2\uparrow$	+	NaOH
sodium carbonate		water	*heat*	carbon dioxide		sodium hydroxide

The provision of *free caustic alkalinity* is beneficial in lower pressure FT and WT boilers for several reasons:

1. It prevents acid corrosion.
2. It increases the solubility of silica.
3. It aids passivation of the steel surfaces.

The formation of a *passive* film of **iron oxide** (magnetite, Fe_3O_4), under sulfite or hydrazine reducing conditions, is optimized at pH of 11 to 12. The downside is that the decomposition of carbonates and bicarbonates produces **carbon dioxide**, the primary cause of *condensate system corrosion.*

NOTE: Condensate system corrosion was an inevitable result of old-style, ***carbonate cycle*** *internal softening programs, commonly employed in HRT, economic, locomotive, Lancashire, and similar boilers.*

Today, in an era of water reuse and higher costs for premium-quality water, condensate line corrosion may be an inevitable and serious drawback when using naturally high-alkalinity water as a MU supply source. Some form of dealkalization pretreatment process generally is provided to high MU demand boiler plants but unfortunately not so often to smaller facilities.

The provision of free caustic alkalinity in higher pressure boilers (say, 300–950 psig) generally is severely limited or even curtailed to ensure a high quality of steam purity and to control the risks of foaming and other problems developing.

For boiler plants over 900 psig (6.21 mpa, 63.07 bar absolute), the water chemistry is particularly carefully controlled, with no free caustic alkalinity permitted. This is partly to reduce the risks of localized **caustic deposits** forming, which may cause **caustic gouging** or *caustic-induced,* **stress corrosion cracking** to develop.

7.1.2 Deposition by Silicates and Other Common Minerals

Apart from calcium and magnesium bicarbonates, most natural sources of MU water commonly contain some small amounts of **silica** and other dissolved minerals, salts, and contaminants. Under a wide variety of operational circumstances, every one of these common materials may contribute to complex boiler scales and deposits, especially the silicates. Thus, it is necessary to ensure that water chemistries are properly balanced and controlled.

7.1.2.1 Silica and Silicate Deposition

Silica is normally present in most sources of MU water, although not to any significant level as soluble SiO_2 but rather as both **colloidal amorphous silica** and **silicate salts**. In any particular water, such

soluble silica as is present (together with silicates) exists in equilibrium with colloidal silica of 10 to 2,000 angstroms particle size and so-called **"giant" silica**, which is essentially colloidal or suspended silica of 1,000 to 2,000,000 *angstroms* particle size.

Typically, the total silica concentration in most surface waters is 5 to 15 ppm SiO_2, but this may be much higher (notably in arid areas), rising to 50 to 70 ppm SiO_2 or higher.

The limit of solubility typically is around 150 to 175 ppm SiO_2 in cold water but increases with alkalinity, pH, and temperature to perhaps $\cong$ 250 ppm.

At pH levels above 9.0, there is an increased tendency for the soluble silica to form **silicate anions** and react with magnesium (and to a lesser extent with calcium) to form *insoluble* forms of **magnesium silicate** that precipitate to form crystalline scales and sludge.

The nature of silicate scaling is complex and may involve a series of steps including:

1. The initial **nucleation** of **calcium carbonate** ($CaCO_3$) crystals.
2. These $CaCO_3$ crystal nuclei then provide **seeding points** for **silicate** precipitation.
3. The development of **magnesium hydroxide** [$Mg(OH)_2$] at the *heat transfer surfaces*, especially at cathodic sites where localized pH may exceed 10. The $Mg(OH)_2$ then reacts with colloidal silica from the *bulk water* to form **silicate scale**.

Where carbonate, phosphate, or sulfate scale–based deposits have been found in boiler systems, analyses show that they almost always contain some silica or silicate as well. Typically, this is less than 8 to 10% unless there is a specific underlying silica-related problem (under such circumstances, the deposit may contain more than 20–30% SiO_2).

Silicate scales are among the most heat transfer–resisting of all scales. They are particularly adherent, requiring special and expensive techniques for their removal. In addition, silica forms particularly elaborate **glassy scales** in combination with a wide range of other minerals.

Some of these scales are described here:

- **Acmite** ($Na_2O \cdot Fe_2O_3 \cdot 4SiO_2$) is formed at high temperature and invariably is found beneath sludges of *hydroxyapatite* or *serpentine* or under porous deposits of *iron oxides*.

- **Alpha quartz** (αSiO_2) is found throughout the boiler and post-boiler sections. It is a very hard, adherent scale, found in the mud drum, on boiler tubes, and on turbine blades as a hexagonal crystal structure.
- **Analcite** ($Na_2O{\cdot}Al_2O_3{\cdot}4SiO_2{\cdot}2H_2O$), a cubic crystal structure, is formed at high temperatures. It is similar to *acmite* and also invariably is found beneath sludges of *hydroxyapatite* or *serpentine* or under porous deposits of *iron oxides*.
- **Natrolite** ($Na_2O{\cdot}Al_2O_3{\cdot}3SiO_2{\cdot}2H_2O$) is an orthorhombic crystal of medium hardness.
- **Nepheline**, variously reported as $[Na_4K_2Al_6(SiO_4)_2]$, ($Na_2O{\cdot}Al_2O_3{\cdot}2SiO_2{\cdot}H_2O$), or ($Na_3KAl_4Si_4O_{16}$), is a hexagonal crystal of medium hardness.
- **Noselite** ($5Na_2O{\cdot}3Al_2O_3{\cdot}6SiO_2{\cdot}2H_2O$) is a hard, adherent scale found on boiler tubes and other areas of high heat-flux density.
- **Serpentine** ($3MgO{\cdot}2SiO_2{\cdot}2H_2O$) is a common silica-containing constituent of boiler waterside deposits. It typically appears as a flocculated sludge; it has a monoclinic crystal structure.
- **Sodalite** ($3Na_2O{\cdot}3Al_2O_3{\cdot}6SiO_2{\cdot}2NaCl$) occurs as a hard, adherent scale on tube surfaces; it has a cubic crystal structure.
- **Xonotlite** ($5CaO{\cdot}5SiO_2{\cdot}H_2O$) is also a hard, adherent scale that is found on boiler tubes and other areas of high heat-flux density.

The formation of **complex silicate scales** takes place at high temperature (usually they are only found in boilers operating at over 300 psig) and high heat-flux density points in the boiler section. The presence of complex silicates such as analcite and acmite may indicate **steam blanketing** problems.

NOTE: Steam blanketing is the static steam–water condition that occurs when boiler water circulation is impeded by foulant or when initial deposition prevents adequate heat transfer and the dispersion of lower density steam or water.

*Steam blanketing results in a **departure from nucleate boiling** (DNB) and typically **dryout** (localized total evaporation) conditions. It also may result in the formation of secondary (silicate-based) deposits that cannot be rinsed or resolublized, overheating problems, and eventual boiler tube or furnace shell rupture.*

Analcite frequently forms as a result of **external treatment carryover** from *alum*-dosed clarifiers.

Extremely thin, glassy silicate scales of less than **"eggshell" thickness** may sufficiently insulate the tubes of WT boilers and the furnace tube of FT boilers for tube failure to occur through deformation and rupture.

Apart from the risk of silica problems within the boiler section, at pressures above 400 to 500 psig **silica volatilization** and distillation occurs, resulting in silica deposition in superheaters and on turbine blades. Under these conditions the maximum concentration of silica permitted in steam is 0.02 ppm SiO_2.

Silica can also etch gauge glass, thus making it difficult to observe the water level. As a result, special **flat gauge glass** is used for boilers operating at over 250 psig.

Because of the problems relating to silica and silicates, silica levels in the FW and BW must be strictly controlled. This normally is not a problem in higher pressure boilers because various methods of pretreatment are typically employed to reduce the concentration of silica in the FW as much as possible. Automatic monitoring and alarm systems are also provided.

Various national guidelines exist for the maximum permissible concentration of silica in boilers. These are typically based on defining pressure operating ranges, with progressively lower silica levels permitted at increasingly higher boiler pressure. Where the boilers are highly rated (high heat-flux densities), however, the maximum permitted limits for BW silica levels should be lowered still further.

NOTE: Guidelines on operating practices taken from various authorities indicate that boilers having a maximum local heat flux of between 44,000 and 82,780 Btu/hr/ft^2/° F (79,250–14,9000 Btu/hr/ft^2/°K, 250–470 kW/m^2/°K) are considered highly rated.

Magnetite is unstable relative to **ferrous metasilicate** ($FeSiO_3$) and so, under certain high-silica BW conditions, *ferrous metasilicate* may form in preference to magnetite. *Iron silicate* scales are exceedingly insoluble and adherent.

It should be noted that, in practice, where lower pressure industrial process boiler plants are operated, the problem of overcoming risks of silica deposition is seldom tackled by the installation of external silica removal pretreatment equipment. Instead, control centers primarily around ensuring an adequate ratio of caustic alkalinity to silica in the BW and limiting the TDS.

NOTE: For lower pressure boilers, the maximum permitted level of boiler water silica (as ppm SiO_2), typically is 0.4 x caustic alkalinity (as ppm $CaCO_3$). This method of control is satisfactory as far as it goes, but it does not solve the problem of the risk of silica deposits in the pre-boiler section.

Where MU water silica is high (say, more than 20–30 ppm SiO_2), action probably is needed to reduce the silica level at source. This may be achieved in several ways, for example, by the use of *anion exchange or flocculation–adsorption processes* using *ferric sulfate or magnesium hydroxide*.

7.1.2.2 Iron Oxide and Other Corrosion Debris Deposition

Iron salts (and to a lesser extent **manganese** salts) are found in many surface water supplies and "industrial water." Both ferrous (Fe^{2+}) and ferric (Fe^{3+}) iron may be present in the water, depending on the pH.

At a pH of 8.5 or more, all the iron is in the *ferric* form, usually as a colloidal precipitate. If the iron level is very low, it tends to be ignored for most general purposes, but if the concentration rises to perhaps 0.3 ppm Fe or more, it causes discoloration upon precipitation and fouling and must be removed.

Iron levels of 1 to 10 ppm Fe often are found in subsurface waters. This may rise to perhaps 25 ppm Fe in seriously anaerobic water; *sulfides* usually are also present.

Where present in boiler MU water, both iron and manganese may present fouling and deposition problems in the pre-boiler section. These problems may extend to the boiler section, and therefore these metals must be removed at source. Typically, this is achieved by oxidation followed by filtering off the flocculated iron. (Process examples are *aeration towers*, *contact with chlorine*, *pressure filters with BIRM® media*, *manganese greensand filters*, etc.)

Where particulate matter (in the form of corrosion products of **iron oxide**) is present in returning condensate, it often contains **copper**, **nickel**, and **zinc oxides** as well. This debris can initiate foaming (through *steam bubble nucleation* mechanisms) leading to carryover. It certainly contributes to *boiler surface* deposits, and the Cu usually also leads to **copper-induced corrosion of steel**.

The presence of these deposits causes overheating at heat transfer surfaces and permits caustic and other salt concentration to develop. This may lead to **ductile gouging corrosion**.

For the most part, iron, copper, nickel, and zinc deposits found in the boiler section are the result of corrosion processes taking place somewhere else within the overall system. Similarly, **mill scale** from new boilers may be released and redeposited elsewhere, plugging BD lines and boiler tubes.

The direct reaction of **ferric oxide particles** with steel heat transfer surfaces (corrosion) also is possible, producing a thick, coarse, and porous deposit of magnetite.

Where **caustic deposits** occur, the resultant corrosion of steel by **caustic gouging** or **stress corrosion cracking** (SCC) mechanisms produces particulate iron oxides of **hematite** and **magnetite**. It is common to see white rings of deposited *sodium hydroxide* around the area of iron oxide formation.

It also is common to observe reddish stains of **elemental copper** in the same area (as a result of the reduction of *copper oxides* by hydrogen generated during the steel corrosion process).

In many smaller manufacturing or factory processes in which live steam is directly employed (such as in a bakery, laundry, etc.), there often is little returning condensate (perhaps only 15–20%). Here, the MU requirement is correspondingly high and the FW may be relatively "cool" (and therefore partially oxygenated). Under these circumstances, it is not uncommon to observe the transport of **ferrous bicarbonate** [$Fe(HCO_3)_2$]) into the boiler and the subsequent development of iron fouling.

Additionally, considerable orange-red **tuberculation corrosion deposits** may develop. The tubercles grow, cause more fouling, permit under-deposit corrosion to persist, and generally act as a **binding agent** for carbonates, silicates, and other precipitates.

We have already noted that the transport of pre-boiler corrosion debris to the boiler section includes the **oxides** of **iron**, **copper**, **nickel**, and **zinc** (sometimes also **chromium**) and in higher-pressure boilers transport minerals may further include:

- **Malachite** [$CuCO_3 \cdot Cu(OH)_2$]
- **Ammonium carbamate** [NH_2COONH_4]
- **Hydrated basic ferric ammonium carbonate** [$(NH_4)2Fe_2(OH)_4(CO_3)_2 \cdot H_2O$]

These alloy corrosion products usually originate in the pre-boiler section but deposit in the boiler at points of *low flow*, such as just beyond bends

in tubes that change direction, *rough spots*, and *areas of high heat transfer*. The deposits that form are sintered, porous, and insulating in nature. They also act as receivers for the concentration of *chloride* and *hydroxide* salts causing **pitting** and **caustic gouging corrosion**.

Some additional corrosion products that may be found as deposits in the boiler section include:

- **Bunsenite** (NiO), a nickel oxide, is often found in deposits (albeit only in low concentrations) with zinc and copper oxides as a result of the corrosion of brasses and cupronickels.
- **Copper** (Cu) is deposited in boilers either by direct exchange with iron or by the hydrogen reduction of copper oxide during the corrosion of steel.
- **Cuprite** (CuO) is formed as a black, nonmagnetic mineral under boiler conditions. The copper originates from *brasses* and *cupronickels* used in condensers and FW heaters.
- **Hematite** (Fe_2O_3) is formed at lower temperatures and higher oxygen concentrations than magnetite. It is a deposit binder. Typically, it is the face-centered cube, *ferromagnetic* form of ferric oxide (γFe_2O_3) that dominates rather than the more stable body-centered cube, rhombohedral, paramagnetic form, sometimes called **Goethite** (αFe_2O_3).
- **Magnetite** (Fe_3O_4) is formed at high temperatures under fully reducing conditions. It is ferromagnetic and has the composition $Fe^{2+}(Fe^{3+}[O^{2-}]_2)_2$.
- **Wustite** (FeO) is a ferrous oxide that may be formed in lower pressure boilers where poor removal of DO takes place. It is often found as a core component of tubercle deposits. The formation of octahedral crystalline FeO is not stochiometric, being slightly deficient in iron.
- **Zincite** (ZnO) originates from *brasses* used in condensers and FW heaters.

7.1.2.3 Deposits Originating from Inorganic Salts and Organics

When sulfates, carbonates, and other dissolved BW salts exceed their individual maximum solubility limits, they form sludges, scales, and deposits. This situation may arise either from a general overconcentration of the BW TDS (high COC) or from the deliberate precipitation of salts of selective ions, as occurs when using *phosphate precipitation programs*.

Salt deposits in the boiler also may give rise to corrosion by acting as *cathodic* areas, relative to *anodic* steel surfaces.

As a general rule, boiler section deposits initially are often soft and porous but are prone to become harder and more adherent as they age. Thus, the presence of hard, dense scales and deposits in a boiler indicates that deposition has been occurring for a considerable time. The deposition of scales often produces a layered effect similar to the rings of a tree, indicating periodic changes in the water chemistry and perhaps providing some clues as to the history of the deposits.

Several common salts have an **inverse temperature solubility** and readily precipitate to form deposits on hot *boiler surfaces* and other heat exchange areas. These include:

- **Calcium carbonate** ($CaCO_3$)
- **Calcium sulfate** ($CaSO_4$)
- **Calcium phosphate** ($Ca_3(PO_4)_2$)

Sulfate, chlorides, and phosphates are common **contaminants** and **contribute to boiler scales and deposits**.

- **Sulfates** in surface MU water sources usually are present at lower concentrations (typically 20–60 ppm) but this level may rise to several hundred ppm in subsurface waters. The maximum solubility of **calcium sulfate** is dependent on temperature but is in the range of 1,800 to 2,000 ppm in cold water. This rate is significantly less in hot BW; where boiler deposits occur, the sulfate scale normally is present as **anhydrite** ($CaSO_4$). Sulfate scales are hard and very difficult to remove, so treatment programs employed must be carefully controlled to avoid risks of scaling.
- **Chloride** salts are present in surface waters at levels similar to those of sulfate and present similar problems in FW and BW. They also are highly mobile and aggressive *depassivating* and *depolarizing ions* and have similar reactions. Their salts are much more soluble, however, and thus do not readily precipitate to form boiler deposits. Nevertheless, chlorides may be present in complex scales such as **sodalite** ($3Na_2O{\cdot}3Al_2O_3{\cdot}6SiO_2{\cdot}2NaCl$), which occurs as a hard, adherent deposit on tube surfaces.

  Deposits become less resistant to rinsing and resolublizing with age, and the interstices fill with salts to become bulkier and more dense. Thus, where *hydrolyzable saline salts* such as **magnesium**

chloride enter the boiler section (perhaps from a leaking surface condenser, where the pressure differential encourages cooling water to leak into the system rather than condensate to leak out), chlorides concentrate in the deposit interstices and hydrolyze to form hydrochloric acid. Localized **acid pitting corrosion** then occurs.

- **Phosphate** is sometimes present in MU water sources (say, 1–2 ppm or more) usually as a result of field and factory run-off or from the deliberate addition as a city water *threshold agent* to prevent corrosion and deposition in the mains. The steady growth in the reuse of secondary water sources such as municipal and industrial waste waters means that phosphate is increasingly likely to be present in MU. If the phosphate remains undetected, it likely will scale and foul FW lines by forming *amorphous* **calcium orthophosphate** [**tricalcium phosphate** $Ca_3(PO_4)_2$] sludge before it reaches the boiler section.

  Where phosphate is used for internal treatment programs, a variety of insoluble phosphate and hydroxide salts are produced to form sludges. If these sludges are not properly held in a suspension by the use of appropriate polymeric dispersants (and then blown down from the boiler within a certain period), they will deposit on heat exchange surfaces as hard, adherent scales.

  Phosphate salts formed in the boiler section include:

  - **Hydroxyapatite** [$Ca_{10}(OH)_2(PO_4)_2$]
  - **Ferric phosphate** [$FePO_4$]
  - **Basic magnesium phosphate** [$3Mg_3(PO_4)_2 \cdot Mg(OH)_2$]

NOTE: In lower pressure FT and WT boilers, internal treatment programs using phosphate are common and a small phosphate reserve is permanently maintained.

Where high residual calcium leakage occurs in the FW, the phosphate reserve is lost and the boiler water alkalinity is reduced. This is not the same problem as ***hideout****, which is the apparent loss of BW phosphate and other salts in higher pressure WT power boilers operating under high load conditions.*

In hideout, the salts reappear and can be determined when the load is reduced.

Problems of deposition often are interrelated with corrosion processes in cause-and-effect mode.

- **Cause and effect in lower pressure boilers.** Operators of lower pressure boiler plants (say, below 250–300 psig) using fully softened MU water normally maintain a relatively high BW total alkalinity (say, 15–20% of TDS, where the TDS can reach 3,000–3,500 ppm). Where the MU water has a naturally high alkalinity, however, the contribution to BW TDS may rise significantly to 30 to 40% (say, 1,200–1,500 ppm total alkalinity as $CaCO_3$). Under these conditions, the very high alkalinity causes the passivated film to deteriorate, with the effect that corrosion may take place and corrosion deposits may form. [Such deposits often contain a variety of iron salts including **siderite** ($FeCO_3$).]
- **Cause and effect in higher pressure boilers.** Conversely, operators of higher pressure boilers may seek to severely limit free caustic alkalinity (which also limits the total alkalinity). They often use *coordinated*, *conjunctional*, or *equilibrium phosphate programs* to eliminate risks to stressed boiler fabric metal caused by **stress corrosion cracking** (SCC) or **embrittlement corrosion**, through the absence of *hydroxyl alkalinity*. In a manner similar to that of *saline concentration* in porous deposits, however, when the water chemistry is not perfectly balanced and controlled, the buildup of **sodium hydroxide** (NaOH) may occur. The resulting effect may be both **caustic-induced SCC** and **caustic (ductile) gouging**, depending on the presence or absence of localized stresses.

NOTE: Caustic gouging corrosion also may occur in LP boilers because the deliberate provision of a caustic reserve is normally a basic waterside chemistry requirement.

Fouling and deposition in boiler sections may occur unintentionally through the application or misapplication of chemical water treatment programs. **Internal treatment-related boiler section problems** may occur in a variety of ways; some examples follow:

1. **"Gunking":** This may occur when beginning the use of *filming amines* in condensate systems or *polymeric sludge dispersants* in FW systems. Here the new program may dislodge old corrosion debris or salt deposits and cause them to redeposit elsewhere (usually ultimately in the boiler section).
2. **General sludging:** Where dispersants of an inappropriate quality or application rate are employed, the result is the poor dispersion and

suspension of general sludges, such as those of *sulfate*, *carbonate*, *silicate*, or *phosphate*, and their subsequent deposition. The sludge may settle and bake on tubes. **Baked-on sludge** often is the simple result of a failure to wash down an offline boiler when draining down.

3. **Flocculation:** Where dispersants are present at too high an active level in a boiler (say, when the "actives" exceed 80–100 ppm or possibly up to 120 ppm), the dispersant may exhibit flocculating properties; normally dispersed sludges then settle out on *boiler surfaces*.
4. Boiler scales and corrosion product deposits also may form from the **thermal breakdown of treatment chemicals**. Breakdown products of chemicals such as *sulfite*, *amines*, *hydrazine*, and *chelants* often are steam-volatile, and subsequent reactions may produce corrosion debris that forms deposits and causes blockages. This problem typically occurs when chemical treatments selected for use are applied under unsuitable operating conditions (as when the boilers are highly rated or raise steam at particularly high operating pressure or temperature).

Internal treatment-related problems may take the form of *organic material* present in deposits of iron oxide corrosion debris and salt scales. The material typically is present as **carbonized organic components** and may originate from water treatment chemicals such as *quebracho*, *wattle*, *pyrogallol*, or other **tannin** derivatives. Also, *acrylates*, *starches*, *sulfonated lignins*, and other **sludge dispersants** may be present.

In addition, organics also may be found in boiler section iron oxide deposits taken from large process industry boiler plants. Here, the organics are more likely to be **hydrocarbons**, such as *oil*, *tar*, or *petroleum coke*, rather than inhibitor treatments. The various mixtures that form all become very insoluble with age and quite dense.

7.2 PASSIVATION AND COMMON CORROSION PROBLEMS

It is a general rule that as boiler design pressure and heat flux increases, so the requirement for a progressively "higher quality" (higher purity) MU water also increases.

As a result of these more exacting operational demands and the reduction in MU water dissolved impurities, basic waterside problems

such as simple *carbonate* or *phosphate scaling* tend to be replaced by increasingly more complicated problems involving various types of corrosion mechanisms and metal oxide deposition. Where these deposits are porous, caused perhaps by the diffusion of ions from underlying metal (as can happen at high pH), *hydroxyl* and *chloride ions* concentrate and initiate more specialized forms of corrosion.

Problems of **short-term** and **long-term overheating**, which leads to *fatigue* and *metal failure*, also are associated with deposition on *boiler surfaces* and restricted BW flow—the particular mechanisms depend on the nature and quantity of the waterside deposits formed.

As a consequence, when a boiler is taken offline (because of *pitting corrosion*, *tube leaks*, or some other problem), it is vitally important to understand the **chain of cause and effect** and to ensure that the correct remedy or work protocol is in place before putting the boiler back in service.

In practice, the potential causes of boiler section corrosion are many and often commonplace. Initiators include *oxygen*, *carbon dioxide*, *acid*, *caustic*, *copper plating*, *chelant*, and even the *water* itself. In addition, mechanical problems may be an initiator of corrosion, which in turn may lead to boiler mechanical failure.

It is generally agreed that the causes and effects of poor water chemistry, mechanical problems, boiler section corrosion, metal failure, and poor boiler plant operation are all closely interrelated. Thus, effective control over the various corrosion processes that may occur in a boiler and its auxiliary equipment is *fundamental* to the realization of the full life expectancy and safe operation of the plant. Corroded and wasted metal cannot be replaced easily, and the failure of a boiler in service is both potentially dangerous and expensive.

Although this chapter looks primarily at relatively common forms of corrosion, we also explore a number of often complex and esoteric boiler section corrosion mechanisms. Many of these types of corrosion will only ever seriously develop in larger high-temperature or high-pressure boilers, especially those requiring knife-edge control and operating under difficult *thermal stress* conditions.

For most small to medium-size, light-industrial factories and facilities operating HP steam boiler plants at perhaps 30 to 150 psig, if and when problems of corrosion occur, they generally are of a more mundane nature.

For the limited number of smaller boiler plants where *serious* corrosion problems do develop, however, it typically is found upon investigation that corrosion does not take place in isolation. Rather, the

corrosion, sludging, and deposition mechanisms are interdependent and develop in a discernible chain of cause and effect. The results of corrosion often represent a failure to adhere to the most basic requirements for good waterside operating conditions.

Where serious problems develop, typically the waterside chemistry is poor and iron corrosion debris, sludges, and general deposition are evident. Perhaps there is no softener or the water treatment program is unsuitable for actual operating conditions. Possibly the protocol for BD is inappropriate (either too much or too little, or it is unrelated to steam demands) or flushing, cleaning, and boil-out programs have not been properly instituted.

Thus, a failure to properly balance and control various external and internal water chemistry parameters may lead to one or more corrosion mechanisms occurring, including several forms involving oxygen. Many types of corrosion are of themselves unfortunately relatively common phenomena, and the mechanisms also are common to all sizes and designs of boiler.

The precise protocols necessary to achieve effective corrosion control will vary dependent on individual boiler design and operation. For example, control of alkalinity is fundamental in controlling corrosion mechanisms. In small to midsize, general-purpose and industrial boilers, it is common practice to obtain adequate BW alkalinity as part of any water treatment program that operates under a **free-caustic regimen**. This approach generally is perfectly acceptable, and such programs normally can be relied on to ensure a clean, scale- and corrosion-free boiler.

Despite global use of free caustic programs, however, it is worth noting that good control over the caustic reserve and other factors is still very necessary to prevent the development of localized and highly concentrated deposits of caustic that may cause specific and very damaging **caustic gouging corrosion**. Such problems are usually associated with power WT boilers but, in fact, also may occur readily in FT boilers.

NOTE: Where free-caustic reserve programs are employed to reduce the risk of caustic gouging, it is vital to maintain boiler surfaces clean and free of sludge. This is especially so in high heat-flux boilers, irrespective of whether they are of FT design or WT design.

With regard to higher pressure industrial and power boilers, the more exacting waterside and operating conditions demanded generally dictate that an alternative approach to corrosion control be employed, which usually precludes the presence of free-caustic.

In these boilers, various interrelated, complex surface chemistry reactions may occur at the metal–water interface, which (apart from the development of a *desirable* protective magnetite film) can lead to the formation of unwanted deposits. These surface reactions are influenced by the specific heat flux, operating temperatures, and the areas and degree of local metal stress resulting within a particular boiler.

In addition, the development of porous deposits on *boiler surfaces* often is enhanced by the presence of small amounts of iron or copper oxides (usually originating from contaminated condensate). This increased rate of deposition may then lead to even more serious problems of **overheating**.

Where a deposit contains an adequate concentration of **sodium hydroxide** and the affected area is stressed to a sufficiently high level, **stress-corrosion cracking** or **caustic embrittlement** (SCC) may occur. This type of caustic corrosion is different from *caustic gouging*, which does not require the presence of stress.

NOTE: For SCC to develop, apart from the obvious requirement for stressed components, the presence of some ***silicate*** *also is necessary.*

As a result of the need to prevent SCC, the standard water treatment program (as practiced by almost all HP boiler operators for many years around the world) has been to severely restrict or totally eliminate the presence of *free hydroxyl ion* in the boiler water.

The primary chemical water treatment program employed to balance and control alkalinity and yet prevent the deposition of free sodium hydroxide includes a **coordinated phosphate program** and some derivations of this approach (such as **congruent phosphate** and **equilibrium phosphate programs**).

It will be noted from the preceding discussion that impurities may induce more than one form of corrosion. The particular types of corrosion and the influence of these impurities work in a developing chain of cause and effect, depending in large part on the specific operating circumstances in question. Such factors include the boiler system basic configurational design, the localized areas of stress, and the temperature of various metal surfaces.

Whatever the various interdependent but background causes of waterside problems, a common overall effect is an inability for a uniform, **passivated surface** to be completely formed or properly maintained on all waterside surfaces, and for corrosion to thus continue unabated.

7.2.1 Boiler Surfaces Passivation

Given that the effective and continuous control of boiler section corrosion is a vitally important function, the establishment and maintenance of the **passivity** of the *boiler surface*'s metal at the metal–water interface is critical.

Passivation under a wide range of operating conditions and in all boiler designs is a goal of *all* BW treatment programs. It is achieved through the formation of a stable, continuous, uniform, self-limited, and nonporous **magnetite** film. (This objective also applies to the maintenance of **cuprous oxide**, the copper equivalent of a film of passive iron.)

The objective of passivation is traditionally achieved by permanently maintaining *reducing conditions* (an absence of oxygen) and *sufficient alkalinity* in the BW. There are various mechanisms that may occur to induce passivated film development:

- In HW heating and smaller, simpler design LP boilers, the anodic corrosion reaction is often stifled by the use of an **anodic inhibitor program** such as an alkaline **nitrite** or **silicate-based**, chemical formulation. The passivated film developed is typically **hydrated iron oxide** ($Fe_2O_3 \cdot H_2O$) in the *hematite* (γFe_2O_3) form. This film is not completely protective, and, if possible, it is preferable to produce **magnetic iron oxide** (*magnetite*, Fe_3O_4) because this is virtually resistant to further oxidation.
- In steam-raising FT and WT boilers designed for general industrial applications and operating at pressures of 50 to 300 psig, the correspondingly higher BW temperatures coupled with the presence of **hydroxyl ions** (e.g., *caustic alkalinity*) and the removal of dissolved oxygen from the FW ensure that a dense, adherent magnetite film is always formed. The hydroxyl ions necessary for the reaction are typically supplied by providing a **free caustic** (*caustic reserve*) **program**. The equations involved are:

Fe^{2+}	+	$2OH$	$\rightarrow$	$Fe(OH)_2$
ferrous ions		hydroxyl ions		ferrous hydroxide

$3Fe(OH)_2$	$\rightarrow$	Fe_3O_4	+	$H_2\uparrow$	+	$2H_2O$
ferrous hydroxide		magnetite		hydrogen		water

- At the even higher temperatures found in HP industrial process or power generating boilers, the oxidation of iron is accomplished by the reduction of hydrogen ions supplied by the HW. The magnetite film is thus formed directly.

$3Fe$	+	$4H_2O$	$\rightarrow$	Fe_3O_4	+	$4H_2\uparrow$
steel		water		magnetite		hydrogen

7.2.2 Oxygen-Influenced Boiler Corrosion Problems

For all types of boilers, from the most simple HW heaters to immense power generating plants, one of the most fundamental objectives of any water treatment program is (as stressed several times) to minimize boiler section waterside corrosion, especially those common types of corrosion involving oxygen. The actions taken to achieve this objective are generally the same, irrespective of boiler size or design. These actions include:

- Permanently maintaining reducing conditions (the exclusion or minimization of oxygen) in the FW/BW
- Providing an appropriate level of alkalinity in the FW/BW
- Ensuring clean metal waterside surfaces
- Imposing maximum limitations on TDS and certain specific ions or salts (such as hydroxyl ions or chlorides)
- Limiting (especially for HW or LP steam boilers used for heating duty) the requirement for MU water to within design specifications to minimize the ingress of oxygen and the risks its very presence extend

Where waterside chemistry and operational control is not what it should be, the opportunity exists for corrosion to develop. Some of the more common forms of oxygen-influenced boiler section corrosion are discussed in the following sections.

7.2.2.1 Coarse Magnetite Corrosion

The formation of a magnetite film, although highly desirable, is itself a form of corrosion. The effective protection of *boiler surfaces* requires the proper development of an adherent, nonporous, self-limited, and stable film. Under adverse conditions, however, such as when

the BW pH is either too high or (especially) too low for the particular operating circumstances, or when finely divided *iron oxide* contaminants are present, the magnetite film formed is less than ideal and tends *not* to be self-limited. This **coarse magnetite** may form in the bulk water as well as on steel surfaces. It tends to be thick and porous in nature.

In particular, corrosion of *boiler surfaces* may result from the direct reaction with **ferric oxide** particles entering the boiler. The usual source of ferric oxide is from corroded circulation loops in HW heating boilers and condensate systems, or in pre-boiler sections in steam-raising plants.

The eventual result is the production of a thick, porous film of coarse magnetite (**ferroso-ferric oxide** or **ferrous-ferrite**), as shown below. This corrosion product is of no operational benefit and further hinders efficient heat transfer.

$4Fe_2O_3$	+	Fe	→	$3Fe_3O_4$
ferric oxide		steel		coarse magnetite

7.2.2.2 Boiler Section Oxygen Corrosion

Oxygen in a large operating boiler may corrode steam–water separators and *boiler surface* components such as the top drum (especially at the waterline) and tubes. **Oxygen corrosion** also may occur in superheater and reheater tubes, especially in places where moisture can collect, such as in bends and sagging tubes.

It should be noted, however, that oxygen corrosion of operational boilers supplied with mechanically deaerated FW, supplemented by the use of an appropriate oxygen scavenger chemical, and under a constant load is relatively rare. This position is not necessarily the same in **idle boilers**, **low-load boilers**, or **chemically cleaned boilers**, and despite all best efforts oxygen corrosion may take place.

Boiler section oxygen corrosion occurs if **high oxygen residuals** are permitted for any length of time (a failure to permanently maintain reducing conditions). This condition may be due to:

- **Air in-leakage**
- **Repeated use of cold water** during boiler start-ups
- **Malfunctioning deaerator**

- **Insufficient oxygen scavenger** to meet the DO demand

Oxygen corrosion also may occur if and when the following conditions below:

- **Passivated layer is absent** because of *acid leakage* or a *poor cleaning program.*
- **Passivated layer is imperfect** because of *surface attack from aggressive ions.*
- **Stress- and thermal-related cracks develop** caused by *rapid load swings.*
- **BW chemistry is unbalanced.**
- **Metal oxide and other deposits are laid down**, as may occur in *peak-loading power boilers.*

Apart from oxygen corrosion, under these circumstances, several other forms of corrosion also may take place, leading to further waterside problems in a "catch 22" chain of cause and effect. Nevertheless, despite the rarity of oxygen corrosion in constant load, large operational boilers supplied with mechanically deaerated FW, the greatest physical number of boilers in daily operation around the world are not large units but rather much smaller plants used for HW heating, LP steam, and general industrial purposes. The vast majority of these are neither supplied with deaerators, nor do they operate 24 hours per day.

Consequently, there exists a very significant potential for oxygen corrosion to occur in many of these smaller boilers. In fact, oxygen corrosion is, unfortunately, all too common in boiler houses around the world.

Oxygen corrosion may occur periodically and generally throughout the entire boiler or (more likely) in a number of localized areas at the same time. The risk of oxygen corrosion in smaller operational boilers is enhanced when:

- Boiler surfaces are dirty.
- FW is cold.
- MU water rates are high.
- Loads are erratic.
- Daily start–stop type operations are used.
- Preventative maintenance practices are poorly implemented.

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- Water losses and other problems result in periods of undertreatment of both oxygen scavengers and corrosion inhibitors and remain unexplained and uninvestigated.

7.2.2.3 General Etch Oxygen Corrosion (Uniform Rate Corrosion/General Wastage Corrosion)

General etch oxygen corrosion seldom occurs in boiler section steam–water circuits, although where steel is inadequately protected by *magnetite* (or *hematite*) and is exposed to water containing oxygen, then general etch corrosion forms, as shown in the following equation:

$$\underset{\text{steel}}{2Fe} + \underset{\text{water}}{H_2O} + \underset{\text{oxygen}}{O_2} \rightarrow \underset{\text{iron oxide}}{Fe_2O_3} + \underset{\text{hydrogen}}{H_2\uparrow}$$

This view of the corrosion process is, however, more often than not too simplified an explanation. First, even when "general" corrosion take place (as in an *idle* or *wet lay-up boiler*), the reaction mechanisms tend to occur at many localized points on the boiler metal surface, typically where cracks and other imperfections in the magnetite film exist. Second, such processes almost always lead to derived forms of "localized" corrosion, which often result in severe metal wastage through the formation of deep pits.

7.2.2.4 Localized Corrosion

Under *localized* corrosion conditions, where highly focused concentrations of oxygen may exist, the oxygen is *cathodic* in nature. Thus, points of lower oxygen concentration as well as the surrounding boiler metal may become *anodic*, relative to the point of high oxygen concentration. The difference in oxygen concentration can be measured as a current flow, and this current reflects the rate of corrosion taking place.

As corrosion products develop, so the rate of O_2 diffusion reduces and the rate of **general etch corrosion** slows down. But in practice, the presence of surface deposits tends to promote various forms of *localized corrosion* such as **tuberculation**, **pitting corrosion**, and **stress corrosion**, and consequently the rate of corrosion continues unabated.

Although these localized corrosion mechanisms all involve oxygen to a greater or lesser extent (and thus may be considered forms of oxygen corrosion), they also often involve other corrosive species. Also, the corrosion processes tend to become more *indirect* in nature, at

which point they may be regarded not as forms of oxygen corrosion but rather as types of **concentration cell corrosion**.

There are various different forms and mechanisms of localized concentration cell corrosion. Unfortunately, because one or more types may be manifest at any one time, the results can be quite devastating.

7.2.2.5 Concentration-Cell Corrosion

Tuberculation, **crevice corrosion**, and **under-deposit corrosion** are all forms of concentration cell corrosion, and they all involve the presence of some oxygen. There are several common factors and mechanisms involved in these various forms of concentration cell corrosion:

- The primary difference between these types of metal wastage and *oxygen corrosion* is that these are all *indirect* forms of attack, induced by **surface shielding** (areas of metal surface under deposits or foulants, or cracks and gaps in the metal that are close to a shielding surface).
- Reactions continue even with very low levels of oxygen present (i.e., as the diffusion rate decreases).
- Metals with protective oxide layers are not immune from attack, especially stainless steels and copper alloys, which may suffer aggressively from crevice corrosion.
- Additional forms of corrosion, such as galvanic corrosion, may also be involved.
- Poor housekeeping with uncontrolled metal oxide deposition usually increases the rate of corrosion.

Although each form of concentration cell may be considered a discrete form of corrosion, in practice, more than one type may occur simultaneously. These forms of corrosion are all characterized by localized differences in concentration of *hydrogen*, *oxygen*, *chloride*, *sulfate*, and other minerals, but especially *oxygen* (producing the so-called **differential oxygen concentration cell**, or **differential-aeration cell**). The basic mechanisms surrounding each of these specific forms of **concentration cell corrosion** are discussed next.

7.2.2.5.1 Tuberculation Tuberculation *concentration-cell corrosion* may be found in all types of boilers, especially HW heating boilers and LP/HP steam-heating boilers.

In these simpler types of boiler plants, corrosion protection generally is provided solely by the use of chemical treatments containing anodic passivators and alkali. Under conditions in which the (oxygen-containing) MU water requirement is expected to be very low, no specific oxygen scavenger is typically employed. This is often not the case in practice, however, for various reasons such as inadequate preventative maintenance, poor BD practice, the infiltration of air or oxygen, or other such reason.

The resulting pattern of events is usually that some initial *general etch oxygen corrosion* develops, leading to the formation of *rust* deposits and the subsequent development of a *differential oxygen concentration cell* under the deposit, resulting in further metal wastage. If this mechanism remains undetected for any length of time (which may be anywhere from 3 months to 1 or 2 years), the result is deep *pitting corrosion*. Where the pit exceeds 50% of the tube wall thickness, the tube must be replaced.

As part of the pitting process, tuberculation tends to develop especially when flow rates are low (as they often are in HW heating boilers). The pitting corrosion initiator may be *shielding* rust or deposits and foulants swept along to the area of lower flow.

The final result of this type of corrosion is the development of **nodules** or **tubercles**, consisting of successive layers of various (normally hydrated) *iron oxides* in both partially and fully oxidized states, which may run the length of the tubes.

The rate of all these corrosion mechanisms increases when the water contains a high alkaline, chloride, or sulfate content.

7.2.2.5.2 Crevice Corrosion Crevice corrosion is less common than tuberculation but may be found in larger boilers (typically WT boilers). Crevices form, for example, when an *alignment backing ring* is used during the butt welding of boiler tube sections; because strain may be present in the area of the crevice, **stress-corrosion cracking corrosion** may result.

The mechanism typically involves some *general oxygen corrosion* around the area of a crevice. As oxygen corrosion proceeds, the oxygen inside the crevice becomes depleted and corrosion debris may further impede the diffusion of O_2 into the crevice. Thus, a change in O_2 concentration gradient occurs and a *differential-oxygen concentration cell* is established with the oxygen-rich area outside the crevice becoming *cathodic* and the internal crevice area becoming *anodic*, thus inducing the development of **localized crevice corrosion**.

In the case of carbon steel, the accumulation of Fe^{2+} in the crevice attracts **chloride ions** (Cl^-) and aggressive *pitting corrosion* may occur.

7.2.2.5.3 Under-Deposit Corrosion In the same way that oxygen becomes depleted in a *crevice*, and a *differential-oxygen concentration cell* is established, leading to localized corrosion of the oxygen-starved anodic area, so the same phenomenon readily occurs in dirty boilers under deposits, sludge, and other foulants.

The rate of metal wastage of this *indirect* form of corrosion may be increased by the presence of other *direct* corrosion influences in the deposit or foulant. Also (and similar to crevice corrosion), there may be *general oxygen corrosion* occurring at the same time or perhaps acting as an **initiator** to the *under-deposit corrosion* process.

This type of corrosion is liable to occur in any part of a boiler where *silt*, *muds*, *scales*, *precipitants*, or *foulants* exist and is by no means limited to ferrous metals. **Stainless steels**, **brasses**, and **cupronickels** are all subject to under-deposit corrosion and deep pitting.

7.2.2.5.4 Pitting Corrosion Pitting corrosion is a general term for a visible sign of *concentration cell corrosion*, where further **induced-corrosion processes** develop, as when *chloride attack* occurs (although pits also may occur with simple *acid corrosion* processes).

In boilers subjected to **dry lay-up**, pitting of bent tubes and water-trapping boiler components may result from exposure to condensed moisture and atmospheric moisture.

In boilers containing pits as a result of oxygen corrosion, the pits may act as a site for additional **stress-corrosion** and **corrosion fatigue** mechanisms to occur.

7.2.3 Additional Forms of Concentration Cell Corrosion

All the various forms of **concentration cell corrosion** described are types of **indirect attack** induced by the effects of surface shielding, although not all concentration cell corrosion mechanisms involve the presence of oxygen.

Additional forms of concentration cell corrosion include those involving **sodium hydroxide** (*caustic*), **chlorides**, and **sulfates**; thus, some control over corrosion may be obtained by limiting **salinity** in the boiler.

These ionic salts all increase the conductivity of BW electrolyte and thus enhance corrosion reaction rates, so that strict limitations on the

salinity content of BW become increasingly important as boiler pressure or heat-flux density increases.

At least as important, however, is the need to ensure **clean metal surfaces** because, as stated earlier, concentration cell corrosion mechanisms commonly occur under boiler section sludges and deposits.

7.2.3.1 Caustic Gouging (Ductile Gouging and Caustic Attack)

Corrosion of steel may take place because of its *amphoteric* nature (it is attacked under either strongly acidic or strongly alkaline conditions). Caustic gouging is a specific form of corrosive attack on boiler steel, effected by a very high concentration of sodium hydroxide (typically >100,000 ppm/10%), as shown here:

Fe_3O_4	+	4NaOH	→	$2NaFeO_2$	+	Na_2FeO_2	+	H_2O
magnetite		caustic		sodium ferrite		sodium hypoferrite		water

Caustic gouging usually occurs only in areas of high heat flux but may also result when heat transfer rates are low, as in horizontal or inclined WT boiler tubes under circumstances in which the steam–water velocity is particularly low. Here, the relatively small volume of BW surrounding the steam bubbles concentrates very quickly, the alkalinity soars, and caustic corrosion develops.

The resultant **sodium ferrite** and **sodium hypoferrite** are washed away by fresh BW and the process repeats itself, eventually resulting in extensive thinning of the steel through the development of *longitudinal gouging* or *grooving*.

The *ferrite* corrosion product hydrolyses to *magnetite* and may move around the boiler. When magnetite is removed and bare steel is exposed, the caustic may react directly with the metal, as shown here:

Fe	+	NaOH	→	Na_2FeO_2	+	$H_2\uparrow$
steel		caustic		sodium hypoferrite		hydrogen

For caustic gouging to take place, it is necessary to have the availability of *free caustic* (or an alkaline-producing salt) in the BW and for some form of *concentrating mechanism* to be present. Concentration may result, for example, by virtue of the presence of existing (porous)

deposits, under or within which the caustic may be found, and it may take place in both FT and WT boilers.

Concentration may also result from **waterline evaporation**. In higher pressure WT power boilers, it may develop as a result of *high-firing cycle operations*, which may lead to **departure from nucleate boiling** (DNB).

NOTE: Caustic gouging does not require the presence of localized stresses or strains to develop.

At pressures of over 900 to 1,200 psig caustic gouging can be a very serious hazard, and **coordinated phosphate programs** (or similar types of program) have been used almost exclusively for very many years as a proven means of control. Under this type of program, the pH level generally is maintained sufficiently high to precipitate any calcium or magnesium contamination but not so high as to permit the presence of excess *hydroxyl ion*, which may initiate caustic gouging.

Apart from other control activities, such as the determination of phosphate, it is always necessary to closely monitor the FW *sodium* (Na) content.

7.2.3.2 Saline Corrosion

The presence of high concentrations of *salines* such as the sodium salts of **chlorides** and **sulfates** may increase the rates of localized corrosion and produce deep pits (especially in the presence of boiler sludge).

Chlorides in particular present a problem because of their tendency to attack and weaken *passive oxide* layers and accelerate metal wastage by **pitting corrosion** and other forms of *concentration cell* processes.

Chloride is both a **cathodic depolarizing agent** (*depolarizer*) and a **depassivating agent**, and the presence of high chlorides in steam–water circuits significantly increases the risk of **stress corrosion cracking of austenitic steels** (type 300 stainless).

Sulfate ions have reactions similar to those of chloride. They are **corrosion-causative agents** (similar to oxygen and hydrogen) of the various types of **concentration cell corrosion**. In addition, they also are *depassivation agents* and may greatly accelerate the risk of stress corrosion mechanisms. Saline corrosion pits resulting from high concentrations of chloride and sulfate salts also may be associated with **low pH corrosion** because *hydrochloric acid* and *sulfuric acid* can form within the pit, under deposits.

7.2.4 Low pH Corrosion

The minimum rate of boiler steel corrosion (i.e., the maximum development of dense, adherent, and protective magnetite) occurs at pH of 11 to 12. However, at significantly lower pH values (acid conditions) hydrogen ions are discharged (*depolarization*), the magnetite layer becomes porous, and corrosion rates increase.

Although relatively uncommon, low BW pH may occur for a variety of reasons under *online* operating conditions, resulting in either general or localized low pH corrosion. Under *offline* conditions, low pH corrosion usually is simply a result of improper acid cleaning procedures.

7.2.4.1 Low pH General Corrosion

Bulk BW having a low pH may can cause general corrosion and may originate from several sources:

- Naturally acidic MU water
- Reverse osmosis permeate water
- Demineralized water
- Seawater evaporator distillate

Low pH MU water sources are likely to adversely affect first preboiler equipment, such as economizers and other front-end components; a severely low pH incursion (say, below pH of 5.0–5.5) also results in general corrosion of boiler section components, including the boiler itself. Under these conditions, iron corrosion debris may form composed of particulate **magnetite needles**.

NOTE: The development of magnetite needles in the BW should not be confused with the transport by FW of particulate iron, which has its origins in other areas of the boiler system.

Clearly, none of these sources of water should be deliberately used for initially filling the boiler or as a FW component without the addition of an appropriate alkaline chemical treatment. Nevertheless, it may happen that untreated acidic waters are used, perhaps because a boiler plant operator assumes that the local (lean, acid) city water is perfectly satisfactory. This example indicates a need to provide not only site training in corrosion fundamentals but also in the purpose and benefits of using chemical treatments.

Where acid process contaminant or acidic water ingress occurs, the bulk BW pH may quickly drop as low as 5.0. This may occur, for example, where there is only limited alkaline buffering of BW because of low cycles of concentration and/or high-purity FW. Where acidic incursions occur, a general thinning of the boiler tubes, drums, and shell rapidly takes place, giving rise to a clearly visible irregular surface.

7.2.4.2 Low pH Localized Corrosion

Localized corrosion is a more common result of low pH water conditions than general corrosion. These conditions may be only temporary, but they may take place on a regular basis; if the cause is not thoroughly investigated, it can lead to extensive pitting and gouging of *boiler surfaces.*

For low **pH localized corrosion** to take place, two conditions are required.

1. There must be a source of acid (or acid-producing salt).
2. A localized acidic concentration effect must develop.

Examples of the first condition include:

- **Acid regenerant infiltration** (e.g., H_2SO_4, HCl) from the regeneration of ion-exchange demineralization plant.
- **Salt contamination** (NaCl) from the regeneration of cation exchange softening plant.
- **Seawater contamination** (e.g., $MgCl_2$, $CaCl_2$) from seawater or estuarine condenser leaks.

In a condenser leak in which magnesium hardness exceeds the bicarbonate alkalinity, the pH may be lowered sufficiently to induce significant acid attack, especially if an internal **all-volatile treatment program** (AVT) is employed:

Mg^{2+}	+	$2HCO_3^-$	→	$Mg(OH)_2$	+	$CO_2\uparrow$
magnesium ion		bicarbonate ion		magnesium hydroxide		carbon dioxide

Examples of the second condition include:

- **Departure from nucleate boiling** (DNB), perhaps as a result of *flame impingement* or other overheating effect
- **Waterline evaporation** in the top drum or shell
- **Acidic process contaminant in-leakage** combining with condensate (or alternatively the decomposition of process organics, resulting in the production of acids)
- **Shielding deposits** that retain corrosive residues originating from escaping steam

Substantial deposit-filled corrosion pits may result from the rapid concentration of only a few ppm of initial acid contaminant in the bulk water. The visual result can be similar to *high pH pitting corrosion*; thus, more sophisticated examination techniques may be required to ensure that the true cause is properly identified.

Very specific forms of *low pH localized corrosion* may develop in large high heat–flux WT boilers. Where subsequent analysis work is undertaken, the results usually provide the basis for a traceable chain of cause and effect. An example of such a chain of cause and effect is detailed in an interesting corrosion case history provided by Maringer, Saavedra, Selby, and Haberman, and published by Tall Oaks Publishing, Inc. A synopsis is provided below (with kind permission of Tall Oaks Publishing).

Extract of Case History Concerning the Reported Failure of Boiler Tubes in a Chilean Methanol Plant, 1,500 psig Waste Heat Boiler

The tube failures resulted from the development of corrosion pits that eventually perforated. The pits contained phosphate-based deposits and were a consequence of this high localized concentration of phosphate (plus the presence of some iron, which acted as a reactant) causing **acid attack**. The corrosive attack was, in turn, traced back to a combination of causative problems, including:

- Higher than desirable phosphate reserves when using a *coordinated phosphate program* (20–50 ppm phosphate rather than 5–10 ppm)
- Gas temperatures in the attack zone of over 1600 °F
- A particularly low sodium-to-phosphate ratio (below 2.1:1, rather than a control of 2.5–2.6:1)

This low $Na–PO_4$ ratio was a result of using an incorrectly blended solid phosphate mixture. The constituent proportions had been calculated based on utilizing *trisodium phosphate monohydrate* ($Na_3PO_4 \cdot H_2O$),

whereas, in fact, *trisodium phosphate dodecahydrate* ($Na_3PO_4 \cdot 12H_2O$) was employed.

7.2.4.3 Acid Cleaning Corrosion

Acid cleaning is not a precise process and many variable factors are involved, which, if not fully controlled, may result in acid corrosion of boiler steel. Under some circumstances, even with the use of **acid cleaning inhibitors**, acid corrosion (i.e., oxidation via hydrogen ions originating from the acid) may take place:

$$\underset{\text{steel}}{Fe} + \underset{\text{hydrogen ion}}{2H^+} \rightarrow \underset{\text{hydrogen}}{H_2 \uparrow} + \underset{\text{ferrous ion}}{Fe^{2+}}$$

The typical results of poor control over an acid cleaning process are *irregular pitting* and a very rough and jagged appearance on the various *boiler surfaces* that may resemble "Swiss cheese."

Most acid cleaning processes do not totally dissolve the available scales, oxides, and other debris, and where *localized crevice shielding* and *redeposition* takes place, it may be difficult to subsequently effect the complete neutralization of pockets of acid. These areas are then subject to vigorous attack once the boiler is bought back online.

7.3 STRESS AND HIGH TEMPERATURE–RELATED CORROSION

In addition to the many different forms of boiler section ferrous corrosion already described, several other less common types occasionally develop. In particular, corrosion processes may evolve that are interrelated with stress, deposition, and/or high temperatures (**thermal effect corrosion**), and together these may lead to metal fatigue (**metal fatigue corrosion**), metal failure, and even more serious problems such as the risk of a boiler explosion.

- Where stress plays a part, the resultant metal failure may be present as either a **transgranular** (*transcrystalline*) or an **intergranular** (*intercrystalline*) mechanism.
- Where overheating effects develop, they may be of either a *long-* or *short-term* nature and may result in **thermally induced corrosion** or **metal failure**.

- Where waterside deposits are evident, they provide a *heat insulating effect* and also permit *under-deposit contaminant concentration.* Under conditions of high pressure, heat flux, or stress, this combination of factors may lead to the development of **embrittlement corrosion** or **stress corrosion cracking** (SCC).
- Where stress factors are present in combination with high temperatures, these may result in both **thermal fatigue cracking** and **corrosion fatigue**. There are various potential stress factors, including:
  1. **Residual stress:** generally from the effects of metal rolling, bending, or welding operations
  2. **Applied stress:** as a result of flame impingement or uneven heating
  3. **Cyclic stress:** developing from on–off and peak-load boiler operations

7.3.1 Stress Corrosion Cracking

Stress corrosion cracking (SCC) or **embrittlement corrosion** describes any of a number of corrosion processes where in a corrosive environment, localized stress accelerates the rate of corrosion that may occur under or within a deposit.

Stress corrosion cracking develops through the localized concentration of a corrosive agent. It typically occurs only in WT boilers operating at over 300 psig, although a particular form known as **hydrogen embrittlement** usually occurs only in boilers operating at over 1,000 psig.

This type of stress-related corrosion process may result in boiler failure through a sudden and violent rupturing of the boiler tube metal. Austenitic stainless steels also are corroded by SCC mechanisms in the presence of concentrated chlorides (**chloride-induced SCC**).

7.3.1.1 Caustic Cracking/Caustic Stress Corrosion Cracking/ Caustic Embrittlement

This form of SCC affects both *carbon steels* and *austenitic stainless steels* (300 series) that are under stress. It is particularly associated with the inducement of boiler waterside metal-surface fractures (cracking) under localized deposits containing high concentrations of *sodium hydroxide* (caustic soda).

Caustic embrittlement corrosion is *intergranular*, and cracks appear along the grain boundaries. The process is accelerated by:

- High internal stresses
- Moderately high temperatures (200–250 °C/392–482 °F)
- Impurities in grain boundaries

In addition to stress, the development of caustic embrittlement requires a caustic corrosive in a concentration of at least 7.5 to 10% NaOH. It also requires some silica to be present (typically ≅ 0.2%). Thus, the prevention of this form of corrosion primarily requires the elimination of either stress or the concentration of corrosive.

In the days of riveted boilers, concentration of caustic took place through the seepage or leakage of BW into rivet holes or seams. **Sodium nitrate** was the classic SCC inhibitor and was applied at 20 to 40% of the caustic alkalinity (2P–M). It is still used today in certain older facilities, although alternative organic-based inhibitors are now available.

Today, boilers are *welded* and *stress-relieved*, thus ostensibly eliminating a primary component of the SCC process; however, modern boilers operate at higher heat fluxes, which imposes a strict requirement for cleaner metal surfaces. The presence of deposits on any waterside surface may provide an opportunity for the concentration of free alkali under the deposit, and so caustic embrittlement *still* occurs today, depending on inherent stress levels and the particular water chemistry involved.

In practice, higher pressure boilers typically operate under **AVT** or **coordinated phosphate** (or similar) **programs**, which do not provide for the presence of free caustic.

7.3.1.2 Hydrogen Embrittlement and Hydrogen Damage

Hydrogen embrittlement (HE) is the result of a *secondary* or *tertiary* corrosion process in steel whereby loss of ductility and cracking occurs, caused by the pressure generated from the reaction of **atomic hydrogen** (originating from water or acid) within the steel, forming molecular hydrogen ($H^0 \rightarrow H_2$) and from the reaction with carbon (from steel) producing *hydrocarbons*.

Hydrogen embrittlement is commonly associated with problems of excessive waterside deposition in boilers operating at over 1000 psig. Where HE takes place, the *primary* form of corrosion generally is either:

1. A low pH reaction (such as **low pH localized corrosion**)

2. A high pH reaction (such as **caustic gouging corrosion**) that produces both atomic hydrogen and deposition

The primary corrosion process exposes the steel surface. This enables secondary forms of corrosion to proceed within a chain of cause-and-effect mechanisms.

The liberated hydrogen diffuses under deposits and into the steel, where it combines to form **molecular hydrogen** at grain boundaries or inclusions, or reacts with *carbon* or *iron carbides* (**decarburization corrosion**) to form methane. These gases build up in pressure because the molecules are too big to further diffuse through the steel, causing *intergranular separation* (cracking) and finally tube or wall section bursting. A typical chain of cause and effect is shown in Table 7.2.

Because of the very real risks associated with HE and other catastrophic forms of corrosion, many of the larger power plants provide for a variety of real-time **automatic analyzers** to monitor *pH* and *hydrogen* (in addition to, e.g., oxygen, sodium, and silica).

NOTE: Background hydrogen levels in HP steam typically are 1 to 3 ppb H_2.

Given that atomic or molecular weights are approximately: Fe = 56, $H_2O = 18$, $Fe_3O_4 = 232$, $H = 8$, *it can be seen from the following corrosion*

Table 7.2 Hydrogen embrittlement chain of cause and effect

Step 1. A *primary* corrosion reaction occurs, exposing steel. Fe_3O_4 (magnetite) + $4NaOH$ (caustic) → $2NaFeO_2$ (sodium ferrite) + Na_2FeO_2 (sodium hypoferrite) + H_2O (water)
Step 2. One or more *secondary* corrosion reaction occur, producing atomic hydrogen, as in the example below: $3Fe$ (steel) + $4H_2O$ (water) → Fe_3O_4 (ferric oxide (coarse magnetite)) + $8H\uparrow$ (atomic hydrogen)
Step 3. Methane gas evolves during decarburization corrosion and builds up pressure, causing **hydrogen embrittlement metal fatigue** and eventual **tube rupturing**. FeC (ferric carbide) + $4H$ (atomic hydrogen) → CH_4 (methane) + $3Fe$ (iron)

reaction that 1 lb of hydrogen gas corresponds to the corrosion of 21 lb of steel:

$3Fe$	+	$4H_2O$	→	Fe_3O_4	+	$8H\uparrow$
iron		*water*		*coarse magnetite*		*hydrogen*
168 lb.	+	*72 lb.*	→	*232 lb.*	+	*8 lb.*

7.3.2 Thermal Fatigue Cracking and Corrosion Fatigue

Fatigue is the failure of metals under prolonged or repeated cycles of stress. It is characterized by local metal structure deformation. The addition of heat or corrosion processes tends to shorten the number of cycles required before failure resulting from *stress fatigue* occurs, and consequently **metal fatigue** is often described as *thermal fatigue* or *corrosion fatigue*. The different forms of fatigue are described in the following sections:

7.3.2.1 Thermal Fatigue

Thermal fatigue is a form of metal failure whereby fracturing occurs under repeated cycles of thermally induced stress. These cycles make take place, for example, because of *stop–start*, *lead–lag*, or *peak-load boiler firing* arrangements.

In thermal fatigue, a **ductile fracture** usually occurs, characterized by considerable plastic deformation, the tearing of metal, and an appreciable expenditure of energy—as occurs when a strip of metal is repeatedly bent.

Because problems of stress, high temperature, and deposition generally coexist (and may be considered interdependent risk factors), thermal fatigue is often associated with **long-term overheating**.

7.3.2.2 Corrosion Fatigue

Corrosion fatigue is a form of metal failure caused by a combination of *thermal cycling stress* (which leads to *thermal fatigue*) and an appropriate corrosion process, such as *caustic SCC*. Corrosion fatigue processes typically include **brittle fracturing**, which is the separation or cleavage of a metal with little or no resulting *plastic deformation*. The **corrosion fatigue** process does not necessarily take place on the waterside of boiled metal; it may be fireside initiated.

7.3.3 Overheating Effects and High Temperature Corrosion

Overheating increases the rate of boiler section corrosion and fatigue, thus leading to premature metal failure. Results of this form of corrosion may include:

- **Bulges**
- **Magnetite blisters**
- **Fractures**
- **Fissures**
- **Creep**—ductile metal deformation
- **Graphitization**
- **Ruptures**
- **Spalling**—hairline metal surface cracks, flakes or splinters
- **Exfoliation**—a form of corrosion exhibited by the throwing off of thin slivers or chips from the surface of the metal

Overheating may be sudden and dramatic, related perhaps to very unusual operating conditions and leading to catastrophic failure (**short-term overheating**), or a much more gradual process occurring over a period of several years (**long-term overheating**).

Persistently high operating temperatures lead to irreversible changes in the structure of the steel and eventual failure.

7.3.3.1 Long-Term Overheating

Long-term overheating is a further example of a chain of cause and effect. It almost always has its origins in the waterside chemistry and can affect both WT and FT boilers.

Typically, either pre-boiler contaminants introduced into the boiler or less than ideal BW chemistry conditions lead to the formation of deposits, which in turn impede circulation, insulate the heat transfer surface, and cause some higher-than-design degree of overheating.

Stratification and *steam blanketing* may add further to the insulating effects and also promote both thermal stress in excess of design limits and waterside corrosion. Over the longer term, considerable metal oxide is formed and **cracking** and **creep** develop.

Further stresses may be caused by the continued mechanical operation of the boiler under adverse conditions, leading to **intergranular**

creep cracking. Eventually metal failure occurs, usually through a **creep rupture** (**stress rupture**).

The rupture initially may affect only a single boiler tube (although many tubes will be weakened), and this tube typically shows limited *bulging*, but the formation of considerable *oxide* and *scale*.

Control of long-term overheating requires modifying water chemistry and a close analytical monitoring protocol to minimize or eliminate the risks of deposits. In many cases, some significant change in boiler operating practices is also required.

7.3.3.2 Short-Term Overheating

Short-term overheating essentially is operationally induced, and there may be many reasons for it. These factors include:

- Major load swings
- Startup or shutdown firing difficulties
- Excessive blowdown
- A lack of water coolant for a brief period

In the WT boiler, a chain of cause and effect that includes short-term overheating may follow this scenario:

1. Tube blockages cause inadequate steam–water velocities;
2. Insufficient water leads to locally elevated metal skin temperatures;
3. This is followed by a rapid failure in metal wall strength;
4. A violent tube rupture results.

The typical rupture pattern has a thick-walled, wide-mouthed appearance (**fish mouth rupture**).

Short-term overheating may take place when the metal temperature exceeds 850 to 900 °F (454–482 °C). Where dry firing occurs, the skin temperature may quickly rise to 1,200 to 1,500 °F (684–815 °C) or higher.

The problem is confined to the hottest parts of high heat-flux WT boilers (primarily very large industrial and power boilers). Low heat-flux areas such as economizers are not affected.

Where short-term overheating takes place, there seldom is any evidence of a buildup of oxides or significant deposits. However upon

investigation it is not unusual to discover evidence of long-term overheating damage with a subsequent brief period of short-term overheating that finally produced boiler failure.

7.3.3.3 High Temperature Corrosion

Various specific forms of high temperature boiler corrosion (such as *hydrogen embrittlement*) may result as a consequence of overheating (caused by *steam blanketing* or *flame impingement*) coupled with other operational problems (such as *deposition*). There may be a chain of cause and effect, resulting in some boiler surfaces operating at higher-than-design temperatures, which in turn leads to corrosive attack and an increased risk of boiler failure.

Where boiler design specifically requires persistently high operating temperatures, however, (and even though these circumstances may not necessarily constitute an overheating situation), the potential exists for certain other forms of high temperature corrosion to occur. Some examples of **persistently high temperature corrosion** are discussed in the following sections:

7.3.3.4 Thermal Oxidation/Metal Burning and Metal Scaling

Depending on the particular component alloy employed (such as a superheater tube alloy), **metal burning** may take place at temperatures of 1,000 to 2,000 °F (538–1,093 °C), resulting in a hole developing in the tube.

Unalloyed steel can be directly oxidized by steam at temperatures over 750 °F (399 °C). Extensive cracks may occur, the steel surface may resemble tree bark, and magnetic oxide deposits are generated at the failure site. **Intergranular oxidation** may take place. In the thermal oxidation reaction, hydrogen is directly released as shown:

$3Fe$	+	$4H_2O$	→	Fe_3O_4	+	$8H\uparrow$
steel		steam		magnetic iron oxide		hydrogen

7.3.3.5 Spheroidization

At temperatures in the range of 850 to 950 °F (454–510 °C), permanent structural changes, such as spheroidization, take place in the boiler steel. In this process, the **pearlite** phase component disappears as the laminar **cementite** gradually changes into spherical grains.

*NOTE: Steel consists of **ferrite** and **pearlite** phases. Ferrite is a solid solution of carbon in iron, whereas pearlite is a mixture of ferrite and laminar **cementite**. Cementite is a carbide, such as ferric carbide (Fe_3C), although part of the iron content may be replaced by other metals including molybdenum.*

7.3.3.6 Decarburization

Additional high temperature changes cause decarburization, wherein carbon in the *ferrite* phase of carbon steel can be oxidized to *carbon dioxide*.

7.3.3.7 Graphitization

In this form of corrosion, the **iron carbide (ferric carbide)** component of steel is decomposed to *graphite* and *pure iron*. The external physical structure of the steel is rarely changed, but the internal structure is significantly weakened.

NOTE: Do not confuse graphitization with graphitic corrosion, which is different. Graphitic corrosion causes the iron in cast iron to selectively leach out, leaving behind a porous graphite structure.

7.4 OTHER FORMS OF CORROSION

There are many other types of corrosion that may occur (some quite esoteric). Two forms of corrosion not yet discussed include chelant corrosion and nonferrous metal corrosion.

7.4.1 Chelant Corrosion (Chelant Attack)

Organic chelant compounds, such as the *sodium* salts of **ethylenediaminetetraacetic acid** (EDTA) and **nitrilotriacetic acid** (NTA) are commonly used in BW deposit control treatments, often in combination with phosphates.

NOTE: EDTA, NTA, and other chelants are also employed in various online and offline boiler plant cleaning formulations.

Chelants have the ability to take waterborne *metal ions* such as Ca and Mg (but also Fe and Cu) and produce soluble *coordinate bond complexes*. Therefore, they can be employed for the control of FW hardness salts and other related problems.

Chelants are particularly useful in maintaining very clean, deposit-free waterside conditions and can be employed in both FT and WT boilers. In practice, however, they are relatively indiscriminant in their reactions and under *unsuitable* conditions may seriously corrode carbon steel, copper, and copper alloy boiler components. Chelants also may react with any available oxygen under BW conditions and temperatures.

Nevertheless, during the last 25 to 30 years the genuine benefits of using chelant-based programs have become more widely appreciated, and a considerable amount of technical information has also unfortunately been disseminated concerning the potential risks for severe **chelant corrosion**. The position of this author is that much of this risk awareness information has been exaggerated and furthermore that some of the advice is suspect.

What is clear is that chelant corrosion takes place only when a number of unfavorable boiler operating factors are collectively present and that the starting point for corrosion is an overfeed of chelant product.

Where a stable, passivated magnetite film exists, there is little risk of corrosion when using these products, and under normal alkaline boiler conditions (above a pH of 10.0), the chelation of **ferric iron** [$Fe(OH)_3$, Fe_2O_3, Fe_3O_4] does *not* take place (so the protective magnetite film is not disrupted).

High levels of either chelant or *oxygen*, however, affect the **redox** tendencies of iron–oxygen reactions. Consequently, overdosing chelant in the presence of some oxygen, or tolerating high DO levels in the presence of chelant, permits the liberation of Fe^{2+} ions (corrosion) from a metal surface and their subsequent chelation, thus preventing the formation of blanketing ferric oxides or hydroxides.

Under modern, highly demanding operating conditions, where very clean boiler internal surfaces and high heat transfer rates are the norm, the thin magnetite film is essentially the *primary* barrier against corrosion. Consequently, the presence of DO must be strictly controlled to avoid waterside surface corrosion problems. This clearly is even more important when chelants are employed. Also, *all* of the many possible operating conditions that may lead to overheating, DNB, and disruption of the passive magnetite film must likewise be strictly controlled.

It is only when an overfeed of sodium salt chelant takes place over a period of time, *coupled with the presence of oxygen and the disruption of the magnetite film*, that a serious chelant corrosion risk exists. Under these conditions, however, other equally serious boiler failure risks also exist that demand appropriate and swift corrective action.

NOTE: Although FT boilers usually do not operate under knife-edge control conditions (as do some large power WT boilers), it is evident that chelant programs generally are not suitable for any FT plant operating without benefit of a deaerator.

Where chelant corrosion does occur, attack may take place either at the *chelant entry point* or at several possible *boiler surface* locations. At the chelant entry point, rapid thinning of the metal takes place in the immediate vicinity. If the injection point has not been stress-relieved, the attack may be exaggerated and metal gouging may also occur. At the injection point, the available chelant is highly concentrated; injection of product should be continuous through a type 304 injection quill (injection nozzle), with the chelant being rapidly dispersed into the body of steam–water.

NOTE: The injection point of chelant should be into the boiler FW as far downsteam as possible from the deaerator and chemical oxygen scavenging point to permit sufficient time for effective oxygen removal to take place.

The injection location also is important, especially where catalyzed sodium sulfite is employed, because of the potential for chelation of the usual cobalt salt catalyst to occur.

Injection also should be well downsteam of any copper-based pump impellers.

Where chelant attack of *boiler surfaces* does take place, the corrosion results in a thinning wastage of the metal rather than pitting. The metal surface most commonly is uniformly dark, smooth, and featureless, and the corrosion often is not immediately discernable to the naked eye.

As flow velocities increase, chelant attack becomes substantially worse, with the flow pattern being reflected in the form of U-shaped depressions and long tails (**comet tails**). Thinning continues until boiler failure occurs through a rupture of the thinned metal surface. In areas of high stress and/or high turbulence, attack is greatly enhanced and may be very localized.

The points of attack are primarily the waterline (where oxygen pitting may also occur), in areas where steam–water velocities are highest, and at points where stresses are inherent. These include:

- The boiler FW pump
- Boiler tube surfaces (especially at the entry points)
- Rolled tube ends

- Baffle edges
- Threaded components

Where chelant corrosion metal failure occurs, an investigation may determine that contributing factors also include localized overheating, steam blanketing, or DNB.

7.4.2 Copper Corrosion

The most serious pre-boiler contaminant is often *copper*, resulting from the **ammoniacal corrosion** of steam-condensate system components and its subsequent transport through the boiler plant.

If copper is present in the boiler FW (normally as the **cupric ammonia complex ion**), boiler surfaces are directly attacked by electrolytic reduction. In strongly alkaline conditions the ferrous ion is present as **ferrous hydroxide** $[Fe(OH)_2]$:

$Cu(NH_3)_4^{2+}$	+	Fe	→	Cu	+	Fe^{2+}	+	$4NH_3$
cupric ammonia complex ion		steel		copper		ferrous ion		ammonia

The resultant plated copper then acts as a cathode to the surrounding anodic boiler steel and extensive corrosion takes place, thus resulting in thinning and weakening of the boiler steel.

Inadequate acid cleaning procedures also may introduce traces of copper into the boiler (typically originally present as copper-containing deposits), which can plate out onto clean metal surfaces and cause localized, **anodic area pitting corrosion**.

Where very high temperatures are involved, the presence of copper deposits may cause **liquid metal embrittlement**.

7.5 CORROSION IN NUCLEAR POWERED STEAM GENERATORS

PWR steam generators (SGs) are essentially complex shell and tube heat exchangers composed of a variety of corrosion-resisting alloys. The closed loop *primary circuit* is on the tube side and the steam generating, working fluid or *secondary circuit* is on the shell side.

Resistance to corrosion and a long operating life is a requirement of all materials employed in nuclear powered SG heat exchangers.

Corrosion and tube failures can produce severe consequences, including:

- Possible shutdown of the station
- Loss of expensive light- or heavy-water primary coolant
- The spread of primary circuit **radionuclides** to the secondary circuit
- The development of high radiation fields surrounding areas of active corrosion

Over the years, with the advent of larger generators of increased pressure and operating output, the challenge of ensuring maximum output without sacrificing long-term structural integrity related to corrosion has increased. The criteria for SG tube material selection is critical, and the selection process is designed to provide resistance to corrosion and erosion on both sides of the tube under precisely controlled water chemistry and mechanical operating conditions.

7.5.1 Nuclear Plant SG Materials Selection

Early SGs employed **austenitic SS** as tube material, but in several parts of the world problems were experienced because of stress corrosion cracking (SCC) from the secondary side. This was caused by an accumulation of chlorides originating from poor precommission cleaning (PCC) following fabrication and site errection, or from the ingress of chlorides into the secondary circuit from inadequate control over high-purity MU water quality or condenser in-leakage. **Monel 400** (70% Ni, 30% Cu) was also used in early SGs for heat-exchanger tube sheets, but corrosion rates of this alloy tend to increase dramatically where oxygen is present (as when low levels of boiling is permitted in the coolant channels of advanced PHWR designs).

Certain **Inconel alloys** have been used with varying degrees of success. **Inconel 600** (70% Ni, 15% Cr, 15% Fe) has been employed because of its improved resistance to chloride-induced, SCC, but it has failed on occasions because of **intergranular attack** and **general etch corrosion**.

Various newer and more corrosion-resistant alloys are now available for use, including *low nickel alloys*, such as **Inconel 800** (35% Ni, 20% Cr, 45% Fe). Low nickel alloys, in particular those with with less than 0.03% *cobalt*, are required to limit the development of a **cobalt-induced, outer-core radiation field** within the SG.

NOTE: Nickel alloys contain ***Cobalt^{59}*** *(a naturally occurring isotope) as an impurity. Corrosion of high nickel-containing alloys on the primary circuit side of the tubes leads to the release of* ***cobalt corrosion products****, which form radioactive* ***Cobalt^{60}*** *(having a half-life of 5 years) when irradiated by neutrons originating in the reactor. The chain of cause and effect leads to the emission of high-energy gamma rays and the development of an* ***outer-core radiation field****, which increases with nuclear reactor operating time.*

Table 7.3 Deposition of boiler section waterside surfaces by alkaline earth metal salts, other inorganic salts, and organics. (Note: Deposition can also take place in the pre-boiler section.)

Deposit material	*Mineral/formula*	*Problem or risk*
Calcium carbonate	Aragonite $CaCO_3$	Low temperature scale.
	Calcite $CaCO_3$	Higher temperature scale.
Calcium phosphate	Hydroxyapatite $Ca_{10}(OH)_2(PO_4)_6$	Flocculated boiler sludge, as a result of residual hardness.
	Tri-calcium phosphate $Ca_3(PO_4)_2$	Calcium phosphate can form as a hard, adherent sclae in FW line, especially if pH is below 8.2–8.3.
Calcium sulfate	Anhydrite $CaSO_4$	Hard, difficult scale.
(Basic) Magnesium chloride	Magnesium chloride hydrate $MgCl_2{\cdot}5Mg(OH)_2{\cdot}8H_2O$	Saline concentrates in porous deposits, resulting in acid corrosion pits.
Magnesium hydroxide	Brucite $Mg(OH)_4$	Common flocculated boiler sludge.
(Basic) Magnesium phosphate	Magnesium hydroxy-phosphate $3Mg_3(PO_4)_2{\cdot}Mg(OH)_2$	Forms with hematite in passivated films at lower temperatures.
Sodium hydroxide	Caustic soda NaOH	Caustic concentrates in porous deposits, resulting in caustic gouging and SCC.
Various sludges	Phosphates, etc.	Baked on sludge.
Treatment chemicals	Sulfites, hydrazine, amines, chelants	Incorrect application results in thermal breakdown, sludges and corrosion deposits.
	Tannins, dispersants, hydrocarbons	Carbonization produces deposits and binders.

Even where low nickel alloys are specified, corrosion, however limited, may lead to the release of other alloying components and the release of more radionuclides such as **chromium**[51], **cobalt**[58], **iron**[59], and **manganese**[54]. Thus, materials selection remains a critical issue in nuclear plant SG design.

Table 7.4 Summary notes: silica and silicate crystalline scales and deposits affecting boiler section waterside surfaces.

Mineral/formula	*Problem or risk*
Acmite $Na_2O{\cdot}Fe_2O_3{\cdot}4SiO_2$	High temperature scale. Found under sludges of hydroxyapatite, serpentine or porous iron oxides. Can result from alum carryover.
Alpha quartz αSiO_2	Hard scale found in drum, tubes, and turbine blades.
Analcite $Na_2O{\cdot}Al_2O_3{\cdot}4SiO_2{\cdot}2H_2O$	Similar to acmite. Presence can indicate steam blanketing problems.
Magnesium orthodisilicate $Mg_3Si_2O_7{\cdot}2H_2O$	Sludge forms from magnesium hydroxide and silicate in boiler
Natrolite $Na_2O{\cdot}Al_2O_3{\cdot}3SiO_2{\cdot}2H_2O$	Moderate hardness scale.
Nepheline *various structures* eg: $[Na_4K_2Al_6(SiO_4)_2]$	Moderate hardness scale.
Noselite $5Na_2O{\cdot}3Al_2O_3{\cdot}6SiO_2{\cdot}2H_2O$	Hard, adherent scale found on tubes and high heat-flux density areas.
Serpentine $3MgO{\cdot}2SiO_2{\cdot}H_2O$	Common sludge, forms from Mg salts and silicate at lower pressures.
Sodalite $3Na_2O{\cdot}3Al_2O_3{\cdot}6SiO_2{\cdot}2NaCl$	Hard adherent scale on tube surfaces.
Wollastonite $CaSiO_3$	Moderate hardness scale.
Xonotlite $5CaO{\cdot}5SiO_2{\cdot}H_2O$	Hard, adherent scale found on tubes and high heat-flux density areas.

Table 7.5 Summary notes: iron oxide and other boiler section corrosion debris deposits.

Mineral/formula	*Problem or risk*
Ammonium carbamate $NH_2Fe_2(OH)_4(CO_3)_2{\cdot}H_20$ Hydrated basic ferric ammonium carbonate $(NH_4)2Fe_2(OH)_4(CO_3)_2{\cdot}H_2O$ Malachite $CuCO_3{\cdot}Cu(OH)_2$	The transport of pre-boiler corrosion debris to the boiler section will includes these minerals. Also the oxides of Fe, Cu, Ni, Zn, and Cr as as noted below.
Bunsenite NiO	Nickel oxides. A result of corrosion of brasses and cupronickels.
Copper Cu	Deposited by direct exchange with iron, or by reduction of copper oxide, during the corrosion of steel.
Cuprite CuO	Black non-magnetic mineral. Originates from condensers and FW heaters.
Eskolaite Cr_2O_3	Chromic oxide. A result of corrosion of stainless steels.
Ferric phosphate $FePO_4$	Found in low temperature passivation film with hematite.
Ferrous bicarbonate $[Fe(HCO_3)_2]$	Transport into FW line and boiler. Common in smaller boilers with a high percentage of cold water MU water.
Haematite Fe_2O_3	Formed at lower temperatures and higher oxygen concentrations.
Magnetite Fe_3O_4	Formed at high temperatures, under fully reducing conditions.
Siderite $FeCo_3$	Formed in LP boilers with high alkalinity BW.
Wustite FeO	Ferrous oxide formed in LP boilers with poor DO removal. Develops as the core of tuberculation deposits.
Zincite ZnO	Originated from brasses used for condensers and FW heaters.

Table 7.6 Summary notes: boiler section corrosion problems involving oxygen, concentration cells, and low pH.

Type of problem	*Notes*
Coarse magnetic corrosion Fe_3O_4 *NOTE: Passivation is a form of corrosion, albeit the resulting magnetite is desirable.*	Thick, porous, bulk water or boiler surfaces deposit. Formed under both high and low pH and other adverse BW conditions. Of no practical passivation benefit.
Oxygen corrosion, occurring as: General etch corrosion/uniform rate corrosion (less common form) Localized corrosion (takes several forms and common where waterside conditions are less than ideal)	Rare in correctly treated boilers but can affect drum waterline and tubes. More common in idle and low-load boilers, where water chemistry is unbalanced, under high MU conditions and after poor chemical cleaning. Also in peak-load boilers, especially where deposition can occur. Localized corrosion can be very serious, causing metal failure.
Localized, concentration-cell corrosion (differential aeration corrosion), occurring as: Tuberculation corrosion Crevice corrosion Under-deposit corrosion Pitting corrosion	All forms of localized, concentration-cell corrosion are "indirect attack" type corrosion mechanisms. They result in severe metal wastage and can also induce other corrosion mechanisms, e.g. Stress corrosion Corrosion fatigue
Other forms of concentration-cell corrosion include: Caustic gouging Saline corrosion	Combination of free caustic and concentrating effect causes severe metal wastage. High chlorides and sulfates, result in corrosion from depolarization and depassivation effects
Low pH corrosion includes: Low pH general corrosion Low pH localized corrosion Acid cleaning corrosion	 Results from acid breakthrough into boiler water with only limited buffering capacity Requires an acid source and a concentration effect Results from both poor cleaning and poor neutralization processes

Table 7.7 Summary notes: stress and high temperature related corrosion.

Type of problem	*Notes*
Embrittlement corrosion occurring as:	Also known as stress corrosion cracking (SCC)
Caustic cracking (caustic embrittlement)	Intergranular corrosion affects both carbon steels and austenitic steels and accelerated by high stress, higher temperatures, and impurities in grain boundaries.
Hydrogen embrittlement (hydrogen damage)	Only in boilers over 1000 psig, leading to violent tube rupture.
Fatigue corrosion occurring as:	
Thermal fatigue cracking (thermal effect corrosion	Cycles of thermally induced stress leads to metal failure.
Corrosion fatigue	Results from a combination of thermal cycling stress and SCC or other corrosion process.
High temperature corrosion occurring as:	Effects of overheating lead to premature metal failure through:
Long-term overheating	Bulges
Short-term overheating	Magnetite blisters
High temperature corrosion	Fractures
Thermal oxidation (metal burning/metal scaling)	Creep/ductile metal deformation
Spheroidization	Graphitization decomposition
Decarburization	Fish mouth ruptures
Graphitization	Spalling of flakes/splinters
	Exfoliation of surface chips
Chelant corrosion (chelant attack)	Complexing of soluble Fe, Cu, and CU alloy ions. (Excess chelant *and* oxygen leads to change in redox potential and corrosion develops.)
Copper corrosion occurring as:	
Transported corrosion debris	Resulting from ammoniacal corrosion of steam/CR lines.
Cupric ammonia complex ion corrosion	Resulting plated copper acts as cathode to surrounding anodic boiler steel, inducing corrosion.
Anodic area pitting corrosion	Results from poor acid cleaning where copper traces are present.
Liquid metal embrittlement	Results from copper deposits and high temperature conditions.

8

WATERSIDE AND STEAMSIDE PROBLEMS: POST-BOILER SECTION SPECIFICS

The generation of clean, uncontaminated steam is a fundamental objective for all facilities. Most users also require the steam to be as dry as possible, although certain applications can tolerate or even require *wet steam.*

Within any particular facility, steam is expected to be delivered to various points of use safely and at controlled temperatures and pressures through relatively long-lasting distribution networks. Where the steam is not excessively contaminated or directly consumed in a process as **live steam**, it should be condensed, collected, and returned to the boiler for reuse. Thus, the post-boiler section of a boiler plant essentially relates to the systems concerned with steam distribution and condensate return (CR).

Steam is widely employed in all manner of buildings and factories, including:

- Commercial premises and institutions
- Food and beverage industries
- Wood pulp and paper manufacturing
- Chemical and pharmaceutical industries
- Oil, gas, and petrochemical refineries
- Textiles, dye-houses, and laundries
- Metal refining and fabrication plants
- General manufacturing industries
- Utilities

Within these industries, steam may be directly employed in a myriad of processes or indirectly used for innumerable purposes, including:

- Space heating equipment
- Process air heaters
- Evaporators
- Turbines
- Retort cookers
- Jacketed kettles
- Heat exchangers
- Submerged coils
- Dryers
- Strippers
- Hydrostatic sterilizers
- Trace heating lines
- Absorption chillers

For all of these various items of equipment and process applications, the supply and distribution steam systems must be able to meet several basic requirements, including:

1. Vary the steam delivery volumes, flows, and pressures to match **steam demand**
2. Provide and maintain appropriate **high heat-content steam**
3. Ensure the preservation of **steam quality** (minimum moisture content)
4. Ensure the preservation of appropriate **steam purity** (minimum of other contaminants)

To this end, steam distribution and CR systems serve to enable the efficient delivery of steam to take place and, once the heat content has been transferred, the subsequent recycling of the condensate.

Consequently, any and all waterside or steamside problems that may hinder or sometimes completely prevent the achievement of these objectives must be addressed. In practice, there are a myriad of potential problems that may develop in the steam and condensate systems, and (as in other areas of the boiler plant) many of these problems are

interrelated, exhibit a pattern of cause and effect, and may have serious safety and financial implications.

Problems that affect the delivery of steam or may compromise its heat content, quality, or purity may occur in several areas, for example:

- Boiler
- Boiler header
- Steam mains
- Distribution and collection pipework
- Valves
- Steam traps
- Flash tanks
- Condensate receivers

Some of the many relatively common waterside and steamside problems that may occur are listed below. Apart from contributing to reduced steam purity and quality, these problems may result in equipment failures and pose serious safety issues:

- Carryover
- Corrosion
- Erosion
- Water hammer
- Leaking steam traps
- Sticking valves
- Reduced heat-transfer capacity in terminal equipment
- Boiler surging and water level instability
- Process leaks
- Contamination by cooling water
- Air infiltration
- Volatile silica

8.1 STEAM PURITY AND STEAM QUALITY

Ensuring that clean, dry, uncontaminated steam is consistently delivered to the required points of use is not an easy task, and the smallest

amounts of contaminants often have a significant and detrimental effect.

- *Steam purity* indicates the degree of inadvertent BW **carryover**, typically reflected by an increase in electrical conductivity from **sodium** and other ions present in the BW TDS. **Iron** and **silica** may also carry over, and the silica may be in a volatile form. Steam purity also is affected by the use of neutralizing amines (as an intentional measure).

  In many process industries, food factories, meat packing plants, textiles plants, commercial laundries and other facilities, wide load swings are the norm rather than the exception, so that maintaining adequate steam purity is often very difficult.

  Boiler manufacturers typically guarantee steam purity only down to 1.0 ppm; however, 0.1 ppm or better is required for HP boilers and in fact is usually achieved when everything is working as it should. Some particularly good boiler designs carry over only to the extent of 5 to 10 ppb.
- *Steam quality* relates to the amount of entrained water transported into dry steam on a weight/weight basis. Because the water may contain TDS, steam quality is generally very closely allied with steam purity.

  The production of dry steam is important because wet steam may damage equipment and machinery, breaking valves and fittings and causing deposits in superheaters and turbines.

  Where condensate forms from the wet steam and drips back through the system, **water hammer** may develop and cause severe damage.

NOTE: Water hammer is caused by sudden interruptions in flow, as when steam meets draining condensate. The steam produces instantaneous surges of pressurized water that hits valves, elbows, and tees at high velocity. This produces a hammering sound and leads to metal stress and possible failure.

8.1.1 Necessity for Steam Sampling

As can be seen from the various bullet points listed at the beginning of this chapter, the permutations of potential problems by industry, process, equipment type, and specific area are extremely wide. Consequently, to preempt such problems developing, or at least to con-

trol to some degree both the causes and effects, it is important to regularly monitor steam and condensate purity and quality.

The frequency and types of tests employed should, of course, bear some relation to the type of facility being considered. If steam and condensate are not tested, *carryover*, *corrosion*, *contamination*, and other potential problems may be missed, which undoubtedly will have a deleterious impact in other parts of the overall boiler plant.

8.1.1.1 Steam Sampling Problems

The larger power generation, process, and cogeneration plants usually have continuous sampling and monitoring programs in place; however, in many smaller industrial or large commercial FT/WT boiler plants, facilities for adequate steam and condensate sampling points are ofttten unavailable. Under these circumstances, appropriate sampling protocols obviously are not followed, and the value of steam sampling and the benefits to be gained from the information may not always be fully appreciated.

1. **Lack of appropriate steam sampling points.** Before undertaking an analysis program at a facility, many times the first problem is simply obtaining satisfactory and representative steam and condensate samples. More often than not, the original plant designer failed to make adequate provision for steam sampling, and a common vented condensate receiver/ or FT may be the only point from which any samples can be taken with reasonable ease and safety. However, the validity of these samples is often suspect, especially if the receiver is also the point in the system for the addition of MU water. With regard to the smallest industrial and commercial LP steam boilers, it may be almost next to impossible to obtain samples without some serious difficulty or safety issues. Consequently, this situation should be corrected when possible (say, when a shutdown period arises), and two or three permanent points should be installed that are reasonably representative of the steam distribution system and application points of use.
2. **Steam Sampling Awareness.** The very common problem of lack of any reliable sample points in the steam condensate system presumably exists on the premise that somehow the smaller the boiler, the less the risk of condensate-related problems or the lower the potential impact of contamination. Unfortunately, this premise is simply not true as some operators can testify when the repair bills arrive or

when the boiler trips out at the most inopportune time. Steam and condensate system problems develop in every size and type of boiler plant at some time or other. The problem is only compounded by not recognizing this fact or attempting to measure the potential impact on the facility before anything serious develops.

3. **Steam sampling protocols.** Sampling for steam purity and quality may be dangerous if suitable protocols are not followed. Additionally, where appropriate sampling techniques are not followed, the samples may be worthless. Special sampling procedures are generally needed, and in many countries these are often available through national standards organizations, for example, **ASTM D 1066-66T** (for *steam purity* testing). Special equipment may also be required, such as a **Larson-Lane analyzer** for steam quality testing.

8.1.2 Steam–Water Separation Effectiveness

Under boiler operating conditions, when steam does not properly and completely separate from BW, both the **steam purity** and **steam quality** are compromised. Consequently, to ensure the production of high purity, good quality steam, the risk of carryover must be reduced to a minimum.

Any action or operating condition that reduces effective steam–water separation leads to some level of BW carryover and a consequential *reduction* in steam purity and *increase* in the water content.

The purity of steam can be measured by an increase in electrical conductivity. Testing for **sodium ions** (Na^+) is particularly useful because almost without exception, all BW contains sodium ions.

The quality of steam can be measured by a permanently installed **throttling calorimeter**.

NOTE: A throttling calorimeter receives steam from a sampling nozzle through a throttling plug at the rate of approximately 100 lb/hr and into an insulated temperature-measuring chamber. The steam is allowed to escape at a controlled rate to provide a constant temperature of 212 °F/100 °C (adjusted for local atmospheric pressure). The escaping steam passes through an expansion orifice, and in dry steam some measurable superheat is produced. Any moisture present reduces the degree of superheat, and this difference can be calculated as a percentage of water present in the steam.

In general, the most demanding requirements for high purity dry steam (as for power generation and sophisticated manufacturing process application) are met by boiler plants operating at over 1,250

psig. As pressure ratings drop, so boiler design becomes simpler and tolerances widen. Equally, mechanical separation devices become less refined, surface water chemistry allowances become more liberal, and the degree of steam saturation increases.

Cause-and-effect analysis reveals that steam purity and quality are both reduced by the degree of carryover taking place in a boiler, and carryover is itself a function of the effectiveness of steam–water separation. In turn, the mechanics of separation are a function of three areas, each with its own variables:

- Design/mechanical variables
- Operational practice
- Steam-water chemistry

8.1.2.1 Steam–Water Separation Devices

Some boiler designs permit very effective steam–water separation, while others have inherently weak designs that inevitably lead to low steam purity. Generally, this may not present a serious problem where the requirement for steam purity is not a primary concern (e.g., as in space heating duty). For this kind of job, many smaller LP steam boiler designs may have little or no built-in mechanical separation devices and simply rely on gravity differences. However, when operating pressures are lower than mandated, where the boiler has relatively little steam space, or where steam header and steam main designs are weak, considerable surging and carryover may occur and the boiler may not be able to operate.

Where separation devices have not been fitted, there is little that can be done to enhance purity and quality beyond ensuring that basic BW chemistry, BD requirements, and general operating conditions are tightly controlled and maintained within narrower limits.

Steam purity and quality are affected by design variables such as:

- **Type of mechanical separation devices** and their internal arrangements
- **Boiler drum dimensions**, including the available *separation surface area* and the *steam space:water space ratio*; optimum separation occurs where the maximum steam–water surface area is available
- **Design pressure, steam generation rates, and water circulation rates.** Boilers should always be operated close to their maximum

design pressure to maximize steam quality. Boilers should also be sized to match demand because too low or too high a capacity encourages surging and carryover

- **FW supply and on-off/modulation mechanisms.** The on-off supply of FW tends to create *cold-zone stratification* within the boiler, leading to reduced steam production rates and **misting (fogging)** in the steam space. Boiler plant designs that provide for the continuous provision of FW through a **modulated FW supply** prevent these problems.

Where very effective steam–water separation is required, primary functional control lies in the efficiency and operating condition of the mechanical devices employed. As pressure increases, the density differences between water and steam decrease, so in order to ensure good separation, large HP boilers may employ several types and designs of both *primary* and *secondary* mechanical separation devices.

These separation devices must be maintained in good working order. Types include:

- **Primary steam separators:** These devices are located horizontally, immediately above the top drum waterline and use *baffles* or *chevrons* and *dry pipe collectors*, or *cyclone* or *centrifugal action* to radically change the steam flow, resulting in the heavier water and contaminants separating out from the steam.
- **Steam washers:** These spray FW or condensate into the steam to dilute, rinse, and remove entrained contaminants. Additional steam drying capacity is required to deal with the spray water.
- **Steam scrubbers:** These use flow reversal in conjunction with a large contact surface area to remove BW mist from steam.
- **Steam dryers:** These provide closely spaced corrugated plates through which steam must pass. *Chevron dryers* and other dryer types reduce the velocity at which the steam passes, causing the impurities to drop out.

8.1.2.2 The Effect of Boiler Operating Variables on Steam–Water Separation

Certain operating variables may seriously affect steam–water separation either independently or more often in combination with adverse

water chemistry conditions. Operating factors that may lead to steam contamination include:

- **Steam load swings.** Optimum steam–water separation comes at constant steaming rates rather than wide swings in demand and load.
- **High- and low-water levels.** Where boiler design provides for a rapid steam-raising potential by limiting the steam space volume, high water levels increase the risk of carryover. Similarly, low water levels reduce the steam–water surface area, and the high turbulence that results can cut out a boiler and initiate excessive *misting*. In heavy seas, maintaining a steady water level in marine boilers is difficult, and BW can be thrown into the steam space (**gulping**).
- **Sudden reductions in steam pressure.** Soot blowing or sudden, very high process steam demands can cause carryover.
- **Steam flow restrictions.** Operating a boiler that has a restricted steam flow due to blockages or deposits in the chevrons, baffles, collecting pipes, splash plates, or pans (perhaps resulting from long-term adverse water chemistry conditions) may cause localized high steam velocities that lead to carryover.

In some quarters it is common practice to operate boilers at a reduced pressure when steam demand is low, Although this saves energy costs, it encourages **entrainment** because *lower* pressure operation requires a *higher* volume of steam to hold the heat energy required and this must travel at a *higher* velocity, literally sucking BW from the steam–water interface. Also, the size of steam bubbles is directly related to steam pressure, and lower pressure steam allows only a reduced number of larger bubbles to form per unit time. The bursting of larger bubbles causes more surface turbulence and results in lower quality steam. It can be seen that the gain is often not worth the cost!

When steam demand is suddenly high, the rapid take-off lowers the pressure in the steam header and mains, and entrainment occurs once again.

Where process industries operate very variable steam demand operations, the use of a **steam accumulator** may provide adequate buffering capacity and minimize steam quality problems. Good operational practices include:

- Boilers should be operated to ensure that steam demand is matched to boiler capacity and that rapid changes in demand do not cause entrainment problems in the steam

- Use a modulating FW system and modulating valves at steam-use points where possible
- Maintain boiler working pressure close to design levels, and use continuous or intermittent BD based on TDS rather than on time

8.1.2.3 Surging and Carryover and Steam–Water Interface Physicochemical Factors

Carryover is the term for BW (containing some level of contaminant) that is entrained in the steam and passes into the steam header and main distribution lines. Carryover is always detrimental to the steam cycle process and produces problems of:

- **Wet steam**, which leads to interrelated *steam quality* issues, as discussed earlier
- **Reduced heat capacity** to the extent of the *partial pressure* of the steam–water mixture
- **Erosion** due to the presence of the entrained water. This problem may be further aggravated by the suspended solids or TDS also present in the BW
- **Low-grade condensate** that may not be suitable for many process applications, due to the contamination from BW solids
- **Variable pH of returned condensate**, which affects FW quality: BW is always alkaline (often strongly caustic) and highly alkaline condensate may cause **amphoteric corrosion** to metal components in the condensate system

NOTE: Although zinc is commonly used as an example of an amphoteric metal, it should be considered that iron and steel are also amphoteric, albeit wider swings in pH are required for corrosion to occur.

- **Deposits and blockages.** When carryover occurs, some of the TDS can be transported through the steam-condensate system, causing sticking valves and blockages in system components; where deposits form in *governor valves*, for example, **turbine overspeed** may result—a highly dangerous situation

  Carryover is itself a secondary result of various phenomena taking place at the steam–water interface. These effects are generally interrelated with the overall BW chemistry, the operating condi-

tions, and perhaps certain mechanical design features. Often, one or more steam–water surface effects may occur simultaneously. These effects are described in the following sections.

8.1.2.3.1 Foaming Foaming is the formation of small, stable, noncoalescing bubbles of steam at BW heating surfaces, which then rise to the steam–water interface but fail to escape when either excessive suspended solids or TDS are present. The water film around each bubble is toughened and stabilized by the impurities (an increase in *surface tension*). Smaller bubbles develop, and the final eruption of steam (**steam surging**) encourages **priming** (**surging**) and eventually **carryover**.

Where excessive foaming occurs, the apparent volume of water present in the boiler drum increases (**light water**). The persistence of foam increases with increases in:

- SS
- TDS
- Colloidal proteins
- Hydrophilic magnesium hydroxide
- Clays
- Silica miscelles
- Organic sols
- Process contaminants such as *black liquor* or *saponified organic oils* (soaps).

NOTE: ***Colloidal clays*** *also can form deposits, and suspended solids have a significantly higher effect on foaming than TDS.*

Process particulate pickup may significantly increase the risk of boiler foaming. This kind of problem happens in the crossover of hot to cold water during manufacturing processes, as in *rubber tire factories*, *food can cookers and retorts*, *plastic injection molding*, and the like).

Foods such as *sugars*, *colloidal pectins*, and *mayonnaise emulsions* are also prime sources of foaming.

In general, **organic contaminants** induce foaming and inorganics increase surface tension, although clearly there are exceptions. For example, sugar *increases* surface tension, while *tannins*, *lignosulfonates*, *carboxymethyl cellulose* (CMC), *phosphinocarboxylic acids* (PCAs), and other **dispersants** *reduce* surface tension and help destabilize foams.

Polyalkylene polyamides and other nonsilicone synthetic *antifoams* are particularly useful in controlling foaming problems. These chemicals also provide *defoaming* and *demulsification* benefits.

8.1.2.3.2 Gulping Gulping is an intermittent form of BW carryover caused by variable water levels. Some WT boiler designs are prone to gulping, and the carryover passes into superheaters.

8.1.2.3.3 Misting (Fogging) Misting is the development of an aerosol of *microdroplets* of BW into steam at the water–steam interface. This is caused by the sudden release of pressure *under* bubbles as the steam they contain is released. Misting occurs where operating pressure is lower than design. Typically, if misting persists in a boiler and raising the pressure does not resolve the problem, then improved steam separation equipment is needed.

8.1.2.3.4 Surging (Priming) The phenomenon of wildly fluctuating and spouting BW levels known as surging is a result of poor operational and water chemistry conditions. Adverse conditions include *too high a water level*, *uneven heat distribution*, *variable load swings*, *too high a steaming rate*, *too low a steam pressure*, and *excessive suspended or dissolved solids*, *alkalines*, or *chlorides*. The maintenance of any boiler steam generating stability under surging conditions is impossible. Surging is closely associated to problems of **foaming** and **misting**, all of which may lead to the **carryover** of BW and **entrainment** in the steam.

Clearly, control of steam–water surface chemistry is vitally important if good-quality steam of high purity is to be produced and distributed. Good control ideally requires:

1. Absence of process contaminants
2. Low levels of suspended solids
3. All contributors to TDS remaining within prescribed limits
4. Smooth, constant steaming conditions

8.2 CORROSIVE GASES IN STEAM AND CONDENSATE SYSTEMS

Oxygen, **nitrogen**, **carbon dioxide**, **ammonia**, **hydrogen sulfide**, **sulfur dioxide**, and other contaminant gases are generally present to some degree in all steam and condensate systems.

- *Oxygen and nitrogen* (air) infiltrate the systems through threaded joints, faulty steam traps, and other breaks, especially when the steam generating operation is of a stop-start nature and periodic system heating and cooling cycles take place. Oxygen also may be present in the boiler and post-boiler sections due to incomplete *pre-boiler deaeration* and *oxygen scavenging*.
- *Carbon dioxide* is present in steam as a result of the thermal decomposition of bicarbonates in the boiler.
- *Ammonia*, *hydrogen sulfide*, and *sulfur dioxide* may result from the decomposition of chemical treatments (although in large boiler plants, ammonia is often deliberately added to raise the boiler, steam, or condensate system pH).

8.2.1 Oxygen Infiltration

The contamination of CR as a result of oxygen infiltration leads to a **high DO removal demand** being imposed on deaerating equipment and oxygen scavengers. Unless regular testing takes place, this demand may easily eliminate the BW oxygen scavenger reserve, and if the problem goes unnoticed for some time, oxygen pitting and tuberculation can and will result.

Depending on the degree of oxygen infiltration, the temperature of the condensate and the presence of other gases such as carbon dioxide, various corrosion reactions may take place in the steam distribution and CR systems. The most basic reaction associated with oxygen infiltration results in **oxygen corrosion**, which can produce deep pitting in the pipework and is described later in this chapter.

Oxygen infiltration coupled with (steam volatile) *carbon dioxide* produces **enhanced condensate line corrosion**. The corrosion rate of *steel* in the system is particularly high when both gases are present.

Copper and *brasses* in the systems are more resistant to corrosion because of a stable oxide film; however, if **ammonia** is present together with oxygen, corrosion of *copper* and *copper oxide* rapidly occurs. The corrosion is an oxidation process and results in the formation of the **ammonia-copper complex** $[Cu(NH_3)_4^{2+}]$. Corrosion of **nickel** and **zinc** components also may occur in like fashion.

Thus, oxygen infiltration gives rise to a range of localized steam and condensate system corrosion reactions and products. These reactions may, in turn, lead to further downstream problems of **corrosion debris transport** when the condensate returns to the FW system.

To consider these reactions and the problems caused, it may be useful to refer back to the basic corrosion mechanisms of iron and water as shown in section 4.5.1. It can be seen from the *second anodic half reaction* that **ferrous hydroxide** is formed from **ferrous ions** and **hydroxide ion** where water (condensate) is present.

Anodic half reactions:	***Cathodic half reactions:***
1. $Fe \rightarrow Fe^{2+} + 2e^-$	1. $1/2\ O_2 + H_2O + 2e^- \rightarrow 2OH^-$
2. $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$	2. $2H^+ + 2e^- \rightarrow H_2\uparrow$

Or more simply:

Fe	+	$2H_2O$	$\rightarrow$	$Fe(OH)_2$	+	$H_2\uparrow$
iron		water		ferrous hydroxide		hydrogen

In the absence of oxygen and at higher temperatures (as in a boiler), the corrosion is often self-limited as **magnetite** is formed:

$3Fe(OH)_2$	$\leftrightarrow$	Fe_3O_4	+	$2H_2O$	+	$H_2\uparrow$
ferrous hydroxide		magnetite (black)		water		hydrogen

However, in a steam-CR system where oxygen infiltrates, the corrosion reaction continues unabated and **ferric hydroxide** is formed.

4Fe	+	$6H_2O$	+	$3O_2$	$\rightarrow$	$4Fe(OH)_3$
iron		water		oxygen		ferric hydroxide

N.B. Compare this to the *third anodic reaction*, which also leads to the formation of ferric hydroxide:

3. $4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$

Over time and at the relatively high temperatures involved in the steam-CR system, some ferric oxide is also formed:

$2Fe(OH)_3$	$\rightarrow$	Fe_2O_3	+	$3H_2O$
ferric hydroxide	*time and high temp.*	ferric oxide (red)		water

Oxygen corrosion, whether in boiler tubes or in condensate pipelines, is recognizable because large pits typically result. Where the condensate pH is low (say, due to the presence of carbonic acid), the pits may be particularly large, but as the pH rises (say, due to the use of neutralizing amines), the layer of *iron oxide corrosion product* becomes more protective and the resulting pits tend to be smaller. The presence of **red ferric oxide** usually indicates an *inactive pit* but **black iron oxide** infers *active pitting*. Condensate receivers are common points for oxygen infiltration (especially in smaller boiler plants).

8.2.1.1 Oxygen Infiltration Resulting from Operating Practices

Gross oxygen infiltration can and will occur under certain kinds of boiler operating practices, including:

1. Where considerable boiler pressure fluctuations occur
2. Where boilers are idled
3. Where boilers are frequently warmed up from cold
4. Where boilers are operated on a lead-lag system

All efforts should be made to eliminate these kinds of operating practices. Thus, where condensate receivers are fully open to atmospheric pressure (vented), efforts should be made to limit the absorption of oxygen at the water surface by raising the water level (where horizontal cylindrical tanks are used) or by covering the water surface (thermally resistant plastic balls are sometimes employed).

Heating coils also may be installed or any other device fitted to eliminate oxygen from the system, especially if the receiver is cool as a result of considerable MU water being required.

Condensate from boiler warmup steam should be wasted or sent for secondary applications to avoid corrosion of the line feeding the deaerator.

8.2.2 Carbon Dioxide Carryover

Where FW contains *bicarbonate* or *carbonate alkalinity* (as calcium, magnesium, or sodium salts), these salts undergo *thermal decomposition* in the boiler, and the steam-volatile contaminant gas **carbon dioxide** is introduced into the steam distribution system, as shown:

$2HCO_3^-$	$\rightarrow$	H_2O	+	CO_3^{2-}	+	$CO_2\uparrow$
bicarbonate ion	*heat*	water		carbonate ion		carbon dioxide

CO_3^{2-}	+	H_2O	$\rightarrow$	$2OH^-$	+	$CO_2\uparrow$
carbonate ion		water	*heat*	hydroxyl ion		carbon dioxide

In areas where the water has a **high natural alkaline hardness**, the potential for contamination of the steam and condensate system by CO_2 may be very significant. And in those plants requiring a high percentage of MU water, the risk of serious **condensate system corrosion** to the steel pipework, valves, traps, threaded joints, and points where noncondensable gases can collect is very real.

Where the bicarbonate is calcium or magnesium, the reaction to produce a sludge or scale proceeds to virtually 100%, and consequently some form of external water-softening process is generally provided. Although the alkaline earth metals are removed or exchanged and the risk of scaling deposits is thereby halted, the resulting **sodium bicarbonate** (along with any naturally occurring sodium bicarbonate or carbonate) will decompose in the boiler to produce carbon dioxide gas, which then carries over into the steam.

In larger HP boiler plants, excess alkalinity in the MU water is generally removed by means of (ion-exchange) *dealkalization*, *demineralization*, or other pretreatment processes, so that the bicarbonate and CO_2 potential is lost at source.

However, most smaller boiler plants do not do this; rather, control usually takes place by curing the *effect* of corrosion by the use of various **neutralizing** and/or **filming amines** rather than by curing the cause.

In larger steam-CR systems or more difficult situations amines themselves are not always totally effective. They can be expensive to employ and are not without their own "side effect" problems.

NOTE: Neutralizing amines are often the first choice to neutralize carbonic acid in the condensate. In very small boiler plant applications they are

commonly found as a constituent of multicomponent FW treatment formulations that include polymer, sulfite, alkali, and the like. When used, they should not be mixed with sulfites catalyzed with cobalt salts because of the likelihood of precipitating ***cobalt hydroxide*** $Co(OH)_2$.

Carbon dioxide carryover also occurs following the deliberate addition of **soda ash** (sodium carbonate) directly to the boiler. Where boiler designs provide for a significant internal drum or shell, the use of *soda ash* and *caustic soda* to prevent calcium and magnesium scales by precipitation reactions (**internal softening**) may be employed.

This use of soda ash as a reactant for FW contaminants is much rarer today than, say, 25 or 30 years ago simply because the steam-water space design and high heat-flux operation of modern boilers cannot tolerate the volumes of carbonate and hydroxide sludges produced.

Carbon dioxide (CO_2) results from the added sodium carbonate, as shown below:

Na_2CO_3	+	H_2O	$\rightarrow$	2NaOH	+	$CO_2\uparrow$
soda ash		water	*heat*	sodium hydroxide		carbon dioxide

The carbon dioxide carryover dissolves in condensed steam, where it is partially hydrated to form **carbonic acid** (H_2CO_3), as shown below. The increase in hydrogen ion concentration causes the pH to be depressed and generally results in a condensate with a pH of approximately 5.0 to 5.5.

CO_2	+	H_2O	$\rightarrow$	H_2CO_3
carbon dioxide *carryover*		condensate		carbonic acid

Carbonic acid promotes a *generalized metal-loss corrosion reaction* with iron (**carbonic acid corrosion**). Typically, attack takes the form of gouging or grooving in wetted areas of the system. Deep thinning and grooving along the bottom centerline of a horizontal condensate return pipe is very common, as is thinning or "*necking down*" of vertical tubes and thinning and pitting of horizontal baffles and sheets at areas where the metal is in permanent contact with condensate.

The initial reaction with the steel condensate pipework is:

$$\underset{\text{carbonic acid}}{2H_2CO_3} + \underset{\text{iron/steel}}{Fe} \rightarrow \underset{\text{ferrous bicarbonate}}{Fe(HCO_3)_2} + \underset{\text{hydrogen}}{H_2\uparrow}$$

The resulting **ferrous bicarbonate** is not particularly stable in condensate, being affected by heat, pH, and the partial pressure of CO_2 in the *steam-CO_2 condensate mix.* Various secondary reactions subsequently take place, resulting in the formation of *ferrous* or *ferric oxides, hydroxides,* and *carbonates* throughout the condensate system.

Where pressure drops and oxygen infiltration can occur, the presence of both gases leads to a reaction that produces **enhanced condensate line corrosion**, which generates more carbon dioxide and becomes self-perpetuating:

$$\underset{\text{ferrous bicarbonate}}{4Fe(HCO_3)_2} + \underset{\text{oxygen } \Delta P}{O_2} \rightarrow \underset{\text{ferric oxide}}{2Fe_2O_3} + \underset{\text{carbon dioxide}}{8CO_2\uparrow} + \underset{\text{water}}{4H_2O}$$

In many condensate systems it is not unusual, in practice, to find condensate return systems where the pH is apparently high (> 7.5) and yet very significant corrosion is taking place. There are several reason for this:

1. Neither neutralizing amines nor filming amines provide complete CR line coverage, especially in large systems. The degree of coverage depends on the blend of neutralizing amines selected, their respective distribution ratios and suitability for the steam pressures involved, and the location of application points and feed rates. Condensate samples may simply show a high localized pH due to the presence of neutralizing amine, which may or may not have any meaningful relationship to the degree of corrosion actually taking place.
2. Ferrous bicarbonate may be transported to a point where little or no amine is available, which then provides the source for various secondary corrosion reactions. Corrosion mechanisms and deposition formation often take place at points in the system well downstream of the original points of steam condensation and initiation of corrosion.
3. Ferrous bicarbonate is a mild base and, as corrosion proceeds, the ratio of bicarbonate to carbonic acid increases to produce a corresponding increase in pH. The high pH is therefore not necessarily

an indication that all is well but rather that it may be too late and corrosion has already taken place (and continues to take place).

These corrosion scenarios show that simply sampling from one or two points in a large, convoluting steam-condensate system is unlikely to detect the real extent of any corrosion problems. Effective control starts with effective sampling, monitoring, and confidence in the validity of the test results.

8.2.3 Other Corrosive Gases and Related Impurities

Although oxygen and carbon dioxide are the most important corrosive gases found in steam-condensate systems, small amounts of other contaminant gases are usually present. These may originate in various ways, for example:

- The breakdown of **organic contaminants** present in the MU water to produce **ammonia** (from *nitrogenous contaminants*), **phenols** and **carboxylic acids** (from *humic and fulvic acids*), and **trihalomethanes** (from the by-products of chlorination)
- The breakdown of internal treatments such as **sodium sulfite/sodium bisulfite**, **hydrazine**, and **amines**
- The deliberate addition of **ammonia** as a pH enhancer for BW and condensate
- Corrosion processes in the boiler section generate **hydrogen**—this hydrogen release is regularly measured in very high pressure boilers as it can be indicative of the rate of corrosion taking place

NOTE: Typically, the upper limit for hydrogen carryover in steam is 10 ppb H_2.

Sulfites are typically suitable for use in 900 psig boilers. If carryover of BW (containing sulfite) into a superheater occurs, however, then at very high temperatures the sulfite may break down to form *acidic* **sulfur dioxide**, which in turn forms **sulfurous acid** and reduces the pH of the condensate.

Hydrogen sulfide also is formed, and this instantly reacts with iron and steel to form thin deposits of *black* **ferrous sulfide** in the superheater tubes:

Na_2SO_3	+	H_2O	→	2NaOH	+	SO_2
sodium sulfite		water	>1000 °F (538 °C)	sodium hydroxide		sulfur dioxide

$4Na_2SO_3$	+	$2H_2O$	→	2NaOH	+	$3Na_2SO_4$	+	H_2S
sodium sulfite		water	>1000 °F (538 °C)	sodium hydroxide		sodium sulfate		hydrogen sulfide

Ammonia [as **ammonium hydroxide** (NH_4OH)] is often employed in higher pressure WT boiler systems as a low-cost means of increasing condensate pH. It can be added to the FW after deaeration, where it provides an additional benefit of raising the FW/BW pH without increasing measurable dissolved solids.

Ammonia also may be present as the result of the partial breakdown of **amines** used for condensate system protection, from **hydrazine**, or potentially even from **nitrate**.

Nitrate is still sometimes used in high pressure boilers (say, 900–1,500 psig) to protect steel against SCC. Under conditions of high alkalinity and high temperature, nitrate is reduced by magnetite to **nitrite**. Some thermal decomposition also occurs, producing nitrite and oxygen. Further degradation reactions occur, which eventually results in ammonia being formed.

NOTE: Some recirculation of ammonia and amine takes place within the overall boiler plant system, although at higher pH much of the ammonia is lost at the deaerator vent. In practice, this recirculation coupled with lower-than-theoretical CO_2 liberation (as a result of the incomplete breakdown of sodium bicarbonate when present in the boiler) typically results in a reduced amine-demand for any particular boiler pressure. This reduced demand, compared with the apparent demand, results in real cost savings.

Where ammonia is employed to raise the condensate pH, several reactions take place, but none of the reaction products are particularly stable. Essentially, *white* **ammonium carbamate** is formed from the reaction of *ammonia* and *carbon dioxide*, and these "damp" feathery crystals may cause blockages in cold areas of the condensate system. The salt is unstable and, if heated, the *ammonium carbamate* forms **urea** [$CO(NH_2)_2$], which then hydrolyzes back to *ammonia* and *carbon dioxide*:

$$\underset{\text{ammonia}}{2NH_3} + \underset{\text{carbon dioxide}}{CO_2} \rightarrow \underset{\text{ammonium carbamate}}{NH_2COONH_4}$$

Although this reaction may cause slight problems, the primary issue concerning ammonia is ammoniacal corrosion of CR system metals where oxygen is present and the pH is over 8.3. Under these circumstances, copper and its alloys and other nonferrous metals are attacked, and severe damage results due to the formation of a stable cupric ammonium complex ion.

$$\underset{\text{copper}}{Cu} + \underset{\text{ammonia}}{4NH_3} + \underset{\text{oxygen}}{1/2O_2} \rightarrow \underset{\text{cupric ammonia complex ion}}{Cu(NH_3)_4^{2+}} + \underset{\text{hydroxyl ion}}{2OH^-}$$

The soluble *copper ammonia ion* passes through the condensate system and plates out as a cathode on steel surfaces in the deaerator, heaters, economizer, and the boiler itself. A secondary galvanic corrosion process is initiated that damages the surrounding steel by forming **ferrous hydroxide** and releasing **copper** and **ammonia**. The ammonia carries over into the steam, and the entire corrosion process repeats itself.

Ammoniacal corrosion of nickel and **zinc** also occurs with similar complexes forming [$Zn(NH_3)_4^{2+}$ and $Ni(NH_3)_6^{2+}$]. The source of these metals is typically FW preheaters.

Yet another problem associated with ammonia is **stress corrosion cracking** (SCC or **caustic embrittlement**) **of brasses** (such as brass valves and other stressed components). Stress corrosion cracking of brass may develop in systems where ammonia steadily becomes available from a suitable source (such as the breakdown of sodium nitrate when it is added to inhibit SCC of steel) because it can concentrate in the steam.

8.3 VAPOROUS SILICA AND OTHER STEAM VOLATILES

As a result of the volatility of silica and its ensuing risks, such as the deposition of hard, **amorphous**, or **glassy silicates** in superheaters and on turbine blades, various actions are commonly taken in higher pressure boiler plants to limit silica vapor in steam. The maximum permissible silica concentration in steam is generally accepted as 0.02 ppm

(20 ppb) SiO_2. Where silica concentrations exceed 0.03 ppm, deposition most likely takes place.

Boiler water silicas may steam distill and may be present in various forms including **silicic acid** (H_2SiO_3) and **silicate ion** (SiO_3^{2-}). They become more volatile at higher boiler pressure, although volatility is decreased slightly with an increase in pH.

Volatile silica is seldom a problem at under 400 psig, where only 0.1 to 0.2% of total BW silica may be present as volatiles. It becomes significant at 900 to 950 psig and above, however, when silica volatiles rise sharply to 1.0 to 2.0% or more of total BW silica.

Actions taken to minimize the risk of silica distilling over into the steam include:

1. Placing limits on permissible incoming FW silica, typically by providing some form of pretreatment. Treatment methods may include the addition of *ferric sulfate* to the **cold lime process** (to form a flocculant of *hydrous ferric oxide*, which absorbs the silica) or the use of *magnesium hydroxide* in **hot lime processes**. These chemistries are quite effective, although there are several more modern technologies now in common use, including *demineralization processes* such as **anion exchange** and **electroionization**, and various *membrane techniques* such as **reverse osmosis** (RO), **ultrafiltration** (UF), and **electrodialysis reversal** (EDR).
2. Controlling certain aspects of BW chemistry such as *alkalinity* and *cycles of concentration*, or modifying internal conditions by the addition of treatment chemicals such as **silica precipitants** (primarily *magnesium salts* or *trisodium phosphate*) or **silica specific dispersants** (high temperature stable *organic polymers*). Alkalinity in particular has a significant effect on reducing volatile silica carryover because it counters the production of vaporous *silicic acid* (only significantly vaporous above 400 psig), formed as shown:

SiO_3^{2-}	+	$2H_2O$	→	H_2SiO_3	+	$2OH^-$
silicate ion		water		silicic acid		hydroxyl ion

NOTE: Where coordinated phosphate programs are employed, the entire rationale is designed to inhibit the presence of free caustic. As a consequence, the alkalinity buffering capacity is severely reduced and the tolerance for silica is likewise diminished.

1. Modifying the mode of boiler operation to reduce boiler startups and wide load swings. Boilers are far less prone to silica vapors when operating at continuous load (provided, of course, that the basic pretreatment and water chemistry controls are in place).
2. The use of steam washing equipment. Apart from the removal of entrained solids and water, **steam washers** are quite effective at removing vaporous silica carryover (typically 60–70% removal).

The mechanisms of silica carryover and subsequent deposition depend on the initial distillation at *high* pressures or temperatures, the final *low* pressures or temperatures, and the rate of decrease.

Essentially, the higher the pressure or temperature, the greater the potential for vaporous silica carryover and steam dissolution. When pressure or temperature falls, the steam becomes supersaturated and various forms of crystalline silica deposition begin to occur. As temperatures continue to fall, the deposits become increasingly amorphous in nature and also more insoluble.

- Silica deposition in the temperature range of 500 to 700 °F (260–371 °C) is primarily **sodium disilicate** [$Na_6(Si_2O_7)_2$; alternatively given the formula β-$Na_2Si_2O_5$]
- Deposition in the 300 to 500 °F (149–260 °C) range is **alpha-quartz** (α-SiO_2), **chalcedony** (SiO_2), and **crystabalite** (α- and β-SiO_2)
- In the range of 100 to 300 °F (38–149 °C) insoluble **amorphous silica** is deposited

NOTE: No prefix indicates a hexagonal crystalline structure.
α- indicates a tetragonal crystalline structure.
β- indicates a cubic crystalline structure.

At extremely high pressures (above, say, 3,000 psig) both **sodium salts** and **copper oxides** may steam distill, passing unchanged through the superheater and depositing out when the pressure falls significantly (to, say, 2,400 psig).

Vaporous copper may be particularly damaging because it forms **cuprous** and **cupric oxide** deposits on turbine blades.

8.4 SCALE AND CORROSION DEBRIS TRANSPORT

The **pickup**, **transport**, and **redeposition of corrosion debris and deposits** can happen anywhere in steam distribution and condensate return systems and are not confined to any particular boiler plant size or pressure rating. For example, *deposit pickup* may occur in a superheater with *redeposition* taking place perhaps in a pressure reducing station, steam trap, or condensate line. The starting point for transport mechanisms is often a combination of BW *carryover* and *condensate line corrosion.*

Where **carryover** occurs, much of the solids content is deposited in the first parts of the steam and condensate system, such as *superheaters*, but the balance can be transported all the way back to the *preboiler system* and from there to the *boiler* itself. Thus, a chain of cause and effect may once again develop in a manner similar to the progression of problems in other areas of the boiler system.

Where TDS and alkalinity are permitted to rise beyond BW control parameters, **priming** (**surging**) can develop and lead to carryover. Some of the deposits resulting from carryover eventually return to the boiler, initiating **steam bubble frothing** and further priming, and so the cycle begins again.

Corrosion of condensate lines is a serious problem. It is compounded where both oxygen and carbon dioxide are present because it causes considerable quantities of **hematite** (Fe_2O_3) to develop. Corrosion of other boiler plant components, such as FW heaters, adds more metals to the mix, and corrosion debris typically includes **iron**, **copper**, **nickel**, **zinc**, and **chromium oxides**.

Corrosion and mineral debris can form in condensate lines from a variety of means, and it is not uncommon for the resultant debris accumulated over many years to slough off and return to the boiler when operating conditions change. The result is often a thick **boiler-bottom sludge** that settles out in the water space or **baked-on sludge**, which mars efficient combustion and water tube heat transfer.

An example of this kind of problem occurs under circumstances where no condensate line treatment program has been employed at a facility until failures occur. Only at that time is a decision made to start feeding a **neutralizing** or **filming amine**. This rearguard action is generally far too late because the amine loosens old debris and returns it to the boiler, thus causing severe blockages along the way.

Filming amines generally produce a much worse fouling condition than neutralizing amines so where *filmers* are required, the typical prac-

tice is to start very gently with neutralizers, gradually add a blend of the two types, and eventually (say, after 4–6 months) revert solely to the use of the filmer. In many cases, a reduced level of neutralizing amine is always maintained.

Where new boilers are married to old steam and condensate systems, similar effects occur because of the transport of debris and the resultant blockages of valves and steam traps. Where the replacement boilers are of a higher rating than the existing boilers, the problems are further exacerbated (often due to *surging*, *faster steaming times*, or *increased steam velocities*).

Where minerals, metals, and metal oxides are picked up, they are, for the most part, undissolved and exist in colloidal or particulate form. When this matter is transported through the steam-condensate system, the result may be any of a range of pre-boiler section problems such as:

- **FW line** and **feed pump blockages**
- **Impingement or erosion-corrosion.** Where exfoliated magnetite from high heat-flux areas, such as superheaters and reheaters, occurs, apart from the damage caused in turbine areas or process components, the particles may be swept into the condensate system, ultimately causing further erosion throughout the entire system
- **Reduced deaerator venting**, **sticking check valves**, and other fouling problems

Notwithstanding the seriousness of these pre-boiler problems, however, it is material (especially **iron oxide** corrosion debris) originating in the condensate system, then transported back to the boiler itself, which carries the greatest risks of long-term operational problems.

The *balance of material* transported beyond the pre-boiler section tends to ultimately deposit on heat exchange surfaces and other internals. In the smallest boilers, this redeposition may be viewed as certainly more than an inconvenience but probably not a critical risk. As boiler size and pressure rating increase, however, so the risk of boiler failure through overheating and other problems dramatically increases, resulting in unforeseen downtime and very expensive repairs. This reality is well understood in large power plants, and consequently the rates, amounts, and locations of **iron oxide transport** and **redeposition** are carefully monitored and typically form the basis for scheduling off-line cleaning programs.

In smaller plants, the iron transported through to the boiler is essentially **hematite**, but in larger plants, this oxide is subject to **thermal**

aging and **reduction** (by hydrazine, etc.) as it passes through the preboiler section. As a result, **crystalline magnetite** predominates in the boiler itself. This transformation process is reduced where silica is present because **iron silicates** preferentially form.

In small boiler systems, the use of CR *system strainers* and high-temperature-resistant *bag filters* are highly recommended to prevent this corrosion debris from entering the FW system. In larger plants, *condensate polishers* or *electromagnetic separators* may be employed. *Condensate dumping* may even take place, although this is a wasteful and expensive process because both water and heat are lost.

Where iron transport takes place, accurate monitoring over a period and under different load conditions is required before filters, polishers, and other components can be properly sized.

8.5 OIL AND PROCESS CONTAMINATION

8.5.1 Contamination from Oils, Fats, and Greases

Contamination from oils, fats, and organic solvents may occur during food and beverage processing or similar operations. These materials inevitably find their way into the FW system, and from there to the boiler, unless adequate precautions are taken.

Oil, **fat**, **grease**, and **hydrocarbon leaks** are particularly objectionable. These contaminants may originate from *cylinder oil* in steam-driven machinery, *preheaters* for *heavy fuel oil*, *hydrocarbon refining*, *chemical* and *petrochemical manufacturing*, *edible oils processing*, *fat rendering*, *printing*, and a host of other activities. Leaks of these kinds may lead to many adverse problems in the boiler, including:

Oily surfaces induce film boiling and the stabilization of steam bubble on the film surface, and overheating results. Oily surfaces also cause other problems, including:

- **Film boiling** at heat transfer areas due to nonwettable metal surfaces
- **Coke deposition** in areas of high heat flux as a result of the oil charring
- **Contaminant binding**, especially where the boiler contains sludge and other suspended matter.
- **Sludging** and the formation of **oil balls** or **gunk balls**

- **Saponification** (the hydrolysis of a fat to a soap under strongly alkaline BW conditions)
- **Hampered chemical treatments** and interference with several types of organic sludge conditioners, such as *tannins*, *lignins*, *carboxymethyl cellulose*, and others
- **Fouling** of conductivity electrodes and other measurement devices

Whatever the source of this type of contamination, it must be quickly and effectively removed from the boiler to prevent the problem from recurring. The standard procedure is to blow down the boiler to the maximum extent possible until the oil is removed. In more serious cases, it may be necessary to drop the boiler and provide a **boil-out** program. A boiler boil-out uses a simple formulation (usually based on caustic or strongly alkaline phosphates) and is employed to re-expose and repassivate the metal surfaces.

Where oil in condensate cannot be eliminated at source, it should be removed by the use of an inline *precoat filter*. The precoating should be either *aluminum hydroxide* or *ferric hydroxide* because both these hydrous oxide gels have an affinity for oil.

8.5.2 Contamination from Industrial Processes

There are many process contaminants that may be inadvertently carried back with the condensate following either the purposeful injection of live steam into, say, an industrial manufacturing process or that can infiltrate the system due to a leaking heating coil, an open surge tank, or similar access point.

Where *condenser leaks* occur, the result is **condensate contamination** from *TDS* and *chlorides*.

In certain processes (such as rubber tire manufacture and plastic injection molding operations), it is common for a valve sequencing system to first provide *hot* steam followed by *cold* cooling water and thus for **cross-contamination** to occur. The result may be the stripping of passivated cooling system surfaces by steam and for the condensate to be infiltrated by cooling water.

NOTE: Where cross-contamination takes place, rapid pitting corrosion of depassivated surfaces may develop. This in turn requires a cleaning and repassivation program to be initiated.

Process leaks into the steam and condensate system may take the form of *phenols*, *glycols*, and various other organics that produce an

objectionable odor, lay down **sticky films** in lower pressure boilers, and **varnish** in high-pressure systems. In this case, there is little that can be done to salvage the condensate and it should be dumped or otherwise rejected.

Process leaks from *food* and *beverage* production or *wood leachates* often produce *sugars*, *colloidal materials*, *pectins*, *emulsions*, and *proteins* that cause **stable foams** in the boiler. These lead to **carryover** and further steam-condensate line contamination. The temporary use of a *demulsifier* or *defoamer* as part of the water treatment program may be of particular benefit, but again the condensate is unsuitable for return to the boiler. Other process leaks include:

- *Dyes* from textile manufacturing that produce **steam discoloration** and may also present some **chemical incompatibility** (with *amine treatments* for example)
- Small particles or gases which can lead to problems of **impingement/erosion-corrosion**
- Acid leaks that cause problems of **fluctuating pH** and **acid corrosion**.

A summary of many of the specific post-boiler section waterside/steamside problems are given in the following table.

Table 8.1 Steam purity, quality, and other operation problems

Type of problem	*Results and notes*
Poor steam purity	Contaminated steam leads to corrosion, erosion, sticky valves, and boiler operation problems.
Poor steam quality	Inadequate steam/water separation results in "wet steam" with reduced heat content.
Poor steam sampling (common in smaller boiler plant)	Lack of sampling facilities and/or poor protocols results in limited awareness of steam related problems and risky conditions.
Poor matching of steam volumes, pressures, temperatures, and heat-content with demand.	A failure to match steam output with demand impacts on both process and waterside conditions.
Corrosive gases including: Oxygen Carbon dioxide Ammonia H_2S/SO_2	Results in: Oxygen corrosion. Carbonic acid corrosion. Greatly enchanced with O_2 present. Ammoniacal corrosion. Sulfurous acid corrosion.
Vaporous silica, present as silicic acid and silicate ion	Crystalline silica deposits Amorphous silica deposits
Scale and corrosion debris transport results in:	FW line/feed pump blockages Impingement and erosion Poor deaerator venting Sticking check valves Fe, Cu, Ni, Zn, Cr oxides Crystalline magnetite
Oil, fat, grease, and hydrocarbon contamination results in:	Film boiling Coke deposition Contaminant binding Sludging and gunk balls
Industrial process contamination results in:	Cross-contamination Malodors and discoloration Sticky films and varnishes Stable foams Chemical incompatability Impingement corrosion Fluctuating pH/acid corrosion

boiler water treatment

Principles and Practice

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9

PRE-BOILER AND POST-BOILER TREATMENT PROCESSES

As has been discussed earlier in this book, boiler plants can only continuously and economically transfer heat to water and effectively produce steam of satisfactory purity if the feed water (FW) and boiler water (BW) quality is properly controlled and appropriate for the particular boiler design and mode of operation. This, in turn, requires that makeup (MU) water and condensate return (CR) qualities are also controlled.

For simple HW and LP steam heating applications, employing perhaps a Scotch marine or firebox FT boiler, the water quality requirements are unlikely to be onerous, but as pressure ratings and heat-flux densities increase (and other factors such as special boiler designs and steam usage applications are taken into consideration) water quality becomes increasingly important. Thus, in general:

- FW and BW qualities are related to boiler pressure and heat-flux density, such that increasingly higher pressure or highly rated boilers tend to require increasingly higher quality and higher purity FW.
- Higher pressure and highly rated boilers often are larger and more complex; consequently, larger boilers usually demand FW of higher quality and tighter water chemistry control ranges than smaller boilers.
- Where boilers are particularly compact or of special design, for any given pressure or heat-flux rating, they are apt to require a higher quality FW than would otherwise be generally provided.
- Where process applications demand particularly high quality or high purity steam, FW and BW quality must conform to a higher standard and water chemistry must be tightly controlled.

- Owners and operators should always provide the highest possible quality of MU water that makes economic sense for their particular boilers, because improving the quality of MU water (and CR) leads to higher quality FW and BW. This in turn provides a payback of reduced heat and treated water losses caused by blowdown (BD), lower "polishing" treatment requirements, cleaner steam, and, for most plants, reduced risks of internal fouling, deposition, and corrosion. Thus, the provision of good to high quality MU water is an essential starting point to the achievement of effective heat transfer and pure steam generation. In practice, it is not uncommon for system designers or owners of some smaller and lower pressure boiler plants to ignore the need for basic pretreatment, believing perhaps that the available water quality is adequate for MU and that any deficiencies can always be compensated for simply by the use of additional chemicals. This assessment is not always true, and although internal chemical treatments are always required, they should generally be regarded as water chemistry "polishers" and added only in small concentrations.
- A further consideration is that boiler plants operate most effectively when the FW and BW chemistry is constant and predictable. Thus, irrespective of a facility's size (or lack of size), a key objective should be to produce FW of a *consistent* composition. Pretreatment equipment processes can often be particularly useful in ironing out variations in the quality of both MU and CR.

Most raw water sources considered for use as boiler MU have been treated or conditioned either by a water utility (providing *city water*) or in-house (providing *industrial water*). They are supplied to the boiler plant clean and relatively free of **suspended solids**, **colloidal material**, **organics**, and **iron**. In hard water areas there also may be some reduction in **hardness** and **alkalinity** provided. Where boiler plant raw water (RW) quality is still unacceptable for the particular boiler plant needs, additional **pretreatment** (*pre-boiler conditioning* or *external treatment*) may be required.

If a higher quality MU water is required, it passes through one or more **purification processes** as part of the pretreatment.

The term *higher quality* generally means FW with significantly lower levels of **TDS** than typically employed in lower rated boilers. Additionally, it implies the reduction of certain specific minerals or ions (such as **silica**, **sodium**, or **alkalinity**) and **noncondensable gases** to meet very low or extremely low concentration specifications.

When the term *higher quality* is applied to CR, it refers to a reduction in **iron** and **copper**. For large industrial or utility WT boilers, this may also include **nickel** and **chromium**. A **polishing process** may be required to achieve this quality.

External treatment does not end with the provision of filtration, softening, demineralization, or polishing, because for all but the most basic of HW heating systems (where MU requirements are minimal), the effective removal of oxygen from FW is also critical. For this process, depending on the overall economics and ultimate use of the HW or steam, a combination of FW heating and chemical oxygen scavenging is generally employed.

Small boiler plants often supplement the heat derived from CR by employing **steam coils**, **steam sparge pipes**, or **electric heaters**, whereas larger facilities use **economizers**, **closed FW heaters**, and **deaerators** (as discussed in Chapter 3).

Although heaters, deaerators, and chemicals are traditionally used for O_2 removal, new **membrane** and **carbon catalyst technologies** have evolved and are discussed in this chapter.

Chemical oxygen removers such as **sulfite**, **hydrazine**, or **diethylhydroxylamine** (DEHA) are added, as appropriate, to the FW line, deaerator storage tank, FW tank, or other receiver. Although oxygen scavengers are typically fed to *external* treatment equipment, they are generally considered to be part of the *internal* treatment program, together with the balance of the chemical treatments (*chemical polishers*).

Most external treatment processes involve the use of large items of capital equipment (although some consumable chemicals also may be used to aid or improve the process, such as *coagulants, flocculants, filter-aids, dispersants*, and the like).

The available range of pretreatment options has widened considerably in recent years, and different methodologies have come to be viewed not as competing technologies but rather as complementary to each other. Consequently, it is now the norm to design pretreatment and purification system trains by blending various primary technology equipment units (or their subsets) together in any of a wide number of permutations to achieve the most cost-effective solution for any specific problem.

Traditionally, the mix of pretreatment equipment required to meet a specific FW volume and quality specification is provided as a permanent installation under a capital project, although today there is a growing global market in **outsourced water services**. Typically, vendors such as **Ecolochem, Inc.**, a world leader in this type of service, provide trailer-mounted, mobile water-processing equipment that can be

hooked up directly to the boiler plant. Standard equipment trains may be provided on long-term lease, processes custom-designed and delivered to fit existing facilities, or, quite simply, treated water purchased to supply all boiler plant needs. See Figure 9.4d for a schematic layout of a mobile plant.

9.1 OVERVIEW OF COMMON EXTERNAL TREATMENT PROCESS TECHNOLOGIES

The term *external treatment* is used to describe all of the different types of essential nonchemical processes employed to condition or remove some or all impurities in water before it reaches the FW pumps. There is often considerable overlap in the scope of common water treatment process technologies, and each of the primary processes can be divided into several subsets, giving rise to a wide range of impurity removal efficiencies for each process.

Where higher quality water is required, there is no single technology that can provide all the answers to impurity removal requirements. Consequently, it is common practice to employ two, three, or even more processes in sequence. In view of the different water sources, final quality requirements, and permutations of technologies and subsets, there is no universally agreed upon order in which the technologies are sequenced. Nevertheless, there are some purification processes that, because of specific technical or economic advantage, enjoy popular appeal and are commonly specified.

Leaving aside **FW deaeration** (which is usually provided as the final type of external treatment in the pre-boiler section), the primary forms of treatment processes commonly employed can be conveniently categorized into three areas:

1. **MU water pretreatment** provides for a basic good quality water. The scope for potential treatment of impurities is consequently extremely wide because it is concerned with an entire spectrum of raw water sources. Commonly, however, we are concerned with removing *suspended solids* and *colloidal material*, *organics*, *iron*, and *manganese*. Pretreatment also covers the partial or total reduction of *hardness*. Processes employed include **aeration** or **oxidation**, *hardness conditioning* or *removal* by **nonchemical treatments**, **precipitation softening** and **ion-exchange**, **natural zeolite treatments**, and *clarification* by **sedimentation** and **media filtration**.

2. **MU water purification:** is concerned with providing higher quality waters. There are many interpretations as to what constitutes "high quality" water, and consequently there are also a seemingly endless number of related specifications. Purification processes include **ion-exchange**, **membrane technologies**, and **electrodialysis**, together with the many subsets available for each technology.
3. **Post-boiler external treatment** is essentially concerned with restoring condensate to a previous high purity condition by removing contaminants resulting from corrosion and steam utilization processes. Processes include **CR purification (polishing)** by **media filtration** and **ion-exchange**, plus **strainer technologies** and **electromagnetic filtration/separation** (EMF/EMS).

9.2 BASIC PRETREATMENT PROCESSES

Control of waterside chemistry starts in the pre-boiler section because the lack of, or inappropriate methods for, water treatment creates significant operational difficulties and impacts the economics of the entire process from start to finish.

All boiler plants, irrespective of design, size, pressure, or location, need as a *minimum* to be supplied with RW of a basic good quality that is consistently clean and clear throughout the seasons. Further treatment may be necessary.

Raw water essentially should be free of suspended matter, natural organics, iron, manganese, and sulfur gases. Ideally, it should also be low in hardness, alkalinity, silica, and bacteria and have a pH level of approximately 7 to 8.

- Where RW of basic good quality is supplied as MU for **HW heating boilers**, no other form of pretreatment is usually necessary. However, an *internal, corrosion inhibitor* treatment–based program should be provided, and periodic **boil-outs** may still be necessary.
- Where RW of basic good quality is supplied for **LP steam boilers** (that is, *firebox, Scotch marine, cast-iron sectional boilers*, etc. at operating pressures below 15 psig) and where the MU water volume demand exceeds 5% of the FW, pretreatment by ion-exchange softening should be additionally provided. This rule also applies to **electrical resistance boilers**, **electrode boilers**, **vertical boilers**, and **coil boilers**.

- For all LP steam operations in which the total hardness of RW exceeds, say, 10 to 20 ppm $CaCO_3$, the use of a softener is preferable to control solely via internal precipitation treatment. Oxygen scavenging and other internal treatment programs should also be provided. Some MPHW/HPHW and lower pressure steam boiler designs may require additional purification beyond simple water softening.
- Where RW of basic good quality is supplied as MU for boilers operating at over 15 psig, irrespective of the CR contribution to FW, additional pretreatment and/or purification treatment is required. At the very least, full softening of MU water is needed.
- Where RW quality is below a basic good quality standard, pretreatment *must* be provided before the water can even be considered as potential boiler MU water.

Pretreatment processes should not be regarded as impurity-specific, stand-alone methodologies because, typically, each form of water impurity may be removed by more than one type of process and individual technologies can be modified to deal with particular RW chemistries.

In practice, for any specific boiler application, the various pretreatment and purification techniques employed are incorporated in a sequential train to provide the most cost-effective or operationally effective treatment solution.

Examples of pretreatment process trains are:

1. **Treatment of a tropical surface water to provide MU for a 75 psig vertical boiler** (rice grower, South America). The water is naturally very soft (only 5 ppm hardness) but colored brown because of organics. A two-stage pretreatment process is carried out in pressure vessels (PV) and involves iron removal using a *BIRM® catalyst*, followed by *zeolite treatment* for organics removal. No separate *deep-bed sand filtration* stage for suspended solids removal is employed because both PV processes effectively provide filtration capacity in addition to their primary functions.
2. **Provision of MU water for 100 to 150 psig FT boiler from a deep-well supply** (large hotel complex, Caribbean). The water often contains iron and sulfur and is seasonally contaminated with salt water. Total dissolved solids (TDS) vary between 1,200 and 2,500 ppm. The process used is **a.** *aeration* for iron oxidation and

sulfur gas removal; **b.** iron removal via polymer-assisted *flocculation*; **c.** *clarification* by *sedimentation* and subsequent *deep-bed sand filtration*; **d.** *ion-exchange softening*; and **e.** purification by *reverse osmosis (RO) membrane process* to achieve a 90% TDS reduction.

3. **Supply of MU water for a medium-pressure (450 psig) WT boiler, from a surface water source with very variable suspended solids and hardness** (sugar refinery, South Africa). The process used is **a.** carbonate removal using *hot-lime precipitation softening* coupled with silica adsorption by magnesia addition; **b.** *clarification* in anthracite filters; and **c.** *cation ion-exchange* for the balance of hardness removal.

Notes on some common pretreatment processes are provided in the following sections.

9.2.1 Aeration and Oxidation

Aerators are often used for iron and manganese removal from deep well waters. Dissolved sulfur gases and some carbon dioxide are also removed, resulting in a slight elevation in pH levels. There are various designs but **pressure aerators**, **aeration towers**, and **spray ponds**, are common.

9.2.1.1 Pressure Aerators

Pressure aerators employ a vertical, **volcanic lava media**–filled PV and receive water at pump pressure. The water is mixed with blown air and fed to the bottom of the bed. Excess air is discharged through an air valve to atmosphere, and the aerated water is collected at the top of the column and then fed to a sand filter for removal of insoluble **ferric hydroxide**.

Improved results may be obtained by substituting the volcanic lava for BIRM® at a bed depth of 30 to 36 inches (76–91 cm) and a flow rate of 4 to 5 gpm/sq ft of media bed surface area. BIRM® acts as a catalyst and normally requires only a periodic backwash to remove surface debris (backwash rate in pressure filter tank is 10 gpm/sq ft).

Optimum catalytic conversion of iron to insoluble ferric hydroxide is achieved when the following conditions are met:

1. Raw water total alkalinity $> 2 \times$ (sulfate + chloride)
2. pH level > 6.8

3. Dissolved oxygen (DO) is required; the minimum DO ppm = 15% total iron ppm
4. No oil or hydrogen sulfide (H_2S) present
5. If iron and manganese are both present, ensure that pH level is below 8.5
6. If only manganese is present, ensure that pH level is between 8.0 and 9.0

The principal reactions for the aeration/oxidation of dissolved iron and manganese are:

$$\underset{\text{ferrous hydroxide}}{4Fe(HCO_3)_2} + \underset{\text{oxygen}}{O_2} + \underset{\text{water}}{2H_2O} \rightarrow \underset{\text{ferric hydroxide}}{4Fe(OH)_3} + \underset{\text{carbon dioxide}}{8CO_2\uparrow}$$

$$\underset{\text{manganese bicarbonate}}{2Mn(HCO_3)_2} + \underset{\text{oxygen}}{O_2} \rightarrow \underset{\text{manganese dioxide}}{2MnO_2} + \underset{\text{carbon dioxide}}{4CO_2} + \underset{\text{water}}{2H_2O}$$

9.2.1.2 Aeration Towers

Aeration towers are often simply constructed wooden towers with or without the benefit of a forced-air draft, over which the well water is distributed. Typically, the tower holds 8 to 10 trays, each with a 3- to 4-inch (7.6–10.2 cm) bed depth of volcanic lava or **coke media** to provide the total 30 to 36" (76–91 cm) depth required. The lava or coke acts as a catalyst for the further precipitation of iron and manganese salts. These salts can be readily oxidized provided there is sufficient alkalinity present. If in doubt, ensure a minimum of 120 to 150 ppm total alkalinity (T Alk or M Alk) as $CaCO_3$.

In practice, aeration towers using coke or volcanic lava tend not to be as efficient as spray ponds in facilitating the precipitation of ferrous hydroxide; consequently, there is usually a requirement for a cationic flocculant to aid the precipitation of the insoluble materials into a larger floc or denser sludge that can be removed by clarification or sand filtration.

9.2.2 Precipitation Softening (PS)

The principal temporary hardness salt in raw water is **calcium bicarbonate**, formed by dissolution of **limestone** (*calcium carbonate*) by

water containing dissolved **carbon dioxide**. The reaction of dissolving the limestone by the acidic gas is:

$CaCO_3$	+	CO_2	+	H_2O	→	$Ca(HCO_3)_2$
calcium carbonate		carbon dioxide		water		calcium bicarbonate

Under hot BW conditions this reaction is reversible, leading to a serious risk of carbonate scale depositing on heat transfer surfaces. Consequently, many large water utilities and industries around the world continue to use the old established, but effective **lime** (*calcium hydroxide*) and **soda ash** (*sodium carbonate*) processes to soften water by precipitating out insoluble hardness salts.

The **lime-soda softening process** reduces the **temporary hardness** (*carbonate hardness*) content of the RW, and often some of the **permanent hardness** (*noncarbonate hardness*) and some **silica** is also removed.

Both **hot** and **cold** processes are employed, although the hot process, which takes place at or above 212 °F (100 °C), is usually preferred for boiler FW applications, because it produces water of lower hardness levels and usually a lower silica content as well. Also, less lime is needed because the carbon dioxide with which it would normally react is driven off at the higher temperatures. Sometimes caustic soda (sodium hydroxide) is used in place of soda, depending on the alkalinity of the water and the chemical costs; however, irrespective of the process or chemicals used, the major precipitants are always calcium carbonate and magnesium hydroxide.

The two basic hot-process designs are **upflow precipitation softening (sludge blanket PS)** and **downflow precipitation softening (uptake funnel PS)**. In both designs RW enters from the top and is diluted by about 15% by condensate from steam heating. Lime and soda enter from the top of the plant and mix with the water, resulting in a precipitated sludge that settles to the bottom of the hopper-shaper plant (4 to 8% is recirculated as "seed"). The upflow design generally results in maximum contaminant removal, while the downflow type is less susceptible to changes in flow rates.

The steps involved in converting soluble hardness salts in the RW to insoluble precipitants that can be subsequently removed by filtration or clarification, are:

1. Raw water analysis and calculation of lime and soda needed.

2. Addition of chemicals, rapid mixing, then flocculation.
3. Sludge settlement and solids-liquid separation.

There are four basic reactions that take place.

1. Removal of any free **carbon dioxide** by lime:

CO_2	+	$Ca(OH)_2$	→	$Ca(HCO_3)_2$
carbon dioxide		hydrated lime		calcium bicarbonate

2. Partial addition of lime converts the **temporary hardness** salt (**calcium bicarbonate**) to carbonate. Fifteen to 20 ppm of the calcium carbonate remains in solution, while the remainder precipitates as an *insoluble* salt. Further amounts of lime convert other temporary hardness bicarbonate salts (Mg, Na, etc.) to *soluble* carbonates:

$Ca(HCO_3)_2$	+	$Ca(OH)_2$	→	$CaCO_3$	+	$2H_2O$
calcium bicarbonate		lime		calcium carbonate		water

$Mg(HCO_3)_2$	+	$Ca(OH)_2$	→	$MgCO_3$	+	$CaCO_3$	+	$2H_2O$
magnesium bicarbonate		lime		magnesium carbonate		calcium carbonate		water

3. Further addition of lime converts soluble **magnesium** or **sodium carbonate** into the insoluble *hydroxide* and further insoluble *calcium carbonate*. In theory it is possible to limit the lime addition to maintain the magnesium salt as soluble carbonate, but in practice some magnesium hydroxide is always formed (say, 10%), so it necessary to compensate for this by the addition of more lime:

$MgCO_3$	+	$Ca(OH)_2$	→	$Mg(OH)_2$	+	$CaCO_3$
magnesium carbonate		lime		magnesium hydroxide		calcium carbonate

4. Conversion of the permanent, noncarbonate hardness salts such as calcium sulfate or chloride produces more insoluble calcium carbonate using soda ash. The total noncarbonate hardness is the sum of the calcium sulfate or chloride present in the original RW plus that formed from magnesium sulfate or chloride in the previous reaction.

$CaSO_4$	+	Na_2CO_3	→	$CaCO_3$	+	Na_2SO_4
calcium sulfate		soda ash		calcium carbonate		sodium sulfate

The total hardness of the treated water may be as low as 35 ppm or so (as $CaCO_3$). The pH level normally should be approximately 9.4 to 9.6 to obtain minimum calcium solubility. If it is much above this level, it indicates an excess of lime; the treated water will not be **stable,** and some **secondary precipitation** can be expected.

Higher than expected hardness levels are usually attributed to inadequate chemical addition or poor sludge recirculation. High turbidity is often attributable to fluctuating hydraulic loading on the process plant.

Some older plants still carry this softening process further by the addition of **mono-** or **di-sodium phosphate** and, although it lowers the hardness to only a few ppm, it ultimately results in additional carbonate alkalinity, which is undesirable. Additionally, the phosphate is too expensive and it is better to simply pass the filtered, lime-treated water through a BX softener.

9.2.3 Clarification

Flocculation or clarification processes are solids-liquid separation techniques used to remove suspended solids and colloidal particles such as clays and organic debris from water, leaving it clear and bright. Certain chemicals used (such as **alums**) also exhibit partial dealkalizing properties, which can be important given that the principal alkaline impurity removed is calcium bicarbonate—the major contributory cause of boiler and heat exchanger scales (present in scales as *carbonate*), although closely followed by *phosphate.*

Most suspended solids in water have a surface electrical charge that provides stability to the particles. This ionic charge is usually a *negative* (−) charge and requires the addition of metal salts or *cationic* (+) polymer **coagulants** to destabilize the particles and permit them to **agglomerate** or come together.

- **Coagulation** takes place over several minutes in a rapid mix tank and encompasses several mechanisms such as *reducing diffuse layer thickness* and *charge neutralization.*
- **Flocculation** involves large polymer chain molecules adsorbing onto more than one particle, causing bridging. Typically, this process is carried out over a period of 20 to 30 minutes with gentle

stirring. Agglomeration of these particles by bridging and other mechanisms creates a sludge mass or **floc** that is heavy enough to sink.

- **Sedimentation** is the sinking process itself, usually carried out in a round or conical-shaped settling tank.
- **Clarification** is the process of separating the clear liquid from the flocculated and settled sludge.

These processes may take place in a series of tanks or a single multizoned, tank.

9.2.3.1 Inorganic Coagulants

Aluminum sulfate, $Al_2(SO_4)_3 \cdot H_2O$, is the commonest alum used. Hydration is typically 14 to 16 H_2O. It hydrolyzes and polymerizes in water and typically is used within a narrow "window" of pH levels of 5.5 to 6.5 to minimize the solubility of aluminum in the treated water. If alkalinity is present (say, due to **calcium bicarbonate**), the following reaction occurs, producing *insoluble* **aluminum hydroxide** [$Al(OH)_3$].

$Al_2(SO_4)_3$	+	$3Ca(HCO_3)_2$	→	$3CaSO_4$	+	$2Al(OH)_3$	+	$6CO_2\uparrow$
aluminum sulfate		calcium bicarbonate		calcium sulfate		aluminum hydroxide		carbon dioxide

Aluminum sulfate is characterized by its low cost and effectiveness in low turbidity and colored waters. However, it is not very effective at high pH levels (over pH 8.0), and acid must be added to reduce the pH level.

Aluminum sulfate generally produces a large sludge volume and is slow to react and often difficult to de-water. It is usually supplied in dry blocks or a ≅ 50% strength liquid. The required dose rate varies considerably, but it is approximately 20 to 100 ppm, as supplied.

NOTE: When using aluminum sulfate, there is a reduction in alkalinity (and pH level), and a supplemental alkali, such as soda ash or caustic, may be fed to the treated water.

- **Ferric chloride**, $FeCl_3 \cdot 6H_2O$: This coagulant tends to be a very low-cost product. Typically, it is supplied as a ≅ 40% by-product solution with a dose rate of 10 to 150 ppm, as received. It performs

best within the range of pH levels of 5.0 to 6.0; it is very corrosive, lowers the pH level of the water, is slow to react in cold water, and is sensitive to process variations. Ferric chloride needs close control for good results.

- **Ferric sulfate**, $Fe_2(SO_4)_3 \cdot 3H_2O$: A solution of this coagulant is corrosive and requires acid-proof equipment. It is not very soluble in cold water, so heating is sometimes provided. The use of 2 to 4 parts of water per 1 part of salt avoids the formation of the hard, insoluble *monohydrate*.
- **Ferrous sulfate (copperas)**, $(FeSO_4) \cdot 7H_2O$: This is similar to ferric sulfate. The optimum coagulation pH level for these last two iron salts is typically 8.0 to 9.0 but may need to be lowered.

As with *alum*, it is necessary to conduct jar tests to identify the most suitable product and optimum application rates, pH level, and so forth. Testing with ferrous sulfate typically requires a starting point application level of around 50 ppm (as 100% active product), while ferric sulfate requires around 25 ppm (as 100% active product).

As with aluminum sulfate, there is a reduction in bicarbonate alkalinity and a lowering of pH levels when using ferric sulfate, producing *insoluble* ferric hydroxide $Fe(OH)_3$, as shown here:

$Fe_2(SO_4)_3$	+	$3Ca(HCO_3)_2$	→	$3CaSO_4$	+	$Fe(OH)_3$	+	$6CO_2$
ferric sulfate		calcium bicarbonate		calcium sulfate		ferric hydroxide		carbon dioxide

- **Polyaluminum Chloride** (PAC), $Al_n(OH)_mCl_{3n-m}$, where m and n are variable. PAC is a primary coagulant and is usually very effective without requiring any change in pH levels. It will not reduce the alkalinity of the water but also does not materially change the pH level of the water, even if overdosed. Typically, it is supplied as a 30 to 50% strength solution and requires perhaps 5 to 50 ppm of product to be applied to the water.

  When used in conjunction with an organic polymer, PAC can be very useful in treating poor quality wastewaters that contain high levels of *suspended solids* and *fats*, which often permits their reuse. It is rapidly becoming the product of choice where the lowest price is not paramount. In any given application, the requirements for PAC are typically less than for other primary coagulants, and it is easily handled. There is a range of PAC compounds, depending on the

degree of **basicity** required (range 16–70%). It is available only as a solution and acts similarly to a combined **alum/polymer** product.

PAC is faster-acting than alum, even in cold water. It produces a compact, fast-settling floc and is effective over a wide range of pH levels (typically 4–9.5). It provides good color removal.

- **Aluminum Chlorhydrate** (ACH), $Al_2(OH)_5Cl$: ACH reacts very similarly to PAC and is available only as a solution. It is a very highly basic product (80%). Upon dilution, PAC and ACH solutions tend to act as highly cationic polymers. After dilution and with time, they also begin to degrade and act like alum. This period may be on the order of 1 to 10 minutes, depending on pH level and temperature, The dose rate is similar to that of PAC. Good turbidity and color removal are achieved with ACH.

9.2.3.2 Organic Polymeric Coagulants and Flocculants

Organic polymeric coagulants and *flocculants* (or **polyelectrolytes**) are polymers of repeating monomer units held together by covalent bonds, These are available in many hundreds of permutations and a wide variety of molecular weights, ionic charges, physical forms, and so on. Combinations of various organic polymers and inorganic coagulants are also now widely used. Polymers are classified as **anionic**, **cationic**, or **nonionic** and subclassified by *molecular weight*, *magnitude of charge, functional group,* and so forth.

Most polymers are available as *dry powders*, *solution polymers* (in which 10 to 50% active strength polymer is dissolved in water), and *emulsion polymers*.

The demand in the marketplace for **emulsion polymers** has grown rapidly in recent years, and they are now available in almost every permutation possible. They consist of micron-sized water and polymer droplets dispersed in a continuous hydrocarbon oil phase with polymer activity levels of 20 to 50% or greater. Generally, the lower molecular weight (MW) polymers (say, those with MW below 1×10^6) tend to act primarily as *coagulants* and may replace or partially replace metal salts, thus resulting in less bulky waste and minimal pH level changes. These polymers are often based on **polyamines** and their derivatives and usually have strong cationic charges. Higher MW polymers are based on **acrylic acid** and derivatives and tend to act as *flocculants* through particle bridging and other mechanisms. Examples of some organic polymers for coagulation and flocculation are given in Figure 9.1.

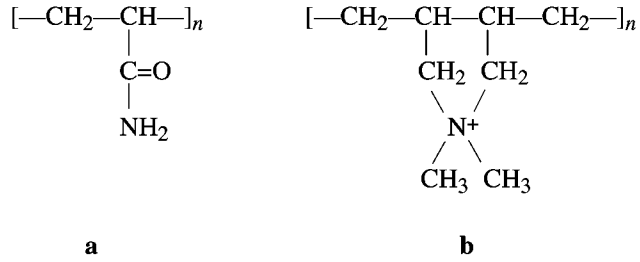


Figure 9.1 (a) Polyacrylamide; (b) polyDADMAC.

There is a very wide range of coagulant and flocculant polymers. Typical organic polymer product groups to choose from include:

- **Acrylamide/acrylate copolymers:** Anionic flocculants, usually 100% active powders or 30% active emulsions. The MW range is high, usually 12 to 22 M, and products are available both in a selection of MW ranges and in gradually increasing ionic charges (say, from 5–100%). Potable water grades (PWG) are available. Application rate is typically 1 to 5 ppm (as 100% active material).
- **Acrylamide/amine copolymer** (and amine derivatives): Flocculants supplied as emulsions in graduated MW ranges of 10 to 18 M and ionic charges of 5 to 100%. Useful in sludge dewatering processes, typically at 4 to 15 lb per ton of dry sludge. Choose perhaps 50 to 80% charge for initial testing.
- **Mannich polymers:** Cationic, solution polymer flocculants with a MW of 5 to 8 M. Very high viscosity at only 4 to 8% active strength solution liquid. A *hydrolyed polyacrylamide,* it is very useful for general municipal waste water treatment. The dose rate normally is 200 to 300 ppm or more.
- **Polyamine/DADMAC (polydiallyldimethylammonium chloride):** Cationic coagulant. Also generally supplied as solution liquids in ranges from 40 to 70% active strength. Low MW, from 0.25 to 0.75M. Useful for reclaiming oily waste waters; typically use at 150 to 300 ppm.
- **Polyamine/EPIDMA (epichlorohydrindimethylamine):** Cationic coagulant, usually supplied as solution liquids of 50% activity or emulsions of 40%. They have 100% charge and MW in the range of 100,000 to 300,000. They are used to partially replace alum when

clarifying raw water at 20 to 100 ppm alum and 5 to 20 ppm polymer, and they can be used for general color removal.

- **Polyacrylamide:** Nonionic flocculant, usually supplied as 100% active powders but also available as 30% or so emulsions. MW ranges typically from 2.5 M to 20 M. Test for suitability using jar-tester apparatus at, say, 1 to 5 ppm. It can be used as a coagulant aid for alum, and PWG are available.
- **Alum plus DADMAC** or **EPIDMA**, and **PAC plus DADMAC** or **EPIDMA**: Various combinations are now available with polymer strengths of from 2.5 to 25%, providing convenience, and often approved by the U.S. Environmental Protection Agency (EPA) for use at up to 60 to 75 ppm product.

There are a number of major, international manufacturers of coagulant and flocculant polymers whose primary markets are high-volume users (i.e., cities, states, and national governments). There are also many smaller regional manufacturers who tend to specialize in niche markets and produce various **polymer blends** (organic polymers blended with various ratios of inorganic coagulants such as *ACH, PAC,* and *alum*). These polymer blends are particularly useful in industrial facilities where process contamination and difficult clarification problems may exist.

As there are literally thousands of polymers on the market, a useful search starting point is **NSF International** (www.nsf.org), an EPA-sponsored, public health and safety company.

Examples of international polymer suppliers are:

- **Ciba Chemical Specialties, S.A.,** which now includes *Allied Colloids* and *CPS*, with brands such as **Percol**™, **Magnafloc**™, **Zetag**™, **and Agefloc**™
- **Cytec Industries, Inc.** (previously *Cyanamid*) supplying **Cyanamer**™ and **Superfloc**™ brands
- **SNF S.A.,** better known as *Floerger,* whose U.S. subsidiaries include *Pearl River*, *Chemtall,* and *Polypure*. Brands include **Clarifloc**™, **Secodyne**™, and **Floerger**™
- **Stockhausen, Inc.** supplying the **Praestol**™ brand
- **Vulcan Chemical Technologies, Inc.** using the **Calloway**™ subsidiary and brand name

Some points to remember when using these polymer products in the field are:

- Benefits of organic polymers may include improved sludge dewatering, wider pH operating range, lower dosage rates, reduced sludge volumes, and stronger flocs when compared with metal salts, but all at a higher cost.
- Metal salt performance is poor outside its pH range "window" because of metal salt solubility and failure to produce precipitates.
- Alums and many solution polymers, or polymers dissolved in water, are corrosive; therefore, use corrosion-resistant tanks.
- Color in water (apart from textile dyes, etc.) often is caused by the degradation of natural organic matter, resulting in colloidal **humic** and **fulvic acids**. These are best removed by precipitation with metal salts, but performance may be improved with high-charge cationic polymers.
- Dry polymers can be stored for up to 2 years, but are **hygroscopic** and absorb moisture from the air. Keep them in sealed bags in a cool, dry storeroom. Batches of polymer solutions made from dry polymers should be used within 24 hours.
- The shelf life of liquid or emulsion products is much shorter than that of dry products, often only 6 months. Emulsion polymers may stratify on storage. Mix gently before using.
- Do not dilute polymers with chlorinated water because the chlorine can break the polymer chain and react with amine groups.
- Liquid polymers can support biological growths. Maintain good housekeeping practice to reduce the risk of contamination.
- Polymers need **activating** by rapid agitation before use. They are more readily activated in soft, warm water (35–40 °C maximum). Maximum viscosity is reached after an **aging time** of 2 to 4 hours.
- Use well-designed, specialized polymer dissolution systems wherever possible (such as those from the U.S. Filter, Inc. subsidiary, **Strandco®**), especially for emulsion polymers, rather than simple dissolving tanks and mixers with propeller-type impellers. This prevents undissolved lumps of polymer (**fish-eyes**) and the breakdown of polymer chains. Always install a strainer to prevent possible pump clogging.
- The maximum solution strength for dry anionic polymers is 0.5 to 1.0% by weight.
- All volume additions of polymers of whatever type should be accompanied by 10 × dilution water at the point of application to ensure rapid dispersion.

- Do not use centrifugal pumps, and keep agitator speeds below 300 to 400 rpm.
- Solution polymers should be fed undiluted into application point areas of high turbulence; otherwise dilute to 5 to 10% strength.
- Emulsion polymers cannot be fed neat. Always add emulsions to water (never water to emulsions) to avoid gel formation. Dilute emulsions to 1 to 2% in-use strength for batch processes.
- Use jar tests to determine the most suitable types of polymers and potential application rates. Tests must be conducted on-site with fresh, representative water samples and fresh reagents.
- A guide for jar testing polymer samples is *first,* a **rapid mix** of 1 to 3 minutes at 80 to 200 rpm to evenly distribute the polymer and provide energy for coagulation. *Second,* a **slow mix** of 2 to 5 minutes at 25 to 40 rpm to allow the floc to build up. *Third,* a **settling period** of 2 to 5 minutes with little or no mixing to permit floc settlement.
- Evaluate jar tests on a 0 to 10 rating (10 = optimum result) for **clarity**, **floc size**, and **settling rate**, with the control given a rating of 5 for each area.
- For each type of polymer, the rate of flocculation and settlement tends to improve with increase in MW; however, very rapid settling may lead to **"fines"** being left in suspension.

9.2.4 Pre-Boiler Filtration

Filtration is the separation of solids from a fluid. While various filtration processes do, in fact, include separation in the ionic and molecular ranges, here we are primarily concerned with particulate filtration. Traditionally, a filter medium is employed to remove particles in the range of 1 to 1,000 micron (μ).

NOTE: $1\mu = 1 \times 10^{-6}$ *meters* $= 4 \times 10^{-5}$ *in. (0.00004 in.)* $= 1 \times 10^{4}$ *Angstrom units*

Traditional types of **gravity** and **pressure media bed filters** (such as *sand* and *anthracite filters*) are widely used to remove suspended solids and improve the clarity of raw water. They are also used following aeration or oxidation and chemical precipitation softening.

Coagulant aids may be used to improve the filtration of flocs, but these are generally only of value if sufficient residence time is available for coagulation to occur before the water enters the filter.

For filtration to be effective and efficient, the suspended solids must be able to penetrate the filter bed to a sufficient depth without clogging the filter so that the choice of **filter media**, **effective grain size**, and **bed depth** is important.

During filtration the suspended solids are trapped between the grains of filter media. Because there must always be space remaining for the water to percolate, there is a limit to the total volume of solid sludge that can be tolerated before backwashing is required. Designers typically set this limit at 25% of the total void volume and, irrespective of the media grain size, the void volume is approximately 45% of the total media volume.

Rough-shaped media beds down more irregularly than does smooth media, leaving larger voids and permitting higher flow rates; however,the bed depth must be increased to achieve maximum water clarity. Generally speaking, the finer the sand, the shallower the bed depth required, although head loss increases.

Pressure filters are available in either **horizontal** or **vertical tank** (vessel) arrangements, with manual or automatic backwashing facilities and with tanks constructed of steel or noncorrosive construction materials. Flow through the filters is normally from the top and then down through the bed.

Backwashing can be by water alone or by an **air scour** and water. Usually where high volumes of water are encountered a horizontal type is used because the tank length can be increased proportional to the volume. However, horizontal tanks are restricted to lower levels of suspended solids because of limitations in media bed depth. They are also prone to the risk of the *underbed* shifting, with a consequential decrease in filtering efficiency.

Vertical pressure filters using only water for backwash are generally loaded with a single layer of sand or anthracite, but sometimes multiple layers of filter media are used.

9.2.4.1 Sand Filters

Pressure sand filters typically have a bed depth of 24 to 36 inches (600–900 mm), with a subfill gravel layer from 15 to 21 inches (380–530 mm), although deep-bed filter designs are also common. The grain sizes employed vary typically from 0.35 mm to 1.0 mm or slightly larger, with 0.5 to 0.6 mm being an average. Depending on the fineness of the filter layer and the filtration rate, the maximum head loss may be anywhere from 0.2 to 2.0 bar (2.8–28.4 psig) and a bed expansion of 15 to 25% occurs during backwash.

Sand filters usually provide efficient SS removal for suspended matter above 30μ particle size, but they may need to be periodically sanitized using *chlorine*, *formaldehyde,* or similar substances (especially filters with very fine grain media). It is not uncommon for filters to contain microbial slimes and therefore act as a source of microbiological reinfection.

Another common problem with sand filters is clogging on the surface of the sand media, resulting in short runs and high head loss. This often is due to the finest grains of sand rising to the top of the media bed. If the problem persists, the easiest solution may be to replace the top few inches of sand with a slightly coarser grain so that some depth filtration occurs.

Filtration rates vary widely, depending on application. Typically, they are employed at 4 to 6 gpm/sq ft of media surface area, with backwash rates of 10 to 12 gpm/sq ft for a period of 5 to 8 minutes. Filtration rates may be as high as 10 to 15 gpm/sq ft, and backwash rates from 15 to 20 gpm/sq. ft.

NOTE: 1 gpm/sq ft = 41 lpm/m²

9.2.4.2 Multimedia (MM) Filters

Dual or **triple media filters** are used to provide a coarse to fine filtration facility. Where an *anthracite-sand media* bed is employed, the anthracite, which is half the density of sand, acts as a **roughing filter** prior to the finer sand bed. The larger and irregular voids within the anthracite bed are particularly suitable for the removal of flocs, and filtration occurs deep within the bed. Where fine crystalline precipitates of *calcium carbonate* or *calcium phosphate* occur, smaller grain sizes may be employed without risk of high head loss or low filter rates.

Triple media (MM) filters use **anthracite, sand,** and **garnet,** with the garnet providing the final and finest filtering quality, so that water with a turbidity less than 5 **nephelometric turbidity units** (NTU) and 20μ maximum particle size can be expected. Media SG, grain size, and bed depths are given in Table 9.1.

Additional notes on MM filters are:

- Bed depth is typically 18 to 24 in of anthracite (0.6–0.7 mm grain size) and 6 to 12 inches of sand.

Table 9.1 Media for MM filters

Media	*S.G.*	*Grain Size*	*Bed Depth*
Anthracite	1.4 to 1.6	0.8 to 1.6 mm	18" to 24"
Sand	2.65	0.35 to 0.8 mm	9" to 12"
Garnet	4.2	0.2 to 0.4 mm	3" to 4"

- Flow rates are similar to that for sand filters, but higher quality filtered water is generally obtained.
- Backwash rates must be lower where anthracite is used to avoid the risk of washing the media out of the filter. Bed expansion is therefore higher, at 50 to100%, depending on grain size and flow rate.

Air scouring is often used with larger filters to improve the cleaning efficiency. The wash cycle is normally a reduced flow backwash in conjunction with air scouring, at the rate of 2 cu ft air/sq ft bed surface area/min, followed by a full-flow rinse with filtered water to resettle the bed.

MM filters tend to be specified where very high clarity cooling water is required, perhaps for certain critical processes or high flux heat exchangers where no degree of fouling can be tolerated. As with sand filters, it may be necessary to periodically sanitize MM filters to prevent biological growth and the harboring of potential foulants.

9.2.4.3 Activated Carbon Filters

Activated carbon filters are employed primarily as RW contaminant removal systems for **chlorine** (by *chemisorption*) and various organics such as **trihalomethanes** (THMs), **petroleum products**, and **pesticides** (by *adsorption*). In addition, they act as physical filters and therefore incorporate sufficient freeboard in their designs to permit periodic backwashing.

Carbon filters find particular application as prefilters for RO and ion-exchange processes in the production of high purity FW. They are also used in **clean-steam boilers** and other types of steam generators where the steam is ultimately destined for application in food or beverage production, pharmaceuticals, electronics, surgical instrument sterilization, and similar processes.

There are various grades of activated carbon, depending on the carbon source and the ultimate application; types include *coconut shells,*

bituminous coal, petroleum coal, and *wood charcoal.* Grades are determined by *abrasion number, iodine number, apparent density, particle size,* and *ash.* All grades are highly porous, with an extremely high absorption surface area. Activation (*thermal carbonization*) takes place in a hearth furnace.

The carbon is available as a powder or as **granular activated carbon** (GAC) and is used up in the absorption process. It is either periodically replaced (say, every 12–24 months) or reactivated in a **hearth furnace.**

Activated carbon is not always very efficient at removing organic contaminants, especially the higher MW chemicals or where higher contaminant concentrations are present (say, 100 ppb rising to perhaps 1 or 2 ppm). For organics removal, filter designs may need a much deeper bed (at least 4 to 5 feet, 1,200 to 1,500 mm), longer contact times (perhaps 60 minutes or longer), a larger carbon bed volume, a lower pH level, and perhaps a carbon grade that is relatively organic-specific.

Organic traps (ion-exchangers) may be more suitable where the organic loading is high. **Ultrafiltration** and **RO** may also prove suitable alternatives.

Dechlorination requires a much shorter contact time than organics removal (perhaps only 60 seconds at pH levels below 7.0 but 3 minutes at pH over 8.5). The process involves reaction with carbon as well as absorption, such that 1 lb of carbon typically reacts (and is used up) with between 3 and 6 lb of chlorine.

- **Liquid face velocity rates** (flow rates) for organic removal are usually less than 1 gpm/cu ft, but for chlorine are typically 2 to 3 gpm/cu ft.
- The absorption potential of carbon is given by its **iodine number** (IN). The IN is a measure of how many milligrams of iodine, present in a 0.02 N iodine solution, can be adsorbed by 1 gram of carbon. Usually the IN is between 850 and 1,200.
- For water applications, activated carbon is usually of 8 to 40 mesh (a mean particle diameter of 0.55–1.7 mm).
- Use hard, abrasion-resistant grades of carbon such as *bituminous coal* and *coconut shell* for raw water pretreatment to avoid the production of fines resulting from erosion.
- Microbiological fouling may develop from time to time, and periodic sterilizing treatment with steam or hot water may be required.

- To backwash carbon requires a minimum of 30 to 35% bed expansion, with a flow rate of 8 to 10 gpm/sq ft for 15 minutes. Because of the presence of fines in new carbon, the initial backwash should be *double* this time period.

9.2.4.4 Bag Filters and Related Technologies

For smaller boiler plants, various **sieves**, **screens**, **cyclones,** and **strainers** may sometimes be used for filtering MU and FW. Also, **bag, ceramic membrane, cartridge**, and **candle** filters, either with a **filter aid** (*precoat* filters) or without (*naked* filters), all of which are typically available in single- and multiple-filter component vessel configurations.

A major benefit of these filters over conventional sand and MM filters is their much smaller footprint and lower capital cost. However, these features are sometimes provided at the expense of either robustness or limited filtering capacity and quality (despite claims to the contrary).

Bag filters are perhaps the most widely used of these types of pretreatment equipment, and they are also commonly employed (and highly recommended) for sidestream application in HW boiler circuits. They are reliable and robust and tend to be available in an almost infinite number of permutations. When sizing, specification items to be considered include *flow rates, vessel materials, housing and support-basket sizes, pipe sizes, connection threads and flanges, outlet positions, code and pressure ratings, gasket materials, bag shapes, bag materials,* and *micron ratings.*

Although generally associated with manual cleaning, it is possible to obtain fully automatic bag filter systems. These have a hydraulic backwashing and bag-cleaning device solidly attached to the steel bag housing.

Bag filters can be particularly useful in situations in which city water may be subject to periodic bouts of dirt or iron particle contamination arising from mains repair and flushing programs. Care must be taken when selecting filters for HW application to ensure that bags and gaskets are appropriate for the conditions. For example, *polypropylene* bags and *buna rubber* gaskets are normally only suitable for up to 200 °F (93 °C). *Teflon* or other high-temperature materials may need to be specified.

Bags are normally reusable after cleaning and may last for several cycles before changing becomes necessary. Bags should be cleaned or changed when differential pressure reaches 20 to 25 psid.

Where particularly dirty water is encountered, special filter bags are available that contain variable micron rating media to provide true depth filtration, low initial pressure drop, and longer life.

The dirt-holding capacity of bag filters is obviously dependent on a wide number of factors, but a unit of, say, 8-inch diameter and 30-inch depth should be capable of holding up to 1.5 to 2 lb. of dirt before the differential pressure becomes extreme.

9.2.5 Basic Pretreatment/Using Natural Zeolite, Greensand, and Synthetic Resins

- **Zeolites** are naturally occurring **hydrous aluminum-sodium silicates** in porous granule form. They are capable of exchanging their sodium base for calcium or magnesium and of expelling these alkaline earth metals for sodium by treatment with salt. Thus, they are a type of *ion-exchange media.* (Some zeolites act as *molecular sieves* by adsorption of water and polar compounds.)
- **Greensands (glauconite greensands)** are also zeolites and are suitable for the removal of ***iron***, *manganese*, and *hydrogen sulfide* from RW. They can operate at a wider pH range than an aeration tower, and the strong oxidizing power of potassium permanganate is used to periodically regenerate the *manganese greensand,* producing higher manganese oxides on the surface of the glauconite greensand.
- Modern **ion-exchange resins** are hard, attrition-resistant, insoluble, spherical beads made of synthetic organic materials. Ion-exchange is the process by which positive or negative ions *(charged species),* fixed to the resin groups, can exchange in (aqueous) solution under certain conditions with other ions of the same sign that are in contact with them, without any apparent change, deterioration, or solubilization of the resin. Cation resins exchange *positive ions* from water (e.g., **calcium, magnesium,** or **iron**) while anion resins exchange *negative ions* from water (e.g., **bicarbonate, chloride,** or **sulfate**).

Synthetic resins are extremely widely used, both pre-boiler and post-boiler. Pre-boiler, they are employed for basic MU water treatment (e.g., *softening*) and various higher quality purification processes (e.g. *dealkalization* and *demineralization*). Post-boiler applications are for *condensate polishing.*

The organic resin material is often a **styrene divinylbenzene** (DVB) **copolymer** in a network or matrix, to which are attached functional groups such as a *sulfonic acid, carboxylic acid,* and *quaternary ammonium.* The nature of these groups determines whether the resin is classified as a **strong/weak acid** *(cation resin)* or **strong/weak base** *(anion resin)* ion-exchanger.

Resins containing these functional groups are generally available in one or more forms; for example, **strong acid cation resin** is typically a *sulfonated polystyrene* type, available either in the **hydrogen form** (H^+) or in the **sodium form** (Na^+). The sodium form of this resin is used for water softening.

Cold process ion-exchange softeners usually contain **gel**-type resins with a lower level of **cross-linking** (4–10% DVB) but a higher softening capacity than softeners following hot-lime/softening processes. Here, a **macroporous** (*macroreticular*) resin is used, with a higher level of cross-linking (16–20% DVB) to provide physical strength against osmotic and thermal shock, but at the expense of a lower capacity.

9.2.5.1 Iron and Manganese Removal Using Greensands

In this method, the greensand is contained in a conventional pressure filter tank and regular backwashing removes the oxidized precipitates. It has a long life expectancy, with an attrition rate of typically only 2 to 3% per year. Before using manganese greensand for the first time, it should be double backwashed and regenerated with 2 to 4 oz **potassium permanganate** ($KMnO_4$) per cu ft of media.

Greensand filter sizing and operation are based on the following data:

- Capacity for Fe is 10,000 gallons per regeneration at 1 ppm Fe/cu ft of media; for Fe/Mn, it is 7,000 gallons per regeneration; and for H_2S, it is 3,000 gallons per regeneration at 1 ppm H_2S.
- Maximum practical limits are 15 ppm of Fe or Mn and 5 ppm of H_2S. Raw water pH level is 6.2 to 8.5, and ideal temperature is less than 80 °F (26.7 °C).
- Size the filter for 30-inch bed depth and gravel underbed, with a service flow rate of 2 to 5 gpm/sq ft. Backwash typically every 24 hours for 10 min at 12 to 14 gpm/ sq ft to achieve 35 to 40% bed expansion.
- Limit pressure drop to 8 to 10 psi maximum. to prevent Fe leakage.

- Continuous regeneration is recommended, adding $KMnO_4$ to achieve a slight pink color at filter inlet. Also, prefeed Cl_2 10 to 20 seconds upstream of $KMnO_4$ to achieve residual in filter effluent.

9.2.5.2 Softening by Ion-Exchange

Sodium cycle softening (**base-exchange softening**) is used primarily to remove the risk of calcium- and magnesium-based crystalline scale formation and deposition. The general reaction is as shown in Figure 9.2.

The reaction is reversible but proceeds to the right during the softening process. In a static situation, the reaction stops when chemical equilibrium is reached; therefore, during softening it is necessary to continuously percolate the water through the ion-exchange media bed to permit successive stages of equilibria to be reached. The reaction is not perfect, and some leakage of unsoftened water occurs, typically 1 to 2 ppm total hardness.

The capacity of the resin to remove hardness is dependent on several design factors, including the flow rate of water through the resin and the amount of regenerant used (**salting rate**).

Softening continues until the bed is saturated with calcium and magnesium ions (**exhausted**) and hardness **breakthrough** occurs. In practice, softening is permitted until a point just before exhaustion occurs (**operating exchange capacity**), when the regeneration process is initiated. During regeneration, the ion-exchange reaction proceeds to the left if a strong sodium chloride solution (*brine*) is used. In industrial applications, the practical regeneration of strong acid cation (softening) resins is often limited to perhaps 70 to 80% of theoretical.

The condition of an exhausted resin bed is an *ionically banded bed*, with the most strongly held ions on the top of the bed. Iron is more strongly held than calcium, which may lead to **iron fouling** problems.

Some practical considerations for a RW softener are:

$$\begin{matrix} Na^+ \\ / \\ R \\ \backslash \\ Na^+ \end{matrix} \quad + \quad Ca^{2+} \quad \Leftrightarrow \quad R-Ca^{2+} \quad + \quad 2Na^+$$

Figure 9.2 Cation ion-exchange reaction.

- Resin is a strong acid cation in sodium form, fully hydrated; typically 53 lb/ cu ft at 45% moisture content (0.85 kg/ l).
- For continuous softening service, it is advisable to install two or more softeners in parallel, on a duty/standby basis.
- The minimum water pressure required is typically 20 psig.
- Total resin volume design requirement is sufficient resin for 8 hours minimum continuous operation; 12 to 16 hours per tank is fine.
- Typical resin exchange capacity is 20,000 grains as $CaCO_3$/cu ft resin (45.9 grams hardness/l resin) at 6 lb NaCl/cu ft of resin (0.1 kg/l) to 30,000 grains at 15 lb NaCl/cu ft. Resin capacity decreases and calcium leakage increases with high sodium to calcium ratios.
- Typical salt brine regenerant concentration is 10 to 25% NaCl; maximum is 36%. Caution is needed when using some types of rock salt because it may contain considerable calcium and magnesium salts. Good quality rock salt is 98 to 98.5% NaCl. Evaporated, recrystallized salt is 99.5 to 99.8% NaCl. See Table 9.2 for concentrations of salt regenerant.
- Resin bed depth is 24 inches minimum, 72 inches maximum (0.61–1.83m).
- Bed expansion (**freeboard**) is 50% minimum (thus, the resin tank must be at least double the volume of the resin requirement). Resin bed expansion is a function of backwash rates and temperature.
- Service flow rate is 15 to 30 bed volumes (BV)/hour, or 2 to 4 gpm/cu ft resin (0.27 to 0.40 lpm/l resin). Linear flow is 4 to 10 gpm/cu ft.
- Regeneration: Backwash rate is 5 to 6 gpm/cu ft for 10 minutes (0.69 to 0.80 lpm/l resin) at 70 °F (21 °C) and 10 gpm/cu ft (1.38 lpm/l resin) at 190 °F (88 °C).
- Regeneration: Typically, brine injection rate is 0.5 to 1 gpm NaCl soln/cu ft resin (0.13 lpm/l resin). Typically, this takes 25 to 30 minutes. Check NaCl strength. It may take 4 to16 hours to achieve suitable strength.
- Regeneration: **Slow Rinse** is 1 gpm water/cu ft resin for 15 minutes (0.13 lpm/l resin).
- Regeneration: **Fast Rinse** is 1.5 gpm water/cu ft resin for 5 minutes (0.2 lpm/l resin.).

Table 9.2 Salt Concentration Indicators

Sodium Chloride % W/W NaCl	*Specific Gravity*	*°Beaume*	*Salometer Degrees*	*Sodium Chloride lb/gallon*
2	1.014	2.0	8	8.462
4	1.028	4.0	16	8.579
6	1.043	6.0	23	8.704
8	1.059	8.0	30	8.837
10	1.074	10.0	38	8.963
12	1.090	11.9	46	9.096
14	1.107	13.7	53	9.238
16	1.124	15.5	61	9.380
18	1.142	17.3	68	9.530
20	1.160	19.1	76	9.680
22	1.179	20.8	84	9.839
24	1.197	22.5	81	9.989
26	1.204	24.4	99	10.047

9.2.5.3 Organic Traps (Organic Scavengers)

The presence of organic contaminants in raw water will foul certain MU water pretreatment and purification processes. Organics will especially foul the strong base anion resins present in ion-exchange demineralization plants, causing a reduction in resin capacity and MU water purity. The loss of purity is typically reflected by a decrease in resistivity (increase in conductivity). Rejuvenation of an organically fouled resin bed may require soaking with a special cleaner followed by a 20 bed-volume rinse (compared to a normal regeneration rinse of, say, 10 bed-volumes).

Where the risk of organic fouling is present, it is prudent to incorporate an organic trap unit in the pretreatment system. **Isoporous** and **macroporous (macroreticular)** types of ion-exchange resin have (apart from a high level of cross-linking, which provides physical strength against osmotic and thermal shock) an improved porosity and a relatively high available surface area, making them suitable for use in organic traps.

Organic removal using these resins is through a combination of *absorption* and *ion-exchange*, typically using **strong base anion resin**,

regenerated in the chloride form with sodium chloride. Sodium chloride is preferred to sodium hydroxide because the affinity for chlorides is stronger and the organic foulants are more easily displaced.

In general, organic traps employing ion-exchange resins are more reliable than activated carbon filters for the removal of higher MW contaminants, for those organics possessing a weak ionic charge (polar materials), and where flow rates are high. If the organic contaminant has no **polar character,** it passes through the resin, but where it is extremely polar, it may be irreversibly adsorbed onto the resin, so that care and selectivity are required.

Where an organic trap is part of a demineralization plant system, it is placed in the train *upstream* of the strong base anion (SBA) resin unit. When the organic trap resin is placed within the same pressure vessel, physically on top of the anion resin (**stratified bed**), in which case, as it forms part of the overall anion capacity, a **weak base anion resin** operating in the free base form is employed.

Organic trap designs are available that employ a combination of activated carbon and cross-lined resin beads without ionic functionality.

9.2.5.4 Multifunctional Water Conditioners

Various types of water conditioning equipment are available to provide multiple pretreatment functions in the same tank or pressure vessel. For the most part, the technologies employed by the manufacturers are not revolutionary, despite considerable rhetoric and deliberately confusing "technical" explanations, as these units simply contain two or three different types of media of differing densities.

In general, these **multifunctional water conditioners** are available from smaller regional distributors who are seldom sufficiently technically proficient and may use gobbledygook and misleading information to add their own "spin" to the manufacturer's promotional literature. This approach is pitiful because the underlying technology is fundamentally sound and the equipment generally is well made and long-lasting.

The market is such that, typically, some manufacturers originally developed small multifunctional water conditioners solely for the residential market, where contaminant removal requirements are generally low and the small equipment footprint provides a space-saving benefit. With the passage of time, they have gradually expanded their range to include larger units suitable for commercial and smaller industrial boilers. However, for larger boiler houses, where water consumption requirements are higher and removal efficiencies are more

demanding, it is doubtful that these multifunctional units are particularly cost-effective when compared to standard, problem-specific softeners and filters.

For 24-hour, continuous conditioning operation, twin-tank multifunctional units are available with top-mounted **Fleck**™ or **Autotrol**™ controllers. These controllers provide water meter–initiated, media *backwashing*, *regeneration,* and *reclassification* functions in precisely the same manner as conventional ion-exchange water softeners.

NOTE: Where RW quality is poor, a ***booster unit*** *is generally required on the front of the multifunctional tank, so that the concept of a single tank is lost. Additionally, where iron- and sulfate-reducing bacteria may be present, periodic sterilization of the bed using chlorine injection becomes necessary.*

Multifunctional water conditioner pretreatment functions usually include combinations of the following processes:

- Removal or control of **hydrogen sulfide, iron, manganese** and **sulfur bacteria.** This is carried out on a (non-manganese greensand) catalytic/filter media bed with or without the addition of chlorine-based oxidizing agents (rather than potassium permanganate), depending on the model size and MU water characteristics.
- Cation exchange of hardness salts, using **potassium chloride** (KCl) as a regenerant, rather than **sodium chloride**. KCl is considerably more expensive than ordinary salt (NaCl), but it is promoted as being medically and environmentally superior.
- Cation and anion contaminant "reduction." This technology uses a mixed-bed of acrylic and ceramic beads, with **potassium chloride** as a regenerant.
- Removal of **hydrocarbons, volatile organic compounds** (VOCs), and **odors** using activated carbon.
- Filtration of suspended particles in the incoming RW and any oxidized Fe/Mn sludge. Here the technology simply uses the natural filtration properties inherent in all types of media.

Where multiple functions are required, units contain double or triple media beds employing, for example, acrylic beads, ceramic beads, and catalysts. **Water Wizard, Inc.** offers a multifunctional unit triple bed under the name **TRION-3**™ .

9.2.6 Nonchemical Treatments (Magnetic, Electrostatic and Similar Devices)

Physical devices (*catalytic devices*) for the nonchemical treatment of water and, more specifically, devices for scale prevention that employ magnetic fields have been part of the water treatment marketplace around the world since its earliest days. These devices include *electronic*, *catalytic*, *electrostatic,* and *magnetic water treatments*. There are also various other types of more recent "alternative" technologies (to chemical treatments) now available in the marketplace. These are being promoted for use in treating all types of MU water, FW, and BW.

For more than 50 years, magnetic devices and other devices have been regularly tested and compared with other water treatment methods, notably chemicals. Although irrefutable, documented evidence of their beneficial effect in industrial water systems still seems sadly lacking, they have enjoyed a profitable share of the water treatment market.

The **U.S. Energy Federal Technology Alert** (FTA) on ***Non-Chemical Technologies for Scale and Hardness Control***, of 3/16/99 (http://www.pnl.gov.fta/11_non.htm) reports:

> *"Today advances in magnetic and electrostatic scale control technologies have led to their becoming reliable energy savers in certain applications. For example, magnetic or electrostatic scale control technologies can be used as a replacement for most water softening equipment. Specifically, chemical softening (lime or lime-soda softening), ion exchange, and reverse osmosis, when used for the control of hardness, could potentially be replaced by non-chemical water conditioning technology. This would include applications both to cooling water treatment and boiler water treatment in once-through and recirculating systems."*

There seems little doubt that catalytic, magnetic, and related nonchemical water treatment devices will continue to claim a small but significant market share. For many buyers of water treatment chemicals and services, or for the operators of building and similar HVAC type water systems, there is the appealing allure of obtaining benefits such as *maintaining good operating efficiency*, *minimal participation in the water management process,* and *no involvement with chemical treatments*, all with *lower maintenance costs* than generally possible with chemical-based programs. Such appeal may significantly outweigh the (often very high) capital purchase or leasing costs of the equipment.

Some of these technologies are summarized below:

- **Magnetic devices:** A magnet(s) is fixed onto, or plumbed into a system, along the parallel axis of water flowing in a pipe. It is claimed that, with careful sizing and fitting, these devices inhibit the formation of scale.
- **Electrolytic devices:** These devices, consisting essentially of a *zinc anode* and a *copper cathode*, are plumbed into a system and in contact with the water (electrolyte); they are claimed to prevent scale by acting in a similar way to a battery.
- **Electrostatic devices:** These devices provide a "static field within the water" via the production of a very high localized voltage (but low current). It is claimed that this field physically affects the dissolved mineral ions and inhibits the precipitation of scale.
- **Electronic devices:** There are various designs, including *square-wave generators*, *sonar effect*, and *frequency modulation (FM) devices*. The signal generated is typically applied to a closed coil, formed by wrapping a signal cable around the outside of a water pipe. These devices are claimed to transfer energy to the ions of dissolved bicarbonate minerals, creating *nanocrystals* and preventing scaling of metal surfaces and holding the minerals in suspension until they can be bled from the system.
- **Catalytic devices:** These nonmagnetic devices use a perforated nonferrous tube to encourage small calcite seed crystals to form and reduce the risk of bulk water scaling. They are promoted for use in hard waters under conditions where supersaturation can easily occur.

9.2.6.1 Review of Nonchemical Treatment Technology

The arguments for and against the use of magnetic devices and similar technologies are periodically aired. These center around:

- Whether benefits are really tangible or merely wishful thinking
- An acceptable rationale of how they work
- The continuing apparent lack of any readily acceptable scientific basis on which to predict performance

Whether magnetic devices and related technologies really do work under any or some limited circumstances is still debatable. It is clear, however, that, in general, the chemical-based water treatment companies remain extremely skeptical, although the market has perhaps

moved a little in the last few years from a position of "They probably never work" to "They probably sometimes work."

The magnetic devices industry continues to do itself no favors by providing explanations that are often pseudoscientific gobbledygook! Even within the industry, manufacturers of magnetic devices cannot agree on what constitutes an effective design, and some suppliers seek to gain marketing advantage by deriding competitive products.

Comments from the catalytic devices industry have at least proposed that FW or MW water quality, recirculating water, and surface temperatures are key factors in determining whether such devices will perform.

Despite the rhetoric surrounding the subject of magnetic water treatment, some "useful" information can be gleaned from technical papers and supplier's literature (extracts of which are reported below), which may help the reader form an informed opinion on the benefits or otherwise of this form of pretreatment.

- The FTA laboratory perspective notes: *"The history of the technologies, as illustrated through primarily qualitative—but some quantitative—assessment in many case studies, has shown that when properly installed, a decrease in or elimination of scale formation will be found. The key here is "properly installed." By this it is meant that a manufacturer or their qualified representative is responsible for equipment integration."*
- The FTA on what-to-avoid notes: *"This technology is littered with disreputable manufacturers or vendors, the actions of whom have given the technology an undesirable history in the eyes of many. Work with a reputable manufacturer through their engineering department or their designated installer. These people have much more experience with the technology than the typical water treatment engineering firm. Be aware of process water requirements since these requirements may dictate the need to install solids separation equipment or iron removal equipment in order to maximize the performance of the technology. Installation near high voltage electrical equipment or strong magnetic fields is to be avoided since these fields will interfere with the performance of this technology."*
- It is known and accepted that magnetic and other applied fields can interact with certain charged species in water and other fluids in such a way that the subsequent behavior of these species is altered.
- There appears to be evidence from certain university laboratories that, although applied magnetic fields do not interact directly with

charged species in fluids, they can result in changes in the crystallization process such as changes in solubility, the rate of precipitation, particle size, or crystal morphology.

- It is reported that various university laboratory–controlled experiments and university-monitored field trials involving magnetic treatment of fluids have shown reductions in calcium carbonate, sulfate, and phosphate scaling in a variety of industries, thus lengthening the operating cycles of industrial equipment before cleaning was required (due to scale formation) and reducing the propensity of calcium carbonate scale to occur over and above that achieved by increased water turbulence. (It is difficult to find, however, actual experimental reports in legitimate publications, or any specific references, either to these reports or to trials that demonstrate the merit of such devices in real-life industrial or commercial applications, despite claims of their existence. It is also noted that some of the university-inspired reports are critical and dismissive of negative comments, yet are equally devoid of substantiated data.)
- Other university experiments have found that under certain scaling conditions, with the right combination of magnetism, temperature, acidity, and water flow rate, the rate of scaling can be halved and that the scale so formed is not in the form of adherent crystalline deposits, but rather a sludge or powder that is fairly easily removed.
- Various theories have been postulated to explain the phenomenom that magnetic fields can change the way in which calcium carbonate precipitates and crystallizes, the most probable one being that the *applied field distorts the electrical charge carried by small particles of calcium carbonate that have already formed in the water*, thus affecting the way in which they adhere to form large particles.
- Designs of proprietary magnetic devices have changed and evolved throughout the years, perhaps partly to improve operating efficiency or widen the scope of application, but also partly to overcome voiced criticism of the supposed mode of action. Products contain either permanent magnets, electromagnets, or both and may require the installation of single or multiple devices for adequate water magnetization. Devices may or may not successfully treat water in a single pass and may or may not require frequent attention to remove internal scale.

  All designs claim to treat the water for control of crystalline scales. Some designs claim to also control corrosion. There does **not** appear to be any claims to nonchemically treat water so as to

control any of the other problems sometimes or often associated with water, such as incoming ***raw water contaminants*** (*hydrogen sulfide, iron*, etc.), ***microbiological fouling*** (*general aerobic bacteria, sulfate reducing bacteria, algae*, etc.), ***process contaminants*** (*ammonia, citrates, oil, plastic beads, wood pulp,* etc.), or ***atmospheric-borne contaminants*** (*dust and dirt, beach sand, steel swarf,* etc.). Suppliers usually require operators to provide bleed or BD facilities to control sludge buildup or precipitation problems due to overconcentration or reactions such as calcium phosphate sludge formation.

- The FTA reports that, *"The operating principles for* **electrostatic units** are much different (than magnetic devices). Instead of causing the dissolved ions to come together and form nonadherent scale, a surface charge is imposed on the ions so that they repel instead of attract each other. Thus. the two ions (positive and negative, or cations and anions, respectively) of a kind needed to form scale are never able to come close enough together to initiate the scale-forming reaction. The end result for a user is the same with either technology; scale formation on heat exchange surfaces is greatly reduced."

Whether electrostatic technology is superior to magnetic device technology is debatable. What is of interest is that, in a 1998 marketing and technical support documentation pack from a major electrostatic unit manufacturer, most of the information supplied related primarily to cooling water applications rather than boilers. The boiler data, such as there was, concerned only smaller, simple systems (e.g., HW boilers and steam ovens).

Also in the pack was a publication, of 1975 vintage, entitled "How Electrostatic Water Treatment Works" *(National Engineer, the Journal of the National Association of Power Engineers)* indicating that perhaps not much has changed in 33 years.

Quite separately, the results of a "properly controlled" trial were published in a 1974 paper entitled "Electrostatic Descaler Testing: an Evaluation" (Meckler, M., *Heating/Piping/Air Conditioning,* Reinhold Publishing Co.). This paper concluded that *"the test descaler was not effective in preventing scale deposition, and we were unable to detect any measurable reduction in corrosion potentials."*

NOTE: The author has, on behalf of engineering personnel, occasionally conducted properly controlled, parallel trials of magnetic devices in hard-working industrial cooling systems. All trials were less than successful.

Additionally, while the author has sometimes observed such devices on large-diameter pipe cooling systems (status unknown), no similar observation has ever been made at any "substantially sized" boiler house.

9.2.6.2 Examples of Nonchemical Technologies for Scale and Hardness Control

Some examples of nonchemical technologies are:

- **Hydromag**® provides electromagnetic water conditioners (connection to an electrical supply required). These are disc-shaped and use "*circular electrical coils embedded in body castings of a high-grade ferrite material (copper-, nickel-, or chrome-plated), with controlled voltages to produce powerful electromagnets of 2,500 gauss flux density.*"

  The design is claimed to work with different flows and pressures in pipework and ensures that "*not only are lines of force concentrated in the correct direction but also water flow crosses these lines at the correct angle (15 times in all), ensuring magnetic conditioning of the water is initiated.*"

  The design is further claimed to "*fully treat full flows of water in a single pass when installed direct to mains supplies, and water treated magnetically maintains its state for up to five days. Treatment results in hardness ions being attracted to other ions (rather than to pipework), resulting in a larger neutral body that has no ability to adhere to pipe walls or other contact surfaces, so that no incrustations or hard scales form.*"

  Finally, the control unit, apart from controlling voltage, has a magnetic polarity reversal switch operated by a variable timer, usually set to actuate every minute that "*cleverly ensures no scale can build up inside the unit, making the entire system maintenance free.*"

- **Superior**® water conditioners. These are tubular-shaped devices that employ *permanent* magnets (no electrical connection). The devices are designed with a cobalt-content alloy core, arranged so that water flows around the magnetic core and perpendicular to the magnetic fields.

  The various sizes and types utilize single-bar, multifield, multipole magnets singly or in factory assembled bar-bundles. They are further designed for "*easy disassembly and cleaning in systems with existing corrosion build-up or iron content in the water.*"

  The devices are claimed to "*ensure that magnetically treated water keeps minerals in a soft amorphous powder form instead of*

the usual hard crystalline structure. This amorphous powder deposits a thin film of aragonite talc on the inside of pipes and the waterside of condensers, which prevents free oxygen in the water from attacking the metal surfaces."

- **Aqua Magnetics**® provide heavy industrial *permanent* magnetic power units that have been developed from a patented *diamagnetic theory*. The units are clustered around the raw water pipe.

  The principle behind the technology is: "*1. Molecules suspended in fluids tend to cluster. 2. A fluid traveling through a pipe or line carries these molecules and clusters. 3. Larger clusters tend to slow in speed and move toward the side of the pipe or line, forming unwanted deposits that restrict the flow of fluid. 4. Immediately, as the flow of the fluid brings clusters of molecules in contact with the powerful magnetic circuitry, clusters are broken apart with a single, instananeous jolt. 5. Free of large clusters of molecules, the fluid proceeds through the pipe or line with chemical characteristics of fluid intact. 6. No system is too old. When preexisting scale is in the flow of the treated fluid, it can become resuspended and gradually removed.*"

- **Ener-Tec**® have patented their **Linear Kinetic Cell** (LKC), which is a screwed or flanged tubular-shaped electromagnetic device. Claims include: "*LKC will treat any volume passing through the unit and the treatment is effective for 4,000 feet downstream. Recirculating fluid systems (including boilers) will retain their net-negative charge for up to 36 hours after the LKC is switched off.*

  "*The LKC influences the water by modifying the charges of scale-forming particles as they pass through the LKC. By inducing an extremely powerful flux force field into the water in the direction of flow and at the speed of light, the LKC's effect is to stretch or rotate the axis of each molecule, so that molecules form a tightly knit molecular chain that carries its own electromagnetic force field.*

  "*The LKC eliminates many problems that are presented by the utilization of permanent magnetic or electrostatic water treatment devices of which you may have heard.*"

- **ElectroStatic Technologies, Inc.** provide **FluidTron** electronic fluid treatment systems in various sizes. These items of equipment generate an electrostatic field of between 20,000 and 30,000 volts DC, at very low amperage.

  It is claimed that, "*The electrostatic chamber forms a local capacitor within the piping system or vessel wall. Tiny particles that would be part of scale, sludge, or bacterial deposits are charged to*

the same electrical polarity as the field within the electrostatic chamber.

"The field will control the development of these deposits by reducing the size of the particle collections and interfering with their ability to bond together and form deposits.

"In addition, the surface tension of the water molecules passing through the chamber is reduced, which allows the water to absorb greater quantities of these scale- and deposit-forming minerals and carry them away in suspension. As a result, scale that has been formed within a system will gradually return to solution and be carried away with the water flow."

- **Fre-Flo Water Systems, Inc.** provide equipment utilizing nonmagnetic, nonelectrostatic, **Fre-Flo™** technology. Rather than try to inhibit the development of scale (as with most types of nonchemical devices), this technology is designed to control bulk water scaling and deposition by deliberately encouraging the formation of a small amount of carbonate seed crystals.

  The core of this catalytic water conditioner device consists of a special perforated heavy-metal bar with a nonuniform, surface-spot latticework structure (the bar is a mixture of metals that includes Cu, Ni, and Zn). It is claimed that when water flows through the bar, the pressure drops drastically, causing dissolved *carbon dioxide* to escape, raising the pH level slightly and resulting in the water being supersaturated with **calcite** (crystalline *calcium carbonate*). The surface spots act as nucleation points for millions of tiny calcite seed crystals to grow to subcolloidal size in a process called **epitaxial nucleation.** The crystal seeds are eventually dislodged into the bulk water by the shearing force of the water flow and remain suspended as discrete particles, rather than agglomerating as scale.

  Some reduction in surface tension is also claimed (due to the formation of calcite and a consequential reduction in the ionic concentration of the water), although this is unlikely to provide any practical benefit.

  Additionally, for previously scaled systems, it is claimed that as new calcite seed crystals flow away from scaled sites, a shift in $CaCO_3$ equilibrium occurs, resulting in a continuous descaling action.

- **BWT-Europe, A.G.** have launched a free-standing electronic device that, similar to the **Fre-Flo™** technology, does not try to inhibit the development of scale but is designed to control bulk

water scaling and deposition by deliberately shifting the hardness–carbon dioxide equilibrium and encouraging the formation of a small amount of carbonate seed crystals (nanocrystals).

The equipment is branded as the **AQA™ total** and uses *a special three-dimensional electrode to produce specific current-voltage impulses to the electrically conductive particles, resulting in a local displacement of the hardness–carbon dioxide equilibrium.*

The so-called nanocrystals are formed in the active part of the "IQ" electrode. Because of the small size of the nanocrystals, they carry an electrical load that prevents coalescence. The nanocrystals in their entirety are able to trap the hardness in the water, which prevents limescale buildup in pipes and heaters.

The difference between this European technology and almost all other nonchemical devices is that it has apparently been tested in accordance with **DVGW** and **OVGW guidelines**, which represent the highest European standards. Also, this product has been endorsed by **Alamo Water Refiners, Inc.** a major and very reputable U.S. equipment manufacturer and distributor.

Nevertheless, it should be made clear that the limescale has not been removed, but merely trapped in nanocrystals and total evaporation will still result in limescale deposits.

As an example, the AQA total™ model 14000 provides 62 U.S. gpm (162 l/m) of limescale-free water from a unit 53 × 32 × 20 inches (H/W/D) and consumes 240 W.

9.3 PRE-BOILER PURIFICATION TECHNOLOGIES

Pre-boiler pretreatment is concerned with providing higher quality MU and FW—that is, water with most, if not almost all, natural impurities removed. There are perhaps as many interpretations of what constitutes "high-quality" water as there are boiler designs requiring it, and consequently there are also many specifications available, each with minor variations on a similar theme. Trying to decide precisely what is required, above and beyond a basic good quality, as provided by the use of pretreatment equipment such as filters, softeners, and so forth is difficult.

A summary of some earlier notes indicates that boilers requiring higher quality MU and FW are:

- **Higher pressure units**, above, say, 580 to 600 psig (40 to 41 bar)

- **Highly rated boilers**, say about 95,000 Btu/hr/sq ft/°K (300 $kW/m^2/°K$)
- **Larger and more complex plants**, e.g., power boilers
- **Particularly compact or special design boilers**, e.g., miniature, packaged multitubed WT boilers and coil boilers
- **High-quality or high-purity steam applications**, e.g., "clean" steam generators for use in hospitals

NOTE:

1. *This summary all but excludes FT boilers of any description from the requirement to have high-quality (i.e., low TDS) MU water. Exceptions are those FT boilers that have very low rates of CR and/or a high alkalinity MU water supply, and some special purpose boilers.*
2. *Boilers of lower pressure rating that have significantly reduced rates of CR should operate with higher quality water (i.e., lower TDS) to avoid fouling and high BD rates.*
3. *Boilers of any substantial pressure rating that receive MU water with naturally high alkalinity should incorporate a dealkalization plant as part of the pretreatment and purification plant.*
4. *Mechanical deaeration is essential for all boilers operating at pressures of over 290 psig (20 bar). Ideally, mechanical deaeration should be provided for all larger boilers operating over 15 psig (1.03 bar) but this is unfortunately often ruled out on grounds of high capital cost.*

There are essentially three primary technologies that are commonly employed today for purification of boiler plant MU and FW:

- **Demineralization/deionization** (DI)
- **Reverse osmosis** (RO)
- **Electrodialysis** (ED)

In addition, it is worth mentioning **ultrafiltration** (UF) because it is often employed as a "*roughing filter*" for each of these technologies. There is still a need to provide a basic good quality water through the use of media filters and other devices as a precursor to purification.

NOTE: Apart from demineralization, other ion-exchange processes that may be considered as "purification" techniques include ***cation exchange***

dealkalization *(anion exchange dealkalization essentially does not reduce TDS),* ***desilicizing****, and* ***condensate polishing****.*

Each type of technology has spawned a very wide range of subset processes, and many of these processes may be considered to compete with each other, both within and across disciplines, as mechanisms for producing higher quality waters. In practice, however, although the element of competition may have been true just a few years ago, today each technology is recognized as having particular benefits (and limitations) that tend to make for complementary rather than competing processes. Consequently, although it is likely that, for any given RW source, process designers can provide a range of treated waters at various purity levels employing any of the individual technologies, they prefer to mix and match processes to suit particular operational and economic design requirements.

Thus, for many high-quality FW applications, various water conditioning configurations employing two or more different technologies are commonplace, several of which appear to have emerged as worldwide "standard" industry processes. Some examples of high-quality water purification processes are:

- Twin-bed DI + mixed-bed deionization (MB) polisher
- UF + twin-bed DI + two-pass RO
- RO + electrodeionization (EDI)
- RO + MB polisher
- ED + MB polisher
- UF + electrodialysis reversal (EDR) + RO

The question of which particular MU water pretreatment purification technology or system of technologies to employ for a higher-pressure boiler plant, special boiler design, or steam process can only be answered by looking at the specifics of each case.

Because of the need to provide a case-by-case process design, there is little to be gleaned in this specific area by referring to recognized industry guidelines that cover WT and special design boilers, such as "**Recommendations for Treatment of Water for Land Boilers**" (BSI 2486: 1997, British Standards Institution, U.K.) or "**Consensus on Operating Practices for the Control of Feedwater and Boiler Water Chemistry in Modern Industrial Boilers**" (1994, American Society of Mechanical Engineers, U.S.A.).

Although there are marginal differences, both references take the stance of recommending a gradual improvement in FW quality, relative to increased boiler pressure. There is no sudden cutoff beyond which it is necessary to seek a higher grade of treated water.

Unfortunately, the same authorities also do not provide any recommendations for FW **silica** content, **sodium** content, or **electrical resistivity/conductivity**, all of which are important constituents of high-quality water and are used as indicators of purity. (Silica and conductivity recommendations are, however, provided for BW quality.)

Nevertheless, it is necessary to provide some rough rule of thumb as a starting point for debate. It may therefore be convenient to consider high-quality MU water at three levels, as shown in Table 9.2 and the subsequent notes.

- **Basic pure water:** This grade can typically be obtained by any standard RO, twin-bed DI, or ED technologies.

  Reverse osmosis requires good pretreatment to prevent membrane fouling and loss of performance. Because it is seldom better than 60 to 70% efficient, there is a relatively high cost for pumping and discharging the additional supply water consumed. Nevertheless, it is good as a bulk water "roughing" process for purification.

  Twin-bed DI often ceases to be economical when TDS levels begin to climb, and it can be subject to bacterial infection and resin fouling. Also, there are cost and safety issues associated with chemical regenerant storage, consumption, and discharge. As a technology, however, DI provides the widest possible versatility.

  Electrodialysis is a well-established technology but suffers from poor recovery rates and is very susceptible to scaling problems. (A derivative, EDI, however, is able to overcome these problems, albeit at a higher capital cost.)

  Ion-exchange resins, RO membranes, and ED membranes all have a typical working life of between 4 and 8 years before replacements become necessary.
- **Very pure water:** To achieve this grade requires a further purification process, over and above that necessary to provide basic pure water. Second-stage processes include double-pass RO, MB polisher, or EDI. Typically, the equipment would be configured in a dual or triple train.
- **Ultrapure water:** To achieve this MU water grade requires the use of several special process features and quality control mechanisms chosen from a wide array of technology "tools." Routes chosen may include the provision of UF both pre- and postpurification, carbon

individual **cations** (e.g., Ca/Mg/Fe/Na/K) and **anions** (e.g., $Cl/SO_4/HCO_3/NO_3$), ideally reported in **milliequivalents per liter** (meq/l). Temperature, pH levels, organics, and silica content are also necessary.

NOTE: Silica is generally not dissociated in water and thus does not affect the ionic balance; nevertheless, because of the potential impact of silica in boiler MU water, it should be reported separately.

Where IX designs are being considered, a one-off sample is simply not appropriate. Real analyses over a period of time are required, and seasonal variations should be properly understood in order to provide a realistic design.

9.3.1.1 Some Basics of IX Resins

See Table 9.4 for general properties of IX resins and Table 9.5 for IX equivalents.

- **Resin bead polymer composition:** Either **acrylic** resins or, more generally, **styrene** (*vinylbenzene,* VB) are cross-linked with typically 4 to 20% **divinylbenzene** (DVB) in a copolymer network or matrix.
- **Cross-linking function:** This adds strength to the resin, so that the higher the CL, the stronger the resin. Capacity drops proportionally as the IX sites are on the VB and are reduced with increased cross-linking.
- **Resin bead structures:** Either **gel** or **macroporous resin** types. *Gel resins* have a lower level of cross-linking, which increases kinetics, capacity, and operating efficiencies, but reduces strength and resistance to fouling. *Macroporous resins* have a sponge-like structure that provides greater stress tolerance and resistance to fouling and physical breakdown, but at a cost of reduced capacity.
- **Generic categories:** There are four types, each with a charged functional group added to the VB/DVB structure: **strong acid(ic) cation** (SAC) with a *sulfonyl* group, **weak acid(ic) cation** (WAC) with a *carboxyl* group, **strong base(ic) anion** (SBA) with a *quaternary amine* group, and a **weak base(ic) anion** (WBA) with a *tertiary amine* group.
- **Cation resins** exchange *positive ions* (e.g., calcium, magnesium or iron) from water, while **anion resins** exchange *negative ions* (e.g.,

Table 9.4 General Properties of IX resins

CATION/ ANION type	*Resin Notes*	*Total Wet Exchange Capacity meq/ml*	*Max. Oper. Temp °F*	*Swelling e.g. Na → H*
SAC(Na)	8% CL, Gel	1.9 to 2.0	280	5 to 7%
SAC (H)	8% CL, Gel	1.8 to 1.9	265	5 to 7%
SAC(NH_4)	8% CL, Gel	1.9 to 2.0	260	—
SAC(Na)	10% CL, Gel	2.1 to 2.2	280	5 to 7%
SAC(H)	10% CL, Gel	1.9 to 2.0	265	5 to 7%
SAC(Na)	Macroporous	1.7 to 1.9	300	4 to 7%
SAC(H)	Macroporous	1.8 to 1.9	285	4 to 7%
WAC(H)	Acrylic	3.4 to 4.2	250	15 to 20%
SBA(C1)	Type 1, Gel	1.4	170	15 to 20%
SBA(OH)	Type 1, Gel	1.1	140	15 to 20%
SBA(C1)	Type 1, Porous	1.3	170	20 to 25%
SBA(OH)	Type 1, Porous	1.0	140	20 to 25%
SBA(C1)	Type 2	1.4 to 1.45	170	10 to 15%
SBA(OH)	Type 2	1.4 to 1.45	95	10 to 15%
WBA(Free Base)	Macroporous	1.3 to 1.4	210	15 to 20%

NOTES:
1. *This is not an exhaustive list of resin types or grades*
2. *Capacity variations reflect differences between manufacturers*
3. *1 meq/l = 21.85 Kgrains/cu ft*
4. *Cation resins are typically 50 to 54 lb/cu ft*
5. *Anion resins are typically 41 to 44 lb/cu ft*

bicarbonate, chloride or sulfate). In twin-bed demineralization processes, the *cation bed* (H^+ form) leads, followed by the *anion bed* (OH^- form).

- **Strong acidic cation (SAC):** Can exchange all cations and is very useful for all types of water. Has good physical and oxidation stability and provides a variable capacity dependent on regeneration levels. A limitation is the operating efficiency of SAC resins. A relatively low cost resin.
- **Weak acidic cation (WAC):** Provides only a partial exchange capacity (only those cations associated with alkalinity). WACs have a much higher (but fixed) capacity than SACs. High operating effi-

ciency but limitations include a relatively high cost, poor kinetics, and poor physical stability.

- **Strong basic anion (SBA):** Can exchange all anions and neutral salts, including **silica** and **carbon dioxide**. Good kinetics and short rinses, but there is a tradeoff between exchange efficiency and resulting quality. SBA resins have a limited life, are thermodynamically unstable, are prone to organic fouling, and cost considerably more than the cation equivalent.
- **Weak basic anion (WBA):** Removes only strong acids (**hydrochloric, sulfuric, nitric**). Does not remove SiO_2 or CO_2. A high operating capacity and regeneration efficiency with good resistance to organic fouling and thermal stability. WBA resins need longer rinse times, have poor kinetics, and cost even more than SBAs.
- **Type 1 and 2 resins:** Refers to SBA resins. Type 1 resins are either "standard" (particularly good temperature and oxidation stability) or "porous" (higher capacity and resistance against organic fouling). The structure of type 2 resins is similar to type 1 but provides for maximum capacity and resistance to fouling.

NOTE: Before use for the first time, IX resins must be conditioned by soaking in water for approximately 1 hour. Resins should then be backwashed to reclassify the bed, so that the fine particles are on the top and the coarse particles are on the bottom. After backwashing, the bed should be allowed to settle and the water drained to 1 inch above the top of the bed. Regeneration should then take place.

NOTE: ***Cation resin cleaning*** *for removal of Fe, Mn, and Cu foulants is achieved by soaking in a* ***phosphonate-citric cleaner*** *(5% + 5%) for several hours or sodium hydrosulfite cleaner (4% $Na_2S_2O_4$) for 4 to 10 hours. If the cations have accumulated within the resin bed, perhaps soaking in an inhibited hydrochloric acid cleaner (10% HCl) is the only alternative. Fouling from aluminum hydroxide floc requires an acid-sequestrant program, such as a* ***phosphoric-citric + sodium gluconate cleaner****. For all these procedures, use an air lance (very slow airflow) and provide ample backwashing and rinsing.*

Anion resin cleaning *employs a* ***caustic cleaning program*** *and consists of a partial caustic regeneration and displacement, followed by a warm brine soak at up to 150 °F (65 °C). Following backwashing, the resin is regenerated with warm 2 to 5% caustic, but the amount is limited to only one-third normal dose (1 to 2 lb/cu ft) with a flow rate of approximately 0.2 gpm/cu ft. Following regeneration, the resin is rinsed at the same flow rate for 10 minutes and then injected with warm 10 to 15% caustic at 6.5 lb/cu ft (same flow rate). A final 10-minute slow rinse is given.*

Table 9.5 Standard IX Resins: Approximate Equivalents

Resin	*Amberlite®*	*Diaion®*	*Dowex®*	*Duo-lite®*	*Imac®*
SAC(Na) 8% CL	IR-120	SK-18	HCR-W2	C-225	C-12
SAC(H) 8% CL	IR-120H		HCRS-H		
SAC(NH_4) 8% CL					
SAC(Na) 10% CL	IR-122	SK-110	HGR-W2	C-255	C-14
SAC(H) 10% CL	IR-252				
SAC(Na) Macro	IR-252	PK-220	88	C-26	
SAC(H) Macro					
WAC(H) Acrylic	IRC-84	WK-11	CCR-2	C-433	Z-5
SBA(CI) Type 1	IRA-400	SA-10A	SBR	A-109	
SBA(OH) Type 1					
SBA (C1) Porous	IRA-402	SA-12A	SBR-P	A-113	S5-40
SBA(OH) Porous					
SBA(C1) Type 2	IRA-410	SA-20A	SAR	A-116	S5-42
SBA(OH) Type 2					
WBA(FB) Macro	IRA-93/94	WA-30	MWA-1	A-378	A-20
Resin	*Ionac/ Relite®*	*Kastel®*	*Lewalit®*	*Purolite®*	*Resin tech®*
SAC(Na) 8% CL	C-249	C-300	S-100	C-100	CG8
SAC(H) 8% CL	C-267			C-100H	CG8H
SAC(NH_4) 8% CL				C-100 NH_4	
SAC(Na) 10% CL	C-250	C-300 AGR	S-115	C-100.10	CG10Na
SAC(H) 10% CL			C-100.10H	SACMP	
SAC(Na) Macro	CFZ		SP-112	C-150	SACMP
SAC(H) Macro			C-150H		
WAC(H) Acrylic	CC	C-101	CNP-80	C-105	WACG
SBA(C1) Type 1	ASB-1	A-500	M-500	A-600	SBG1
SBA(OH) Type 1				A-600OH	
SBA(C1) Porous	3-A		M-504	A-400	SGB1P
SBA(OH) Porous				A-400OH	
SBA(C1) Type 2	2-A	A-300	M-600	A-300	SBG2
SBA(OH) Type 2					SBG2-OH
WBA(FB) Macro	A-329	A-101	MP-64	A-100	WBMP

Table 9.5 Standard IX Resins: Approximate Equivalents (continued)

Amberlite® is a trademark of the Rohm & Haas Company
Diaion® is a trademark of Mitsubishi Corporation [previously Diamond Shamrock Corporation (USA)]
Dowex® is a trademark of Dow Chemical Company
Duo-lite® is a trademark of Rohm & Haas [previously Dia-Prosin (France)]
Imac® is a trademark of Rohm & Haas [previously Imacti (Holland)]
Ionac/Relite® is a trademark of the Sybron Corporation
Kastel® is a trademark of Dow Chemical Company [previously Montedison Sp (Italy)]
Lewatit® is a trademark of Bayer Corporation
Purolite® is a trademark of Purolite International
Resintech® Is a trademark of Resintech, Inc.

9.3.1.2 Some Basics of IX System Designs

For many years the standard method of restoring IX resins within a vessel was **co-current regeneration**, whereby the regenerant flows in the same direction as the service water flow—downward from the top of the vessel. This method is inefficient and time-consuming. It also results in incomplete regeneration of the resin at the bottom of the vessel (the *polishing zone*). As a result, co-current regeneration in new plants is all but nonexistent in most parts of the world. In its place came **counter-current (reverse-flow) regeneration**, which emerged as the dominant technology more than 30 years ago and is still used today in a wide variety of designs. Here the regenerant flow is from the bottom up, which provides the most concentrated regenerant exposure to the polishing zone and cuts down on vessel outage time. Traditionally, regeneration took place within the IX vessel, and a **freeboard** was necessary to provide space for backwashing the resin. BX softening and other relatively simple IX processes still employ either *full* or *partial* freeboards. For many DI processes, however, this vessel space is considered wasteful and unnecessary and new operating designs have since emerged.

Since the 1970s more sophisticated IX designs available in the marketplace have utilized vessels completely full of resin (*packed-bed designs*) with counter-current regeneration and single or multiple resin configurations in the same vessel, or have provided external regeneration in both *batch* and *continuous regeneration processes*. The original packed-bed designs were pioneered by *Bayer AG* during the 1950s. Current design technologies include:

- **Hold-down beds:** This design uses the traditional 30 to 50% freeboard space for internal backwashing, but retains or *holdsdown* the resin in a

compressed state during *counterflow regeneration* by means of *water injection*. This ensures that proper restoration takes place. In hydraulic systems, the eluted water and spent regenerant emerges from the middle of the vessel. Supply water enters from the top down, with the treated water emerging from the bottom of the vessel. Because of hydraulic instability problems with some types of equipment, other designs have emerged, including the use of *inert resins, membranes,* or *inflatable compression systems,* to achieve the same hold-down objective.

- **Packed-beds:** Here the vessel is full of resin, which results in considerable efficiencies such as a smaller vessel size, a 20 to 30% reduction in regenerant consumption (both acid and caustic), and a 10 to 15% increase in cation capacity between regeneration cycles. There are many different packed-bed designs, primarily developed by the various major manufacturers of IX resin. Packed-bed designs include *Schwebebett*™ and *Compound*™ *bed* designs by **Bayer AG**; *UPCORE*™ from **Dow Chemical Co.**; *Amberpack*™ from **Rohm and Haas, Inc.**; Fluidlite™ from **Purolite;** and the downflow service/up-flow regeneration types from **Degrémont**.

  In a fully packed bed, conventional backwashing cannot take place inside the vessel, so packed-bed designs compensate for this either by having some degree of partial freeboard or by providing external backwashing. The supply water typically is from the bottom up to the top, but this design may vary.

Both hold-down bed and packed bed systems may be designed to hold single or multiple resins in the same vessel. Single resin beds are often called **monobeds**. Multiple resin bed designs provide for either *single compartment* or *double compartment* variations. Bed designs are also termed *mixed, stratified, layered,* or *sandwiched*. Notes on some bed designs follow.

- **Stratified beds:** In some bed designs, and by use of carefully graded resins with specifically different densities, it is possible to combine both *weak* and *strong* resins in a single compartment vessel, in a stratified manner. There is a 100% freeboard. Supply water is from the top down, with the weak resin on top and the strong resin below. The treated water emerges from the bottom of the vessel.
- **Stratified packed-beds:** A double compartment design that holds stratified weak and strong beds but without any freeboard. Designs vary, but typically the flow is opposite to that of the hold-down

design, so the supply water is from the bottom up, and, thus, the weak resin is at the bottom with the strong resin on top.

- **Mixed beds (MB):** A 100% freeboard is provided. Cation/anion resins are intimately mixed in the bed for highest exchange quality, but they are split during backwashing (due to density differences) for double compartment regeneration. Supply water is from the top down. During regeneration the SBA is on top and the SAC is underneath. Acid is *in* from the bottom and *out* at the top level of the SAC (SAC–SBA interface). Caustic is *in* from the top of the SBA resin and *out* at the interface.
- **Trio-beds (triple beds):** This is an MB double compartment design with an intermediate-density *inert resin* added to physically split the cation/anion resins during regeneration to minimize leakage.
- **MB packed beds (sandwich polisherers):** An SBA–SAC MB polisher unit but within a packed bed.

Compact bed IX designs, such as the *Schwebebett,* use packed-bed and **fluidized-bed** functions to eliminate channeling.

Other IX designs employed to reduce resin volume include, for example, the **Permutit** (now **Vivendi/U.S. Filter Corp.**) **Scion®** *short cycle deionizer design* and the **Scion-Hipol®** (which has a cation polishing unit on the two-stage deionizer).

A further novel reduced-resin design is the **ISEP®** from **Advanced Separation Technologies, Inc.** This employs a carousel holding 30 fixed bed columns of resin that continuously rotate to match 20 fixed top and bottom ports. This design also provides for high purity water and reduced regenerant demand and wash volumes, but at a significant capital cost.

Clearly, it is necessary to be fully aware of FW purification objectives because IX process selection can otherwise be totally bewildering.

9.3.1.3 Some Practical Functions of IX Systems

We are primarily concerned with IX purification processes that focus on general industry and larger commercial and institutional boiler houses and mechanical rooms. In this context, various potentially appropriate *dealkalization*, *desilicization,* and *demineralization* processes are discussed below.

9.3.1.3.1 Dealkalization Processes As noted elsewhere, for steam plants operating at over 15 psig and for many special purpose boilers,

a typical basic good quality FW specification provides for full softening as a minimum requirement. Where the water has high natural alkalinity, this is often reduced via an IX dealkalization process in conjunction with BX softening.

There are different types of IX dealkalization, depending on the nature of the supply water, the final water quality needs, and the operating preferences.

Most processes will provide for *degassing* (*decarbonation*) by means of a **degasser,** which provides an up-current of air through a tower filled with polypropylene packing counterflow to meet a cascade of water saturated with **carbon dioxide**. The degassed water collects in a sump at the base of the tower. After degassing, the CO_2 content is normally less than 5 ppm.

Where the alkalinity is reduced to only 1 ppm (as $CaCO_3$), the pH level is approximately 5.6; for 10 ppm alkalinity, the pH is approximately 6.6. Because of the acidic nature of the degassed water, it is customary to raise the pH level to perhaps 7.0 to 7.5 using raw water or caustic soda, as appropriate, before proceeding to any further conditioning stages.

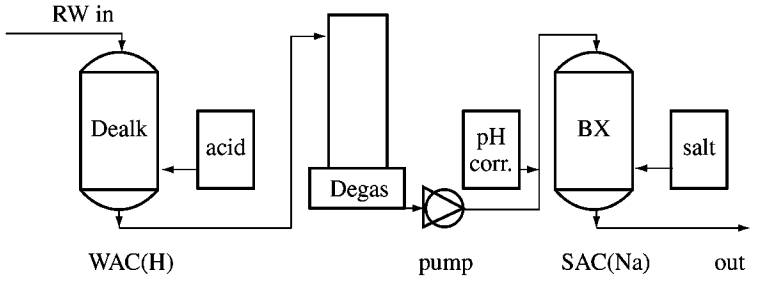
Some examples of dealkalization processes are provided below:

- **Dealkalization by SAC(H)/Degassing:** The hydrogen form cation resin exchanges all cations, converting bicarbonates to carbonic acid, which is removed by degasser. The effluent is both softened and dealkalized but acidic, thus requiring neutralization. Additionally, the TDS of the treated water is reduced by an amount equivalent to the alkalinity originally present.

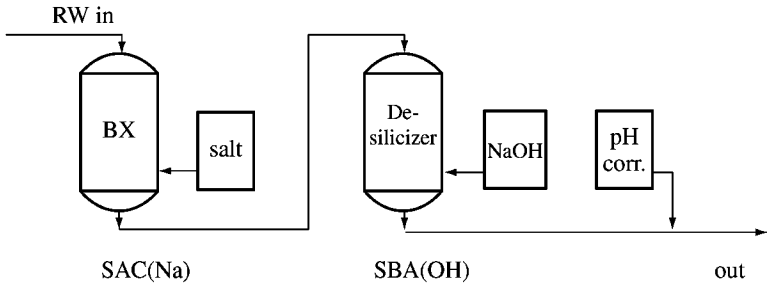
  Where the supply water is of *low hardness* but *high alkalinity* (the major contributor to alkalinity is **sodium** rather than **calcium**), neutralization by a small addition of RW *before* the degasser adds back a small amount of calcium but no further alkalinity. Where the supply water is of *high hardness* and *alkalinity* but has lower levels of **chlorides** and **sulfates**, neutralization *after* the degasser, using caustic soda, is the preferred practice.

  NOTE: If caustic is added before the degasser, sodium carbonate alkalinity is produced.

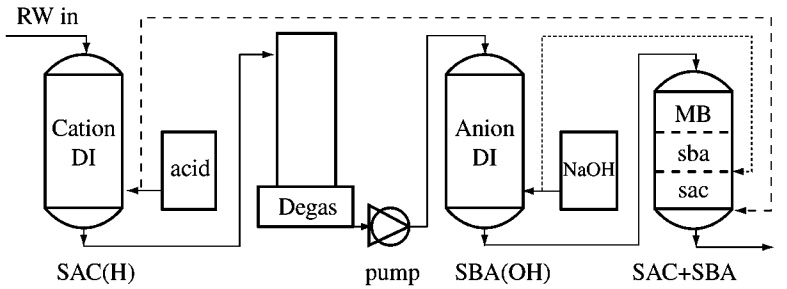
- **Dealkalization by WAC(H)/Degassing**: This process is excellent for waters high in alkaline hardness and reduces the treated water TDS by an amount equivalent to the alkaline hardness originally present.



a



b



c

Figure 9.3 (a), Dealkalization by WAC(H)/Degas/BX softening by SAC(Na); (b) BX softening by SAC(Na)/Desilicization by SBA(OH); and (c) demineralization by SAC(H)/Degas/SBA(OH)/MB.

Where the supply water is high not only in alkalinity but also in nonalkaline hardness ($CaCl_2$, $CaSO_4$, etc.), then, in practice, the process includes a subsequent **softening** stage (i.e., **WAC(H)/Degassing/BX**). The weakly acidic cation removes only the weakly ionized salts such as **calcium bicarbonate** [$Ca(HCO_3)_2$], so the BX process is employed to remove all remaining nonalkaline hard-

ness salts, providing fully softened water. To ensure that regeneration is based on dealkalizer exhaustion, the BX is sized to provide 5 to 10% additional capacity.

Correction of pH level via caustic soda (after the degasser and before the BX) is standard practice. Because both acid regeneration and caustic pH correction are practiced, it is usual to isolate the plant from the mains by providing a break tank. The full plant therefore tends to be *break tank, RW booster pump, acid measuring tank, WAC, degasser, degassed water booster pump, pH correction,* and *BX*. A schematic layout of this type of plant is shown in Figure 9.3a.

NOTE: Hydrochloric acid is usually employed as a regenerant to avoid risks of calcium sulfate formation when using sulfuric acid. (If H_2SO_4 is used, it must not exceed 0.8% w/w strength.) HCl can be used at 120% of theoretical to obtain the maximum capacity and quality, but at the expense of some mineral acidity during the early part of the run. Therefore it is prudent to operate at only 100% of theory, which provides minimal alkalinity leakage and loss of capacity.

The benefit of WAC over SAC is the extremely high exchange capacity and lower (almost theoretical) regeneration efficiency. There is some additional cost in capital equipment and higher resin prices, but this is more than compensated for by lower operating costs. Weak acid cation resin capacity is flow-sensitive, so flows must match design criteria. The overall dealk/degasser/BX is the most popular IX process of its kind in the world today, followed by BX/SBA(Cl).

- **Dealkalization/softening by single vessel stratified bed WAC(H)/BX/Degassing:** In this top-down process the WAC (H) resin is stratified on the SAC (Na) bed, which produces fully softened and dealkalized water with no mineral leakage. There are two stages of regeneration: *acid* followed by *salt* (with an intermediate rinse). The salt has no effect on the WAC but replaces the SCA (H) with Na. This process has the benefit of a small footprint due to the use of a single vessel, but operating costs are higher.
- **Dealkalization/softening by SAC(H)/BX/blend/Degassing:** This process is very suitable for water sources of variable hardness and alkalinity levels and ratios. It passes a portion of the RW through the SAC (H) and the balance through a BX (the process is called **split-stream dealkalization and softening**). The first vessel removes all cations, producing **mineral acidity**, while the BX replaces all

cations, producing sodium salts, such as **sodium bicarbonate**. Upon blending, mineral acidity reacts with sodium bicarbonate to produce a neutral salt and further carbonic acid.

Both IX units remove hardness salts, and by splitting the RW stream based on incoming water analysis and treated water needs, any level of alkalinity can be produced. As in other dealkalization processes, the treated water TDS is reduced proportional to the alkalinity removed.

- **Dealkalization by SBA(Cl):** The use of chloride anion exchange for the dealkalization of naturally very highly alkaline waters for boiler MU is very popular because it involves no acid regenerant or acid-resistant equipment. Consequently, it is a safe process from a handling perspective, capital costs are significantly reduced, and the salt regenerant is inexpensive. The drawback is that there is *no reduction in TDS* and consequently, in process boiler applications where there is limited CR, the costs of BD are high and quickly outweigh the savings in capital costs.

  In practice, as softening is also required, the process train is **BX/SBA(Cl),** and salt brine provides the regenerant for both units. Also, the quantity of SBA (Cl) regenerant is increased by 5 to 10% through the addition of NaOH solution to improve regeneration efficiencies.

9.3.1.3.2 Desilicization Processes It becomes increasingly necessary to remove or control silica as boiler operating pressures rise. Where IX processes are considered, at *lower pressures* softening or dealkalization are often provided, and at *higher pressures* demineralization, in some form, becomes the norm. However, at *medium pressures* (say, 300–650 psig), it is not generally necessary to go to the expense of demineralization, and yet some control over silica is often necessary. Consequently, softening followed by silica removal may be considered as a suitable process.

- **Softening and desilicization by BX/SBA(OH):** This process tends to be suitable when RW sources are relatively low in TDS and where BW cycles of concentration may reach 30 to 50 times or more. Under these circumstances, the BW silica content may exceed normal operating limits (approximately 90 ppm SiO_2 at 300 psig, reducing to approximately 30 ppm SiO_2 at 650 psig). The desilicization process is low in capital expenditure because an acid-resistant plant is not required. The regenerant for both units is caustic soda (Na for the SAC in the BX and OH for the SBA desilicizer).

The BX converts all cations to **sodium** and the desilicizer exchanges all anions, including silica, for **hydroxyl ions**, thus effectively changing the treated water into a dilute caustic solution. This is normally a suitable proposition for boiler MU because the FW pH level typically required at these presssures is 8.5 to 9.5. A schematic layout of this type of plant is shown in Figure 9.3b.

9.3.1.3.3 Demineralization Processes As in dealkalization, there are various IX demineralization process configurations possible depending on the nature of the supply water, the final water quality needs, and the operating preferences. Demineralization may take place in anywhere from one to four vessels per train, depending on the specific purification process.

Where silica and carbon dioxide removal is necessary, the anion unit should contain SBA (OH) resin, and the degasser should precede the anion.

- **Demineralization by SAC(H)/WBA(OH):** Removes virtually all TDS *except* silica and carbon dioxide. The weakly basic anion cuts operating costs through a significantly enhanced capacity and reduced regeneration demands. However any **sodium slip** from the cation unit passes through the anion and increases the conductivity of the treated water.
- **Demineralization by SAC(H)/Degassing/WBA(OH):** Removes virtually all ionic TDS and carbon dioxide, but not silica. It is a cost-effective process.
- **Demineralization by SAC(H)/WBA(OH)/Degassing:** Removes virtually all ionic TDS and carbon dioxide, but not silica. It is a cost-effective process.
- **Demineralization by SAC(H)/SBA(OH):** Removes virtually all TDS, including carbon dioxide and silica. The TDS in treated water is normally below 2 to 4 ppm. Conductivity is below 10 to 15 μS/cm, but this depends on the degree of sodium slip from the cation. Any slip is converted to **sodium hydroxide** in the anion unit (**salt splitting**), causing a sharp increase in conductivity and increased silica solubility. The lack of a degasser drains the anion unit capacity and requires increased caustic for regeneration.
- **Demineralization by SAC(H)/Degassing/SBA(OH):** Removes virtually all TDS, including carbon dioxide and silica. The degasser reduces the loading on the anion exchanger. Silica is reduced to 0.02 to 0.15 ppm SiO_2.

- **Demineralization by SAC(H)/WBA(OH)/Degassing/MB:** Removes virtually all TDS, including carbon dioxide and silica. When the RW is high in chlorides and sulfates, the use of a weakly basic anion reduces both the operating costs and the size of the MB.
- **Demineralization by SAC(H)/WBA(OH)/Degassing/SBA(OH):** Removes all TDS, including carbon dioxide and silica. This is perhaps the most cost-effective method overall of producing higher quality water when the anion loading is high. The bulk of the anions are removed in the weakly basic unit, leaving the final strongly basic resin to remove silica, any residual carbon dioxide, and remaining anions.
- **Demineralization by SAC(H)/Degassing/SBA(OH)/MB:** Removes all TDS, including carbon dioxide and silica. This is a standard process where the RW is high in alkalinity and silica. The MB acts as a polisher with infrequent regeneration. **Silica** and **sodium** are both reduced to below 0.02 ppm as $CaCO_3$. Conductivity is below 0.1 μS/cm. A schematic layout of this type of plant is shown in Figure 9.3c.

9.3.2 Membrane Purification Technologies

There are a number of membrane technologies commonly available and, although a brief description of the primary types is provided below, we are primarily interested in *reverse osmosis* (RO).

- **Microfiltration** is widely used in food and beverage industries for clarification, concentration, recovery, and sterilization applications, and for pharmaceutical and biological use. Microfiltration pore sizes range from 0.1 to 10 μ. Some microfilter designs employ **ceramic membranes** (also used in *ultrafiltration*, although the pore sizes are much smaller), which are constructed from multiple layers of *sintered alumina* to form an asymmetric monolithic element. Ceramic membranes have the benefits of operating at any pH level, up to 300 °C and 150 psig.
- **Ultrafiltration** (UF) is used for the separation and concentration of macromolecules and colloidal particles. Ultrafiltration membranes usually have larger pore sizes than RO membranes, typically 1 to 100 nanometer (nm). Operating pressures are generally low (30–100 psig). Applications include electropaints, gray water, emulsions, oily wastes, and milk, cheese, and protein processing.

  Ultrafiltration is particularly useful as a pretreatment "roughing" filter for the type of ion-exchange resin beds and EDR technologies

used for processing boiler MU water. In UF systems, small molecules such as water, simple sugars and alcohols, and all ionic species, pass through the membrane (usually constructed of *polysulfone*, *polyethersulfone*, *polyvinylidene fluoride,* or *polyamide*), but resin foulants such as **colloidal** and **polymerized silica**, **oils**, **fats**, and **bacteria**, as well as larger molecules are retained.

- **Nanofiltration (NF)** is employed for applications such as water softening, the removal of color, dyestuffs, and **trihalomethanes**, and treating contaminated ground water. The NF pore size is approximately 1 nm. This process does not reject dissolved substances as well as RO. Nanofiltration systems are sometimes called **membrane softeners** because they reject double-charged hardness ions (Ca/Mg) but are not so effective with single-charged ions (Na/K). They are widely employed in the drinking water industry.
- **Hyperfiltration (Reverse Osmosis)** is a form of membrane distillation or desalination (desalting) operating with membrane pore sizes of perhaps 1 to 10 Angstrom units. The various individual RO component technologies have improved tremendously over the last 20 to 25 years, and resistance to fouling and permeate output rates have benefited. Nevertheless, all RO plants remain susceptible to the risk of fouling, and adequate pretreatment and operation is essential to minimize this problem.

  Globally, the RO process is extremely widely used for bulk drinking water, boiler FW, and ultrapure water for electronic and pharmaceutical applications. Membranes are available in a number of sizes, although for any good-sized application an 8-inch diameter by 40-inch length membrane is the norm. Reverse osmosis membranes are now available that offer higher salt rejection rates at lower applied operating pressures, thus lowering the energy requirements of the process. For example, 8-inch membranes, having, say, 440 square feet of surface area, can typically produce 11,500 gallons per day at a 99% salt rejection rate. The difference between *low pressure*, *standard,* and *premium membranes* may be a 40% drop in operating energy costs.

9.3.2.1 Reverse Osmosis

Reverse osmosis is at its best when employed to significantly reduce TDS in water. It is effective at all levels of TDS, although not to the same degree of efficiency. As such, it is often entirely suitable as a purification technology for boiler MU water. It is efficient at removing

colloids, bacteria, and higher molecular weight organics (unlike IX). However, RO will not remove **carbon dioxide** unless the water is made alkaline. Also, it is seldom as effective as IX for removing **silica**. This deficiency can sometimes be improved by the use of selective *silica deposit control agents* (polymers).

Where replacement of pretreatment and purification equipment is required, RO is often the technology of choice to supplant softeners, dealkalizers, and demineralization units, whether the boiler is a 100 psig unit for HVAC, an aging 1,000 MW fossil-fuel power plant, or a 2,000+ MW supercritical supplying power and district heat.

The basic reason for this migration trend is that RO systems are now available from a host of OEM manufacturers in a wide variety of relatively low-cost, skid-mounted, modular forms, and are excellent at bulkwater TDS removal.

Some OEMs produce many of the individual components required for their systems totally in-house, although there are also a large number of specialist equipment manufacturers for pressure vessel (PV) housings, high pressure pumps, and the like. World-class membrane manufacturers include **Trisep**, **Koch**, **Fluid Systems**, **Hydranautics**, **Du Pont**, **Osmonics,** and **Dow**.

See Figure 9.4a for a schematic layout of a carbon filter, softener, and RO train, and Figure 9.4b for a schematic layout of an ultrafiltration, RO, and mixed-bed polisher train.

9.3.2.1.1 Primary Components of RO Most larger RO plants for boiler FW application are comprised of four key component areas:

- High-pressure pumping system
- Pressure vessels (PVs) and membranes
- Frame, distribution piping, and controls
- Pretreatment (e.g., filters, softeners, or antiscalents) and posttreatment (permeate flush and clean-in-place systems)

A good estimate is that each of these areas comprise 25% of the capital cost. Membrane replacement and a pump rebuild may be required after 5 to 6 years, so some provision for these costs should clearly be made because they are not insubstantial.

Softening and raising the pH level of the RW tends to increase the rejection rate of **silica**, **boron,** and **total organic carbon** (TOC). It also tends to increase silica solubility, thus reducing the risk of silica deposition on the membrane.

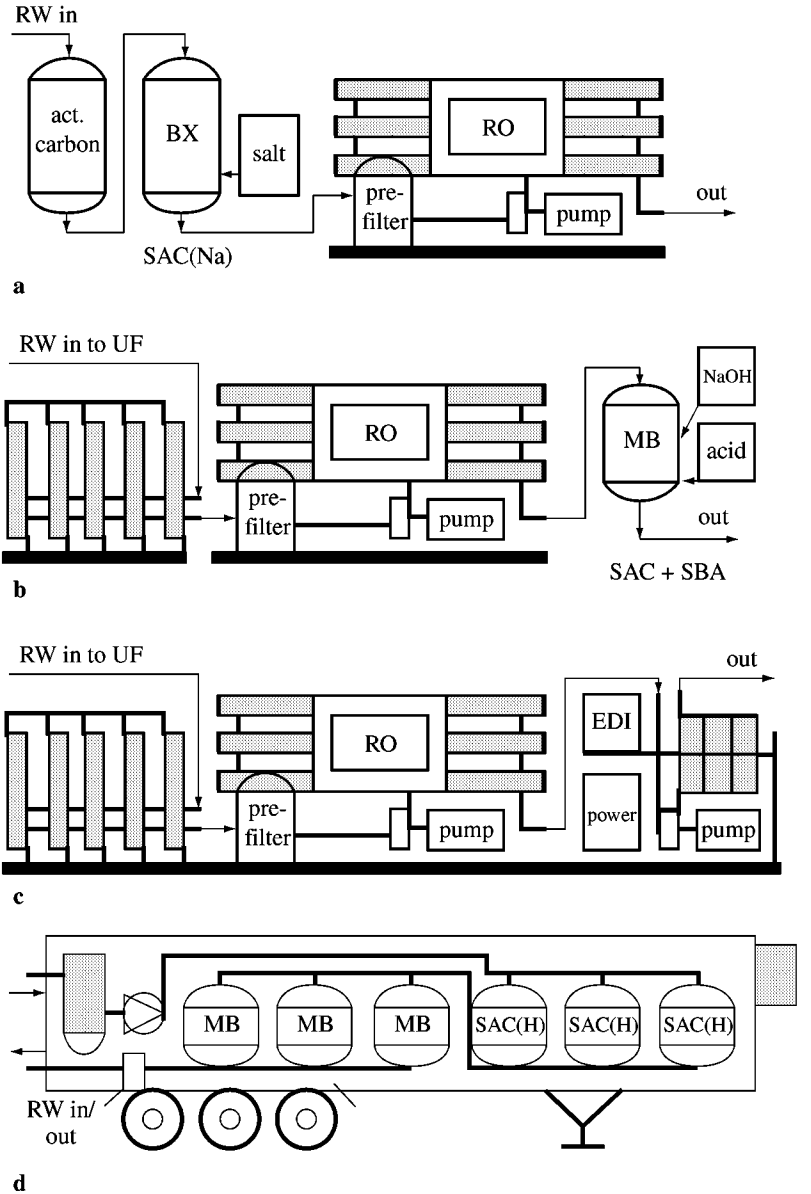


Figure 9.4 (a) Basic pure MU water scheme: CF/BX/RO; (b) very pure MU water scheme: UF/RO/MB; (c) very pure, membrane only, MU water scheme: UF/RO/EDI; (d) mobile condensate polishing scheme: bag filter SAC(H)/MB.

Typically, RO plants require a RW supply with a **salt density index** (SDI) of below 3.0 (ideally below 1.0) to prevent excessive membrane fouling.

The heart of an RO plant is the **semipermeable membrane**, which rejects salts dissolved in the pressurized raw water (RW) and permits "pure" water to pass. Where a salt solution and a pure water source are separated by a membrane, natural **osmotic pressure** forces the transfer of pure water across the membrane to dilute the salt solution until equilibrium is reached. In an RO plant, the applied pressure is much greater than the natural osmotic pressure, and a percentage of the RW passes through the membrane, producing high-quality permeate with typically 92 to 99% of the original TDS removed, while the balance of the RW (the **brine reject** or **concentrate water**), containing a much higher level of TDS, is rejected to waste. Membranes for water treatment applications are constructed in two basic design configurations (**hollow fiber permeator** and **spiral wound cartridge**) and of several different materials, such as:

- **Cellulose acetate** (CA), which is of poor chemical stability, tends to hydrolyze over time, is subject to biological attack, and can operate at only a limited pH range of 3.0 to 6.5 at 0 to 30 °C. It is widely available at low cost and is tolerant of continuous low-level chlorine exposure, such as is found in many city waters.
- **Aromatic polyamide** (*aramid*) is of excellent chemical stability and can operate over a pH range of 4.0 to 11.0 at 0 to 35 °C. It is not susceptible to biological attack, but cannot tolerate chlorine.
- **Thin film composite** (TFC) is an ultrathin barrier membrane on **polysulfone** support layer, of good chemical stability. It has a wide operating pH range of 2.0 to 12.0 at 0 to 40 °C, but cannot tolerate chlorine. TFC membranes are better at rejecting silica than CA membranes.

There are two primary membrane designs:

- **Hollow fiber modules**, or *permeators,* are precisely machined units containing bundles of fine hollow fibers, positioned parallel to and around a perforated center FW tube, with only one or two bundles per pressure vessel. They are widely used for brackish and seawater supply applications. Hollow fiber modules exhibit a low **flux rate** (*permeate flow per unit membrane per unit time*) and foul easily, but

they tend to have high **conversion factors** (*the percentage of feed flow converted to permeate*), typically 50 to 55%. This makes them suitable for both small and large RO systems. They are easy to troubleshoot, and the bundles are easy to change in the field.

- **Spiral-wound elements** are the first choice for many industrial boiler FW applications because of lower element cost, robustness, good response to cleaning, and a high flux rate. (They are also widely used for brackish and seawater applications.) Spiral-wound elements are made from two or more permeate leaves wrapped around a plastic, permeate discharge tube. Each leaf consists of two flat-film membranes, supported and separated by a polyester fabric or plastic net material. Single spiral-wound elements rarely exceed a 10 to 15% conversion factor, however, so designers provide a variety of parallel and series system configurations to overcome this problem and produce efficient RO systems. This low conversion factor makes spiral-wound RO systems less suitable for very small systems and may make troubleshooting of individual elements difficult in multielement PVs.

9.3.2.1.2 Design Considerations for RO Reverse osmosis plants are typically assembled onto carbon steel or stainless steel frames using permutations of components from the hundreds of individual "standard" stock items commonly available, including a wide range of membranes, each with their own range of design features and applications.

This interchangeability of components gives rise to very many RO configuration permutations and provides for a wide flexibility in system design, but may make the direct comparison of competing RO plants difficult at times.

Most RO systems, however, can be categorized according to the three broad classes of water they are designed to treat, as noted below:

NOTE: Generally speaking, the higher the TDS of the RW source to the RO, the higher the applied pressure required to produce a constant permeate water TDS. Also, for practical reasons, the rate of permeate recovery tends to decrease with increase in source water TDS.

- **Tap water.** As city water, mains supply, and the like, tap water is typically under 1,000 to 2,000 ppm TDS. It requires an RO plant operating with an applied pressure of 150 to 300 psig and permeate recovery rates of 80% down to perhaps 50% of the RW supplied

(although very small, simple design RO units may produce only 15 to 30% recovery rates).

- **Brackish water.** Usually associated with salty water, brackish water TDS levels range from 2,000 to 20,000 ppm or more. Most industrial sources of RW supply may be well water, surface waters, or the like, but do not specifically have to contain high levels of sodium chloride. The RO applied pressure required is from 250 to 600 psig, and the permeate recovery rates are typically 60% down to perhaps 40%. There is a tremendous variety in so-called brackish water sources, and correct membrane selection and other design criteria are critical to manufacturing an efficient RO plant.
- **Seawater** is increasingly being used as a RW source for industrial water, drinking water, and boiler FW because of both a lack of suitable alternatives in some areas of the world and constantly improving RO water production–cost ratios. Seawater TDS levels vary around the world, from approximately 36,000 to more than 45,000 ppm. As TDS levels increase, the RO applied pressure requirement typically may increase from 800 to 1000 psig or more to maintain recovery rates (usually 25–35%).

Most larger RO plants for commercial or industrial boiler plant applications work with city or brackish water sources of some description and tend to use perhaps *spiral-wound*, **thin film composite polyamide** (TFC) cartridges of 40-inch length and 4- to or 8-inch diameter, fitted into GRP or stainless steel PVs holding from two to seven cartridges. The required permeate volume for any given RW analysis is achieved by linking one or more PVs together, thus collectively containing sufficient numbers of the most suitable membrane cartridge.

When assessing the potential for RO as an RW treatment option and reviewing "standard plant" specifications, it is important to compare the rated **membrane capacity** against the available water source to be treated. Reported RO membrane capacity may be based on a temperature of 77 °F (25 °C) and perhaps only a 1,000 ppm TDS RW. This level of TDS may be much lower than the potential source of RW and the temperature also may vary, making corrections necessary. At *lower* water temperatures, the viscosity *increases* and the RO flux *decreases* (output *decreases*). This increases the number of membranes required to provide the desired flow.

It is almost always necessary to obtain one or more computer projection printouts from RO plant manufacturers to ensure correct RO

design, with the best balance of variables (e.g., RW feed flow rate, brine reject water flow rate, recovery rates, flux rates, and maximum applied pressures). If, for example, flux rates on first-stage membranes are higher than the manufacturer's recommendations, membrane fouling is likely to occur.

Various RO design techniques can be employed to maximize permeate quality or recovery percentages. **Double-pass** RO plants permit the permeate to flow through a second set of membranes to further reduce the final permeate TDS, thus providing very high quality water, suitable for high pressure boiler plants, and providing a competing technology to **deionization** or **ED**.

Concentrate recycle RO plants allow some of the brine reject water to recycle back through the plant, which improves the permeate recovery rate. (The reduced flow of brine reject water does of course have a proportionally higher TDS level.) Various types of high pressure, corrosion-resistant pumps are used, including *multistage*, *centrifugal* and *plunger pumps*, each with their own benefits and area of application.

Energy recovery turbine systems are available for very high pressure RO (seawater) plants, whereby brine reject water under high pressure can be used to spin an energy recovery turbine, reducing the RW hp requirements (and hence electricity costs) by 30 to 32%.

Standard features of larger RO plants often include:

- **Automatic periodic membrane flush** to remove recent surface deposits, thus reducing the risk of membrane fouling
- **Permeate flush tank**, from which an initial fill of permeate water is used to flush out the system on shutdown
- **High permeate TDS water reject system** to maintain permeate quality
- **Programmable logic control** (PLC) systems, which automatically control the RO process to sustain output and quality specifications
- **Clean-in-place** (CIP) units for periodic membrane washing and removal of *organic deposits*, *inorganic scales,* and *biofouling*

Reverse osmosis plant are always subject to an insidious and gradual loss of permeate volume output or quality deterioration due to membrane fouling. The rate of decline is strongly influenced by the input RW quality. Therefore, any and all features, such as those above, that can be employed to delay the onset and degree of fouling and extend membrane life are to be recommended.

9.3.2.1.3 Pretreatment Requirements for RO In addition to CIP and other fouling control systems constructed within the main body of the RO frame, it is *vital* that all due consideration be given to providing the correct kinds of RO RW pretreatment, in order to further reduce risks of membrane fouling. Options for pretreatment include:

- **Aeration**: may be required to remove any hydrogen sulfide in the RO RW, such as may be found in deep well waters.
- **Chlorine addition** may be a prerequisite to sanitize the RO RW supply line and oxidize any organics (followed by *dechlorination* using sodium bisulfite after the *MM filtration* stage). Where chlorine is required, it is usual to provide a 20- to 25-minute contact period by means of a temporary storage tank. This is followed by a repressurization pump system.
- **Ion-exchange softening** is sometimes specified to remove all calcium and magnesium ions or to at least reduce the hardness salts down to a tolerable level. Reverse osmosis system design engineers may limit the percentage of permeate recovery by controlling the brine reject water quality LSI to a level of perhaps +1.6 to +1.8. The use of softeners may be beneficial in allowing higher permeate recovery rates. Similarly, those chemical additives using more sophisticated technologies also tend to permit higher design recovery rates by extending the LSI of the brine reject to, say, +2.0.
- **Acid addition** is commonly used to convert bicarbonates into the more soluble sulfate salts to reduce the alkalinity of the RO RW, which in turn modifies the brine reject water LSI. Sometimes it is required to maintain the pH level within membrane limits. Additionally, it may be used in conjunction with a reduced dosage of antiscalent chemical to reduce the overall chemical treatment costs.

  Acid is normally added into the low pressure RO RW supply line and requires a static mixer to ensure rapid and even distribution of the acid. Problems may occur at this point if the mixing is not complete before the resultant lower pH level water reaches the high-low pH controller because the controller will shut off the RW feed supply to the RO (to avoid damage to the membrane), only to open the valve again moments later, resulting in pulsating feed supply. The problem may be due to use of an electronic pump set for high pump-stroke length and low stroke frequency, rather than the other way around (low pump-stroke length, high frequency), which permits

"slugs" of acid to enter the RW feed line. Or it may be due to a poorly sized static mixer or insufficient pipe run before the pH controller. **Extreme care is needed when using sulfuric acid, as not only does it present a serious personal danger from mishandling but also it can damage membranes beyond repair.**

- **MM pressure filtration** has tended to become standard practice in many parts of the world as RO pretreatment and is designed to reduce the maximum RW turbidity below 1 NTU and the SDI below 5.

  Some designers push the RW flow rate through MM filters to as high as 15 gal/sq ft/min. This generally is too high and may lead to poor filtration. Also, the resultant cost savings due to a reduced filter size is seldom warranted because the filter is a relatively minor cost as a proportion of the entire RO scheme. A better maximum is perhaps 9 to 10 gal/sq ft/min, with 5 to 6 gal/sq ft/min being preferred.

  Where an RO is designed for continuous operation, dual or triple MM filters are required (similar to ion-exchange softening) and, because an RO plant can operate only at a fairly constant RW supply rate (it is basically either *on* or *off*), additional water must be available for filter backwashing.

- **Cartridge filtration** is standard practice incorporating a 5μ cartridge filter unit in the RW supply line, immediately before the RO high-pressure pump, as a final preventative measure. (This is usually more to protect the pump against damage, rather than the membranes.) Typically, these filters need replacing every 1 or 2 months, which may present an unforeseen maintenance cost. An alternative to these cartridge filters are **bag filters** with *multilayer, progressive depth,* and *bypass-transport systems*. These bags hold the dirt *inside* the bag, rather than on the *outside* as with cartridge filters, and have 10 to 20 times the holding capacity of conventional cartridges. They also may be reusable.

- **Chemical dosing** is also generally required and most often employs a polymeric organic antiscalent on a continuous basis and proportional to the supply of RW fed to the RO. Chemical dosing may often be used in conjunction with softening or acid dosing. The selection of a chemical product is determined in part on the brine scaling indices permitted for any particular RO design.

9.3.2.1.4 Chemical Treatments for RO Antiscaling and Antifouling Duty Typically, organic antiscalents supplied for RO applications are 35% w/v "active" materials and dosed at between 2.5 and 6 ppm chemi-

cal product, (depending on the composition of the source water analysis). Some chemical products are available at up to 50% w/v "activity," but they require a proportionally lower dose rate. Higher strength chemicals are often extremely viscous, which may present pumping problems.

*NOTE: The **calcium carbonate** limit that RO system designers typically require is +1.6 to 1.8 LSI in the **concentrate** or **reject water**, and the **calcium sulfate** design limit typically calls for a maximum reject water **saturation ratio** of 1.6 to 1.8 times solubility product.*

Some chemical product manufacturers claim a need for higher dose rates (say, up to 10 ppm) to minimize scaling and fouling tendencies, but this is usually prohibitively expensive and may well prove to be an overdose.

Powdered inorganic chemicals are also available as low-cost alternatives. There is consequently a wide range of chemical treatment formulations used, including those based on the following products:

- **Polyphosphate**, often with *sodium chloride*. This is a very "low-tech" approach, relying primarily on the **threshold** mechanism of polyphosphate to prevent calcium carbonate deposition at the membrane–water interface. Products based on this simple technology are subject to many limitations and probably are inappropriate to most industrial RO situations.

  An example of a multiphosphate approach to formulations is:

Multiphosphate antifouling RO formulation	
SHMP	28.0%
STPP	6.0%
MSP	12.5%
Water	53.5%
	100.0%

- **Acrylic acid** and **sodium polyacrylates.** Products based on *acrylic acid* or *sodium polyacrylates* are commonly used and generally perform satisfactorily on source waters with a TDS below 2,000 to 3,000 ppm and without specific additional risk factors such as a high silica content (say, above 20 to 25 ppm as SiO_2). Typically, available polyacrylate products tend to be those of approximately 2,000 to 4,500 MW, with the lower MW materials generally being the most efficient scale inhibitors. Some polyacrylate products are

marketed as being suitable for "almost all RO applications," which undoubtedly is an ambitious claim.

A premium antiscalent product in this group is **Flocon® 100** from **Great Lakes Chemical Corporation** (originally the brand was owned by Pfizer, then Ciba-Geigy, then FMC). *Flocon 100* is a 35% w/w, 2,000 MW acrylic acid polymer. An alternate and much more concentrated product is **Good-Rite® K-752**, a 62.5% w/w, 2,100 MW acrylic acid polymer from **Noveon, Inc.** (formerly BF Goodrich Company).

- **Polyphosphinocarboxylic acid**. Products based on this chemical tend to be suitable for brackish waters up to say 10,000 to 15,000 ppm TDS and where high **sulfates** are present (200 to 300 ppm as SO_4). A feature of this type of chemical is not only its ability to deal effectively with carbonate and sulfate scaling in higher TDS waters but also the fact that it has dispersant properties of benefit in physically moving potential foulants away from the membrane surface.

  A premium antiscalent product in this group is **Belros® 435** from **Great Lakes Chemical Corporation** (originally the brand was owned by Ciba-Geigy, then FMC). *Belros 435* is a 35% w/w, phosphinoacrylic acid–based product, similar in chemistry to the **Belclene® 161** (also from Great Lakes) used as a high-stability dispersant in BW internal treatment formulations.

- **Polymaleic acid (PMA).** The use of chemicals based on PMA and some derivatives has become standard practice for very brackish waters and seawater distillation processes around the world, where the TDS may reach 50,000 ppm TDS, or where total hardness levels exceed 500 to 1,000 ppm $CaCO_3$. Its use in RO systems is growing. However, PMA has limited dispersing properties and may need to be formulated with a dispersant chemical to provide satisfactory performance with some RO designs. It is claimed that PMA is also a successful **silica** deposit control agent and therefore may be incorporated into formulations where this is a problem.

  A premium antiscalent product in this group is **Belros® 285** from **Great Lakes Chemical Corporation** (originally the brand was owned by Ciba-Geigy, then FMC). *Belros 285* is a 35% w/w, neutralized PMA-based product.

In addition to these products, many other specialist chemical formulations are available. For example, products may incorporate a proprietary polymer for very high *silica* control or blend in a *carboxylate/*

sulfonate/nonionic functional terpolymer for high *iron* control (**Flocon® 260** is an example of an iron control polymer.)

Formulations for these problems tend to require higher dose rates, which may prove expensive for some applications. An example is a 2 ppm dose rate of specific **silica polymer** product for every 10 to 12 ppm SiO_2, or a 10 to 20 ppm dose rate to RW for blended products that incorporate an **iron control** terpolymer.

Additional controls for high silica waters are:

- Limit total silica to below 240 ppm as SiO_2
- Limit Fe and Al to 0.05 ppm total metal in the supply water source
- Limit magnesium *times* silica to 220,000 for pH levels under 7.5 and 110,000 where the pH level is over 7.5 (where magnesium is reported as $CaCO_3$ and silica as SiO_2)

9.3.2.1.5 Chemical Treatments for RO Cleaning Duty There is a very wide range of chemical treatments and services available for on-site cleaning and membrane regeneration. The **G.E. Betz** company, **Argo Scientific**, for example, is a major supplier of this kind of technology. Also **Avista, KingLee, Professional Water Technologies**, and others.

The type of membrane cleaning required depends on both the type and degree of fouling experienced, but typically it is either *organic* (**bacterial slimes, natural organics**, or **process foulants** and **nutrients**) or *inorganic* (**silica, carbonate, sulfate**, or **phosphate deposits**).

Organic contamination often becomes much worse when nutrients are absorbed onto carbon filters and the bed acts as a support for biological growth, thus necessitating the need for periodic disinfection programs. **Formaldehyde** and **sodium bisulfite** are commonly employed for this purpose, although **2,2-dibromo-3-nitrilopropionamide** (DBNPA) is generally more succesful. DBNPA is produced by Dow Chemical Company as **Dow®** *Antimicrobial 7287* (20% solution) and *Antimicrobial 8536* (5% solution).

Formaldehyde is used at 0.1 to 1.0% concentration for system disinfection and long-term storage. *Sodium bisulfite* may be used at 500 ppm for 30 to 60 minutes per day to control biological growth. It also may be used at a 1% strength for long-term membrane preservation. A **hydrogen peroxide** and **peracetic acid** combination is also sometimes used (0.2% maximum concentration of hydrogen peroxide).

Disinfection of heavily fouled systems generally requires a lowering of the pH level to between 6 and 7 and addition of DBNPA at 25

to 50 ppm of 5% for several hours in a soaking and recirculating action program. **Isothiazolinones** are also employed.

NOTE: The above applies to composite polyamide and polyvinyl derivative membranes. Do NOT use chlorine, which is suitable only for cellulose acetate membranes.

Removal of general organic fouling is best achieved by alkaline cleaning based on **caustic**, **EDTA**, and a surfactant such as **sodium dodecyl sulfate** or **sodium lauryl sulfate**.
Removal of *iron* and *inorganic scales* is achieved by the use of formulations containing 5 to 10% of acids such as **phosphoric** or **citric acid**.

Membrane cleaning generally requires a 3 to 5% strength cleaning solution to be circulated through the PVs for 1 hour at a flow rate of perhaps 35 to 40 gpm (130 to 150 l/m) for 8-inch membranes and 9 to 10 gpm (35 to 40 l/m) for 4-inch membranes. After cleaning, drain and flush the cleaning tank, refill with chlorine-free rinse water, and rinse to drain for several minutes, or as long as is needed to remove all traces of foam and cleaning residues.

An example of a combination formulation is:

Low pH RO membrane cleaner	
NaOH commercial 46% solution	2.0%
Citric acid	10.0%
EDTA commercial 38%	5.0%
Sodium lauryl sulfate	2.0%
Sodium polyacrylate	2.0%
Water	79.0%
	100.0%

Where **membrane storage** is required after cleaning, a 5% **glycerol** solution containing 0.5 to 1.0% weight *formaldehyde* often is employed. The membranes should be totally immersed, with all inlet and outlet valves closed. This solution should be changed every 30 days.

9.3.3 Purification by Electrodemineralization

Electrodemineralization includes a number of subset technologies, including **electrodialysis** (ED), **electrodialysis reversal** (EDR), and **electrodeionization** (EDI). Electrodeionization is sometimes termed **continuous electrodeionization** (CEDI) or **continuous deionization** (CDI).

9.3.3.1 Electrodialysis

The ED process is a reliable, membrane-based, electrically driven demineralization technology that is more than 50 years old. It is suitable for the production of basic pure water from lower TDS supply sources. Commercial ED units consist of hundreds of individual cells in a *modular membrane sandwich arrangement*, bounded by electrodes and linked to a direct current (DC) rectifier-controller. The total treated water flow is a function of the number of cells in the ED unit.

Each cell contains three water-filled compartments, with the central compartment having both a **cation-** and an **anion-permeable membrane**. When current is applied, a cathode (−) in the first compartment attracts cations (+) from the central compartment through the cation-permeable membrane. The negatively charged membrane (a *polysulfonated cross-linked polystyrene*) prevents the migration of negative anions. Simultaneously, the anode (+) in the third compartment attracts anions (−) from the central compartment through the anion-permeable membrane. The positively charged membrane (*cross-linked polystyrene holding a quarternized amine*) prevents the migration of positive cations. Consequently, water flowing in the central compartment becomes progressively deionized.

Electrodialysis is a particularly economic process for low-salinity waters when compared to RO because, although the initial capital cost may be 10 to 15% higher, it generally requires no pretreatment, it produces a higher recovery rate (around 80–85%), it has a lower operating and maintenance cost, and the membranes last twice as long (up to 10 years).

Electrodialysis is, however, not so efficient when dealing with water having a high *calcium* loading bacause there is a tendency for scaling to occur. Mechanisms to overcome this include devices to periodically reverse current polarity, or **sodium cation ion-exchange softening** may be employed. Where higher TDS waters are encountered, **hydrogen cation ion-exchange softening** can be utilized. High-silica waters can be treated by the prior addition of alkali which ionizes the silica for removal at the anion membrane. Electrodialysis is a viable "roughing" process for mixed-bed demineralization, thus high-purity water may be produced by means of a BX/ED/MB train.

9.3.3.2 Electrodialysis Reversal

Electrodialysis reversal is a development of ED and is also employed either in its own right for the production of basic pure water or as a component in a larger system for very pure or ultrapure water.

This technology is programmed to provide frequent short periods of electrical polarity reversal (say, 1 minute every 30 minutes or so), which reduces the scaling potential inherent in the ED process when treating higher TDS waters. Although the pure water flow rate is discontinuous, recovery rates are higher (typically 90%), silica removal is also high (typically over 90%), and the need for additional capital to provide basic pretreatment (e.g., softeners) or pH level adjustment is avoided. Also, the membranes can tolerate low levels of chlorine (say, 0.3–0.5 ppm Cl, as typically present in city waters), unlike the TFC membranes commonly found in "packaged" RO plants.

As with ED, RO, and other membrane techniques, the primary operational cost of EDR is that of pumping water through the system, and pumping costs are proportional to the TDS of the incoming water. Cost for the actual electrodialysis is low.

Electrodialysis reversal can produce water of below 5 μS/cm conductivity (sometimes lower) the membranes are essentially impervious to fouling, and the polarity reversal provides an excellent membrane and cell compartment cleaning mechanism. This technology lends itself to an all-membrane approach (**triple-membrane process**) for the production of high-purity water employing UF/EDR/RO.

9.3.3.3 Electrodeionization

A further derivative of ED is EDI, whereby cell pairs are arranged in plate-and-frame format with each cell-pair being provided with a *cation-* and an *anion-permeable membrane* and spacers to permit water flow. The cell-pair consists of a **dilute stream compartment** (producing a high-purity *product water*) and a **concentrate-reject stream compartment** (producing a high TDS stream flowing to waste). Cell-pairs are again bounded by a set of DC current electrodes, as in the ED process, and are grouped together as an **EDI stack** with a parallel-flow arrangement to provide the desired flow rate.

The novel design of EDI is that the dilute stream compartment contains mixed IX resin (similar to an MB polisher), which provides two important benefits:

1. When incoming TDS is initially high, the resins (in salt form) provide additional electrical conductivity, which aids ion movement across the membranes.
2. When the dilute stream becomes progressively depleted in ions, the increase in mass transfer resistance at the water-resin boundary

layer provides for the development of high-voltage gradients. This causes the *lysing* of water molecules into hydrogen (H^+) and hydroxyl (OH^-) ions, which in turn serves to continuously regenerate the resin without the need for acid or caustic.

Although EDI may be used as a process for the production of basic pure water, in practice it suffers from the organic fouling potential of resins and the scale fouling potential of ED when higher TDS water sources are utilized. Appropriate pretreatment is therefore required. As a consequence, EDI is best suited for the production of very pure and ultrapure water by acting as a polisher to follow bulk water deionization by RO. Under these circumstances, it competes with both double-pass RO and MB units.

Where low to moderate flow rates are encountered, it is likely that EDI is less expensive when both capital and maintenance costs are considered. For high flow rate systems, there is little to choose between the three technologies, although the EDI does have the advantage of not producing acid or caustic waste streams.

Reverse osmosis/electrodeionization (RO/EDI) plants are available in modular form to suit any desired input-output water quality and flow rate. A RO/EDI system should be capable of producing high-purity water of perhaps 5 to 20 μS/cm conductivity (0.2–0.05 MΩ/cm resistance). By providing a second EDI stack in series, it is possible to achieve even higher quality of up to 0.055 μS/cm conductivity (18.2 MΩ/cm resistance).

Both RO/EDI and RO/MB have overtaken twin-bed DI/MB as preferred technologies, and it is likely that RO/EDI will eventually emerge as the ultimate winner because of its lack of any chemical requirements for regeneration. However, there are several excellent EDI designs currently available in the marketplace from world-class manufacturers. As these designs are different, they do not all provide identical performance under specific operating conditions. Examples of EDI designs/manufacturers are:

- **Ionics, Inc.**
- The **E-Cell**™ (from **General Electric**) as used by **Osmonics, Inc.**, **Chemitreat PTE** (Singapore), and others
- **U.S. Filter** with its **CDI**™ system
- The **XL**™ from **Electropure, Inc.**, which finds its way into systems produced by several original equipment manufacturers (OEMs).

Optimum performance is generally provided by a totally integrated but modular system with a high performance/low flux EDI design to provide for maximum rejection of *silica* and other troublesome elements such as *boron*. See Figure 9.4c for a schematic layout of a UF/RO/EDI train.

9.4 POST-BOILER CONDENSATE CONDITIONING

The various mechanisms for external (i.e., nonchemical) treatment of steam condensate are essentially concerned with restoring the condensate to a previous high-purity condition by removing contaminants resulting from corrosion and steam utilization. Technologies employed range from the use of simple **bag filters** and **strainers**, through self-cleaning **pressure leaf filters** and **electromagnetic separators**, to **condensate polishing** (which, in practice, may be quite complex and simultaneously encompass both filtration and ion-exchange processes).

Where condensate is severely contaminated due to excessive iron content, high pH levels, or alkalinity, carryover, or process intermediaries, it is common practice to consider dumping the condensate. This obviously is not a particularly sensitive course of action in an era of high-profile environmental issues and is additionally expensive because of disposal costs and the loss of valuable heat content.

Today, there is almost always a relatively low-cost, "low-tech" solution available as a viable alternative to dumping condensate. Most CR recovery or polishing solutions employ a fixed installation, but mobile retrofits increasingly are being provided by outsourced service providers. See Figure 9.4d for a schematic layout of a mobile boiler condensate conditioning plant.

9.4.1 Condensate Strainer–Filter Units

As with the basic pretreatment of MU water for smaller boiler plants applications, various **sieves**, **screens**, **cyclones,** and **strainers** may sometimes be used for filtering condensate, essentially to remove iron oxide particles. Also **bag**, **cartridge**, and **candle filters** (with or without a **filter aid**) are employed (see section 9.2.4.4).

Because of the HW temperatures involved, *metal basket strainers* tend to be popular, but *in-line bag filters* using high temperature–resistant bags are also widely used. The benefit of strainers and bags over cartridges and candle filters is that where iron oxide transport is the primary problem, the iron particles are trapped inside and cannot fall off or otherwise recontaminate the CR system.

9.4.2 Electromagnetic Filtration and Electromagnetic Separation (EMF and EMS)

Electromagnetic separators sometimes are used as "filters" for the removal of **ferromagnetic iron oxide** from condensate and thus prevent it from being transported back to the boiler.

NOTE: EMS systems are legitimate technologies and should not be confused with magnetic devices proposed for pretreatment of MU water.

EMS equipment generally consists of an electrical control unit and one or two tall cylindrical pressure vessels of small diameter, permanently installed in the condensate line. Each vessel is filled with iron balls, needles, or plates, and strong magnetic fields develop in the interstices between the balls when an electric current is applied. Iron oxide particles are attracted to the magnetic poles (where the magnetic intensity is greatest) and are retained; in addition, the applied magnetism reduces the physical spacing and filtration of particles takes place.

Periodically, the current is switched off, which demagnetizes the equipment, and the filter is backwashed to remove trapped iron oxide.

The efficiency of EMS systems is adversely affected by the presence of oils and greases in condensate, and this should be removed by other means.

Clearly, the efficiency of the EMS is dependent on the magnetic character of the transported iron oxide and other particles, and if they are not magnetic, then no filtration occurs. Unfortunately, it is not unknown for installed EMS units to be ignored or their true function to be in doubt. Consequently, they may have to operate for long periods without any effective backwash or maintenance program being provided.

9.4.3 Condensate Polishing

For almost all larger boiler plants, the relatively high cost of producing MU water and the heat energy inherent in condensate deems it necessary, wherever possible, to recover for reuse condensate to the greatest extent.

Recycled condensate often is of higher quality than FW, although in facilities with extremely long runs of steam and condensate lines, or where amine treatments are not used (e.g., some food processors, hospitals, drug manufacturers, etc.) and in high heat-flux power boiler plants, there is a tendency for the condensate to be contaminated by **iron** and smaller levels of **copper**.

NOTE: Where iron and copper corrosion products develop in CR systems, typically the copper is approximately 10% of iron level.

Under these conditions, it often makes sound economic sense to install a **condensate polisher** as a means of restoring condensate quality and recycling it. Although the concept of condensate polishing encompasses equipment such as strainers and electromagnetic separators, in common parlance it has come to mean the restoration of condensate to a previous high-purity condition by means of *ion-exchange resin* technology.

There is a very wide range of condensate polishers available, and it is important to properly understand the background to the problem to make the correct selection and ensure the economic viability of the project.

Essentially, condensate polishers are pressure vessels containing ion-exchange resins in some form and configuration. There are primarily two different types of duty performed:

- **Filtration of suspended solids,** primarily particulate iron oxides. Here the preferred media/process is *powdered-resin precoat filters.*
- **Exchange of ionizable materials,** primarily dissolved iron. Here the preferred media/process is *resin bead deep-bed polishers.* Resins may be operated in different cycle modes and where, for example **ammonia**, **morpholine,** or **AVT** programs are employed, specific operating conditions are necessary to avoid adverse effects of the ammonia anion cycle.

In perhaps more than 70% of cases, the major problem is the physical removal of particulate matter, but also in more than 70% of cases, the polishers selected utilize resin bead deep-bed polishers, which are not necessarily the optimum solution.

- Powdered resin filtration is approximately 90 to 95% efficient, whereas deep-bed polishers are perhaps 60 to 70% efficient.
- The ion-exchange capacity of a powdered resin precoat filter is perhaps only 6% that of a deep-bed polisher.
- Polishers may be installed either *full flow* (in-stream) or *partial flow* (side-stream). Flow rates vary enormously, anywhere from 1 to 100 gpm/sq ft of surface area, although 25 to 50 gpm/sq ft is typical.

Although condensate polishers mitigate corrosion problems in the condensate, FW, and boiler, it should be remembered that they do noth-

ing to protect the steam piping. As in most areas of water treatment, there is a chain of cause and effect. Where condensate corrosion problems develop, it may be advantageous to go to the root cause and eliminate it rather than embark on an expensive condensate polishing project.

9.4.3.1 Powdered-Resin Precoat Filters

Powdered resins systems (80–600 mesh) typically operate at lower pressure drops, generate less waste water, take up less space, and cost much less when compared to deep-bed polishers. However, they operate at only 3 to 4 gpm sq ft (although the filter element area is large) and are designed to be disposable, so that the powdered resin must be replaced whenever the bed is reconditioned. Sometimes inert resins or cellulose-based fibers are used either in place of powdered resins or as a premix, where they function as both *filter aids* and *absorbents*.

In large power plants, precoat filters are traditionally used only when freshwater condenser cooling is employed because brine or seawater condenser leaks would quickly overwhelm the limited ion-exchange capacity available. They also are commonly used for continuous filtering of suspended corrosion products under variable power load conditions and when frequent boiler startups are necessary.

NOTE: Condensate from the startup of large boilers often contains up to perhaps 40 to 50 ppb Fe, 150 to 200 ppb Cu, and 4 to 5 ppb Ni.

It has been observed that, in some older power plants designed with precoat filters installed ahead of deep-bed polishers, the deep-bed units were not needed because of effective filtration by the precoats. Where precoat filters are installed, it is sometimes the practice to make use of **hydrazine** (or hydrazine substitute) to convert **amorphous iron oxides** to **crystalline iron oxides**, which enhances filtration.

9.4.3.2 Bead Resin Deep-Bed Polishers

A wide variety of polishing bed designs are employed. These may be either externally or internally regenerated and supplied with various grades of *tough gel* or *macroporous* resins. The selection of a deep-bed (i.e., 36–48 inches, 900–1,200 mm deep) polisher depends on the specific operating circumstances. Types of polishers include:

- **Cation polishers:** Where there is a need to keep costs as low as possible, some process industries (such as the pulp and paper industry) use SAC gel resins in the sodium (Na^+) form to remove iron.
- **Cation/anion polishers:** Co-generators and other lower heat-flux power generators often employ cation/anion polishers. The ratio tends to be 60% cation to 40% anion.

NOTE: Ratios of resins used for CP must also consider the cost element because anion resins are considerably more expensive than cation resins.

- **Cation/MB polishers:** This is a common combination in general process industry. The lead cation unit is generally in the hydrogen ion (H^+) form, which protects the MB against iron fouling and provides for very effective Fe and Cu removal. This arrangement is also very useful in the power industry, where there is a risk of condenser in-leakage, as the lead cation unit, which tends to take most of the Fe and Cu removal load, provides additional protection to the MB units.
- **Naked MB polishers:** This is an industry term covering both stand-alone and noncoated MB polishers. They are widely employed and are generally designed for larger installations, operating typically in banks with a 36-inch (900 mm) bed depth, 40% SAC resin and 60% SBA, 60 to 130 BV/hr, and external regeneration. The 40/60 resin volume ratio provides close to a 1:1 equivalent mix.
- **Cation/anion/MB:** This is a traditional design but is often too expensive and basically unnecessary when the primary demand is for particulate filtration.
- **Triple polisher:** This design is sometimes found in high heat-flux, nuclear, and near-critical power units. Typically, the lead cation is in the hydrogen form with an 11- to 12-inch (280–300 mm) bed depth. The intermediate polisher is an anion bed in the hydroxyl form with a 15- to 16-inch (380–400 mm) bed. The trailing unit is a second H^+ cation polisher with an 11- to 12-inch bed. MB beaded resin polishers may typically be operated in either **hydrogen-hydroxide cycle** or **ammonia-hydroxide cycle**. Each operating systems has its benefits and disadvantages:
- **Hydrogen-hydroxide cycle:** Provides the most favorable operating cycle and results in near neutral water of very high quality. The (hydrogen form) *cation* resin converts **silica** to **silicic acid** (H_2SiO_3), which is then retained by the (hydroxide form) *anion* resin but breaks through first due to its very weak nature. Poor

regeneration, aging anion resin, and high water temperature all lead to early *silica breakthrough*, so the (expensive) anion resin must be kept in good condition. In hydrogen-hydroxide cycles, the **carbon dioxide** is unaffected and is ejected with any air. Where **ammonia** is present from **AVT**, **amines**, **hydrazine,** or just plain ammonia addition, the cation resin is rapidly exhausted by exchange with the ammonium ion (NH_4^+), so additional cation capacity is required.

- **Ammonia-hydroxide cycle:** Running costs are less than in hydrogen-hydroxide cycle, with cations operating in the ammonia form, but quality is compromised. Where ammonia is present and the hydrogen form cation resin becomes fully converted to the ammonia form, ammonia eventually breaks through into the effluent (**ammonia break**). The higher operating pH level causes complex silica compounds to be formed that that become more difficult to remove. Where carbon dioxide is present, **ammonium carbonate** is formed, and the carbonate can quickly exhaust the anion resin. Anion resins also may operate in an **amine cycle** form (from **morpholine**) with similar benefits of low operational cost but resulting in potential problems caused by the high operating pH level of the CP.

So far, the discussion has primarily centered around the contamination of condensate due to iron and copper. However, large process industries often produce condensate containing **oil**, **grease,** and other contaminants, and these must also be removed because they are not only damaging to the boiler plant waterside, but may can adversely affect condensate polisher components.

The type of oil-removing equipment used may be *alum* or *caustic precoat* **coke filters**, **diatomaceous earth filters**, or **coalescing filters**, sometimes employing *oleophilic resins* as oil strippers. **Phenolic formaldehyde demulsifiers** are also sometimes used.

Deep-bed condensate polishers are commonly used for nuclear reactor power plants. Due to the extreme operating conditions, the resin is sometimes taken out of service as frequently as every 3 weeks for ultrasonic cleaning. This process removes the iron oxides and other particulates filtered out by the resin media.

Deep-bed condensate polishers also are used to provide protection against **condenser in-leakage** in fossil-fueled sub- and supercritical boilers. Where condenser in-leakage occurs, it results in contamination of the condensate by Na, Cl, Ca, and Mg.

NOTE: Condenser in-leakage may develop during winter heating loads when velocities are high. The increase in velocity adds to condenser stress, occasionally resulting in ***circumferential fatigue cracking*** *of condenser tubes and weeping of condenser water. In fossil fuel–powered boilers, this may result in calcium deposits, overheating, and tube failure. Where it is not possible to shut down the boiler, a modification to the internal water treatment program to include chelant chemistry (possibly at a reduced boiler loading) may provide a "temporary fix" until a proper repair can be scheduled.*

Where condenser in-leakage develops in nuclear reactor boilers, **calcium hideout** may occur in the reactor water, implying that some leakage of Ca and Mg may have occurred from the condensate polishers. There also may be some **sodium** or **chloride leakage** from the polishers (under good conditions, the polisher effluent usually contains below 0.1 ppb Na).

Clearly, this problem is serious because the minimum polisher effluent quality is determined by the maximum impurity concentration in reactor water, and current industry guidelines limit chloride and sulfate to below 5 ppb in reactor water.

The sulfate level in the reactor water is a good indicator of sodium contamination, and it may be observed by an increase in the pick-up rate of sulfate, from perhaps 0.2 to 0.4 ppb to 3 to 4 ppb.

9.5 NOVEL PRETREATMENT OXYGEN REMOVAL TECHNOLOGIES

All boiler operations utilize some form of basic chemical oxygen scavenging, and most larger facilities also employ mechanical deaeration prior to chemical polishing. Alternatives to these essentially independent techniques exist and have been steadily gaining in popularity for application in larger boiler plants and in other types of ultrapure water applications.

Since the early 1980s a chemical-equipment combination technique has been available utilizing *hydrazine* and a *catalytic carbon filter bed*, and since the early 1990s *gas transfer membranes* have entered the market and proved to be particularly effective.

9.5.1 Oxygen Removal Using Catalyzed Carbon Bed Technology

Despite the potential carcinogenic nature of **hydrazine,** it is still widely employed as an oxygen scavenger and is effective at higher temper-

atures where the reaction rate is rapid. At lower water temperatures, the reaction slows down and traditional catalysts do not provide any significant improvement.

Ecolochem, Inc. has taken the standard process and utilized a carbon bed as a true catalyst, thus enabling the oxygen scavenging reaction to take place rapidly and to full completion at variable water temperatures. The patented **DEOX®** process further utilizes downstream ion-exchange to remove any carbon leachables. Deoxygenated water is then stored using a bladder, nitrogen blanket, or other standard engineering technique to ensure that reoxygenation does not occur.

The oxygen removal reaction using a **carbon bed catalyst** is as shown below:

N_2H_2	+	O_2	→	$N_2\uparrow$	+	$2H_2O$
hydrazine		oxygen	*carbon bed*	nitrogen		water

The treated water typically contains less than 10 ppb oxygen and may be below 3 to 4 ppb.

9.5.2 Oxygen Removal Using Gas Transfer Membrane (GTM)Technology

Celgard LLC markets **Hoechst Celanese** modular membrane technology (**Liqui-Cel®**) to remove both oxygen and carbon dioxide from boiler MU water and FW.

These **gas transfer membranes** or **membrane contactors** employ microporous polypropylene hollow fiber membranes arranged in a modular design. Oxygenated water flows on the shell side of the hollow fibers, and a strip gas (such as nitrogen) or a vacuum is applied to the inside (*lumenside*), with the hollow fibers acting as a support medium for intimate contact between the water and gas phases.

The aqueous stream is at higher pressure than the strip gas (or vacuum) and fast diffusive transport of dissolved gases takes place. Gas transfer membrane technology is suitable for deaeration of boiler feed, building water, and other applications, and produces water with DO levels down to 1 ppb O_2.

Interestingly, both GTM and DEOX processes can be combined with other technologies, such as RO/GTM/EDI and RO/GTM/DEOX/DI/MB.

10

INTERNAL TREATMENT PROGRAMS

As discussed in the introduction, boiler water (BW) treatment programs enable the waterside chemistry of boilers and their associated systems to be controlled within certain agreed upon and relevant parameters and specifications. They provide a countermeasure against a wide range of adverse conditions that may strive to develop and hinder efficient boiler operation or cause serious damage.

Various **internal treatment chemicals** are employed as components of these programs. In all but the simplest or lowest efficiency boiler plants, they complement *external conditioning processes* (pre- and post-boiler) and *BD control* by providing a "fine-tuning" or "polishing" function.

There is an extremely wide range of potentially useful chemical treatments available, and for any boiler system, proper selection, utilization, and control are vital considerations that may largely determine the ultimate success of the overall program. These chemicals usually are organized by *type of compound, function, mode of action,* or similar classification, but, because many chemicals are multifunctional in character, may be used in either a primary or supplementary (**adjunct** or **conjunctional treatment**) role, and additionally may be branded (especially many modern polymers) or otherwise disguised, such classifications may be quite arbitrary.

This chapter discusses the various types of programs available, the chemicals employed, their properties, and the ways and means by which they can be incorporated into BW formulations, with relevant examples. In addition, recommendations and guidelines for control are provided.

Chapter 11 completes the discussion on internal treatment programs with information on **program primary support chemicals,** including *oxygen scavengers* and *condensate treatments* (vapor phase inhibitors) and **adjuncts.**

Sludge conditioners were originally regarded as *program support chemicals* (especially older chemistries such as **starches** and **lignins**), but with the advent of modern *deposit control agents,* such as **phosphinocarboxylic acids,** these materials are now incorporated in all-polymer and all-organic programs and various blended multifunctional programs and are discussed later in this chapter.

The various formulatory raw materials necessary to produce these programs are available as either commodity, semispecialty, or specialty chemicals worldwide. Although today all water treatment companies, no matter their size or location, have virtually the same opportunities for materials sourcing, some depth of experience is required to provide blended (and branded) products that have genuinely beneficial properties and the potential for competitive differentiation.

In addition, it should be stressed that all these functional products and their various chemistries are merely tools to be employed in the operational management and maintenance of boilers and BW surfaces. To maximize the potential benefits available, these BW treatment programs must be utilized in the most suitable way, which in turn requires:

- The optimum application methods and points of feed
- Appropriate monitoring protocols
- Correct interpretation of analytical results
- Constructive advice on waterside chemistry control

There is no substitute for proper training and experience in the application of BW programs. Both operators and service company field personnel must be able to demonstrate competence so that the potential for added value is realized.

10.1 OUTLINE OF INTERNAL TREATMENT CONTROL AND PROGRAMS

Functional areas within the boiler plant system where internal chemical treatments are employed include:

- **Corrosion control.** This area includes control over various general and specific forms of **pre-boiler** and **boiler section corrosion.** Broadly speaking, functional corrosion control encompasses a combined approach that includes:

- Oxygen scavenging
- Maintenance of passivated films
- pH level and alkalinity control

For any specific boiler plant, good control also may necessitate the use of certain other *conjunctional treatments* to support the primary chemical treatments such as **sodium nitrate** for protection against *embrittlement.*

- **Scale and deposit control.** This is primarily control over the deposition of *hardness salts* and other scale-forming minerals.
- **Sludge control.** This includes control over a variety of *foulants.*
- **Carryover control.** This necessitates control of *foam, priming (surging), misting,* and *process contaminants.*
- **Specific contaminant control.** This includes control over a wide range of specific problems associated with the presence of relatively high levels of *silica, iron, copper, sodium, chloride, caustic,* and the like. (Quantifying "high level" is case-specific because it varies with each ion or compound and operational circumstances, although starting-point recommendations are provided by the American Society of Mechanical Engineers, British Standards Institution, and other authorities.)
- **Steam/condensate line corrosion control.** Control over steam and condensate line corrosion requires the control of *oxygen, carbon dioxide (carbonic acid),* and *ammonia.*

NOTE: Control over some problems, such as the supersaturation of dissolved solids, short-term and long-term overheating, and boiler priming (surging), relies as much on good operation as on the use of appropriate chemical treatments.

10.1.1 Types of Internal Treatment Program

Internal treatments for BW are chemical formulations having potentially beneficial single-function, dual-function, or multifunctional effects. Globally, many thousands of BW formulations are available, and for the most part, each may be loosely classified into one or another type of commonly recognized chemical program, as described below.

- **Anodic inhibitor programs:** These programs are based on ingredients such as *nitrite, silicate,* and *molybdate* chemistries and usually are formulated as light-duty multifunctional programs in HW heating and LP steam boiler systems.
- **Tannin programs:** These programs are based on blends of certain *natural* or *synthetic tannins* and provide **oxygen scavenging, passivating,** and **sludge-conditioning functions**. They can be formulated into complete multifunctional programs or simple blends that are supported by other functional chemicals or programs. Tannin programs are employed in a wide range of commercial and industrial boiler types and pressures.
- **Coagulation and precipitation programs:** These programs are extremely widely used and employ various types of *phosphates* as a precipitant to provide control over the unwelcome deposition of hardness scales. *Carbonate* and *polysilicates* were once commonly used, although less so today.
- **Chelant programs:** These programs are commonly prescribed for both FT and WT boilers and are employed either as replacements for or used in combination with *phosphate precipitation programs.*
- **All-polymer programs:** There are many types of all-polymer programs, Today, with the wide availability of many specialty polymers, they are proposed for application in almost every type of boiler from the smallest to the largest. They typically are multifunctional products, replacing *precipitation programs* and *sludge conditioners* and providing control over specific problems such as **iron transport**, which can affect many boiler plant facilities. In practice, many all-polymer programs are more properly called **all-organic programs** because they may contain organics, such as phosphonates, that are not necessarily polymers.
- **Chelant-, phosphate-, or polymer-based, dual- or multifunctional programs:** Every water treatment service company offers several types of dual- or multifunctional programs based on either *chelant* or *phosphate,* together with *polymers* and related organics. The various combinations of chemistry, ratios of primary ingredients employed, and activity levels offered have given rise to an enormous number of permutations. Some early program examples included *carbonate/polymer, phosphate/carbonate, chelant/phosphate,* and *chelant/phosphonate.* The development of more modern polymers led to *chelant/polymer* and *phosphate/polymer,* and multifunctionals such as *chelant/polymer/phosphate* and *alkali/polymer/phosphate.*

- **Coordinated phosphate programs:** These programs are formulated to avoid the formation of *hydroxyl alkalinity* **(free caustic)**. They tend to be employed in higher pressure WT boilers and require very careful control. Variants include **congruent control** and **equilibrium phosphate treatment**.
- **All-volatile programs (AVPs):** These programs are employed in higher pressure boilers (generally power boilers) and utilize only volatile chemicals, such as *ammonia, amines* (such as *diethylhydroxylamine* or DEHA), and other **vapor phase inhibitors** (VPIs).

In addition to full- or part-treatment formulations **(boiler compounds)**, the art and science of BW treatment usually requires the application of certain *primary functional chemicals* and *secondary functional chemicals (adjuncts)* to provide a comprehensive program, as outlined below:

- **Program primary support chemicals** encompass **oxygen scavengers** and **condensate treatments**.
  - Oxygen scavengers include *inorganics* such as **sodium sulfite** and *organics* such as **hydrazine**.
  - Condensate treatments include *neutralizing amines* such as **morpholine** and *filming amines* such as **octadecylamine** (ODA).
- **Adjuncts** include **antifoams** and **defoamers**, some **problem-specific polymers**, and **alkalinity boosters**.
  - Antifoams control foam after it has developed and defoamers are preventative products. Natural products such as **castor oil** and **linseed oil** were long ago replaced by synthetics including **polysilicones** and **polyethoxylates**.
  - Problem-specific polymers include **terpolymers**, used for *iron dispersion, iron transport,* and *silica control.*
  - Alkalinity boosters are typically based on **potassium hydroxide** or **sodium hydroxide**.

10.1.2 Historical Perspective of External and Internal Treatments

From the earliest days of steam production, it was recognized that a complementary combination of external and internal water treatment was a vital requirement of boiler operating practice. The justification for investment in external conditioning was (and continues to be) based

on specific boiler operating conditions and economic factors. Regardless of the degree of FW purification achieved, however, protective treatments were almost universally used as insurance against corrosion, scale, and other potential sources of problems.

With lower heat-flux ratings and higher ratios of internal water volume to heating surface than is the norm today, complex external treatment was not always necessary; where deemed necessary, it was often limited to basic *sedimentaion* or *filtration* techniques employing **inorganic coagulants** and **flocculants,** typically followed by the use of **natural zeolites** (see sections 9.2.3.1 and 9.2.5 for additional information).

Filter alum (aluminum sulfate) $Al_2(SO_4)_3 \cdot 18H_2O$ was widely used as an external coagulant (at pH values of 5.8–6.8) and continues to be available today. It was generally supplied as alum bricks, but usually is supplied today in granular or concentrated liquid form.

NOTE: Filter alum does not always contain 18 molecules of ***water of crystallization****; some grades are only 14 to 16* H_2O.

Filter alum reacts with *carbonates, bicarbonates,* and *hydroxides* to produce a variety of reactions, as shown below:

$Al_2(SO_4)_3$	+	$3Ca(HCO_3)_2$	→	$3CaSO_4$	+	$2Al(OH)_3$	+	$6CO_2$
aluminum sulfate		calcium bicarbonate		calcium sulfate		aluminum hydroxide		carbon dioxide

$Al_2(SO_4)_3$	+	$3Na_2CO_3$	+	$3H_20$	→	$3Na_2SO_4$	+	$2Al(OH)_3$	+	$3CO_2$
aluminum sulfate		sodium carbonate		water		sodium sulfate		aluminum hydroxide		carbon dioxide

$Al_2(SO_4)_3$	+	6NaOH	→	$3Na_2SO_4$	+	$2Al(OH)_3$
aluminum sulfate		sodium hydroxide		sodium sulfate		aluminum hydroxide

Copperas *[green vitriol* or *ferrous sulfate* ($FeSO_4 \cdot 7H_2O$)] was also employed as an external coagulant (at pH values of approximately 7.7). It forms a turbid precipitate, and when oxygen is present (as is usual), a slimy precipitate of *ferrous hydroxide* also may form in addition to *ferric hydroxide:*

$$\underset{\text{ferrous sulfate}}{FeSO_4} + \underset{\text{calcium bicarbonate}}{4Ca(HCO_3)_2} + \underset{\text{oxygen}}{O_2} + \underset{\text{water}}{2H_2O} \rightarrow \underset{\text{ferric hydroxide}}{4Fe(OH)_3} + \underset{\text{calcium sulfate}}{4CaSO_4} + \underset{\text{carbon dioxide}}{8CO_2}$$

In the 1940s, copperas began to be replaced by **sodium aluminate** ($NaAlO_2$), which is formed by dissolving the precipitate aluminum hydroxide [$Al(OH)_3$] in a strong solution of NaOH. It does not lower the pH level and is still used today in the form of prills and beads. It is used in conjunction with *sodium carbonate* or *sodium hydroxide* and breaks down again in solution forming $Al(OH)_3$, which precipitates together with any Ca, Mg, Na, and Si, resulting in flocculated sludges such as **calcium aluminum silicate**, a natural zeolite. In addition, *magnesium* in solution forms the flocculant **magnesium aluminate** ($MgAl_2O_4$).

NOTE: Sodium aluminate is sometimes given the formula $Na_2Al_2O_4$.

External treatment also meant the removal of calcium and magnesium hardness by *zeolite softening* using either a variety of *silcate-based,* natural zeolites [such as **analcite**, ($Na_2Al_2Si_4O_{12}{\cdot}2H_2O$)], or manufactured *carbon zeolites.*

Silicate zeolites could be regenerated by salt (similar to modern BX softening), although the exchange capacity was low, generally from 2,000 to 12,000 grains per cubic foot, depending on their porosity and resistance to clogging, fatigue, and physical breakdown.

Zeolite softeners were limited in application because of their potential for rapid fouling by *ferric hydroxide* or *calcium carbonate,* and a narrow operating pH range of 5.8 to 8.3 was therefore preferred to minimize this problem.

*NOTE: **Sodium aluminosilcate zeolites** are still widely used as anticaking agents, as desiccants, and for removing hardness from wash waters.*

Carbon zeolites could be regenerated by acid and were forerunners to modern SAC(H) resins. They proved useful at removing iron, as well as *calcium* and *magnesium,* and did not contribute any silica to the water.

Internal treatment was often based on recommendations dating from the 1920s. The deliberate addition of **soda ash** *(sodium carbonate)* to the BW to form carbonate sludges (rather than, say, sulfate scales) that could be removed by BD was a common program. If unde-

sirable **sulfate scale** was to be avoided, the quantity of *carbonate* required was calculated based on the level of sulfates present in the BW and the boiler gauge pressure.

It was expected that an **eggshell thickness of scale** would form, but that it would be relatively soft and easily removed (despite normally containing some *silicate* and *sulfate*). However, a disadvantage of this method of internal control was that the carbonate degraded to form *carbon dioxide,* and at higher pressures the rate of breakdown was so great that the necessary carbonate reserve required to prevent sulfate scale often could not be maintained. (Never mind the danger to the steam and condensate lines from the production of carbon dioxide and ultimately carbonic acid.)

Phosphates were proposed as alternatives to carbonate because they did not break down. Various types were employed, including **mono-** (NaH_2–), **di-** (Na_2H–), and **trisodium phosphate** (Na_3PO_4), with or without water of crystallization.

Also introduced was **sodium metaphosphate [Hagan® phosphate** or **Calgon®**, represented at the time by the formula $(NaPO_3)_6$, although it tends to have a different formula today].

Phosphate selection was based on the relative cost of anhydrous or crystalline grades and the amount of natural alkalinity present in the BW. The quantity of phosphate required could be determined by calculating the hardness present using a **standard soap solution test** (a test in widespread use in the 1970s and still employed today in some countries).

NOTE: Depending on operating conditions, alkalinity, pH level, point of feed, and so forth, when phosphate is present in the BW, calcium salts precipitate primarily as either insoluble ***tricalcium phosphate*** *[$Ca_3(PO_4)_2$] or* ***hydroxyapatite*** *[$Ca_{10}(OH)_2(PO_4)_6$].*

It was well understood that in high-magnesium waters, the magnesium could be removed as the *hydroxide* [$Mg(OH)_2$] provided adequate caustic was present in the BW, and that *silicate* could be removed by the presence of additional magnesium.

Colloidal silicates, zeolites, and sodium aluminate were also employed as internal treatments. However, sludges and scales were often voluminous and not easily removed, and the need for **sludge conditioners** became necessary. Navy engineers had used natural **tannin** extracts from *chestnut,* South American *quebracho,* and *cutch* (Indian mangrove) since the 1890s for this purpose, as well as **lignins**. These organic materials began to be used for land boilers also. Other

organic sludge conditioners employed were extracts from boiled dead animals, **potato peelings** (colloidal starches), **cornstarch, flaxseed oil, agar-agar** (from seaweed), and **sodium humate**. Later developments included **sodium polyacrylate** and **sodium polacrylamide–acrylate**, which was perhaps the first *copolymer* used and was really a flocculant rather than a dispersant-type sludge conditioner.

Oxygen removal to reduce corrosion was equally important, and external treatment employing new designs of *open FW heaters* and *deaerators* were supplemented by internal oxygen scavengers—first **tannic acid,** then **glucose derivatives** and **sodium sulfite**. Interestingly, claims at that time for the level of oxygen reduction were often below the available test methods' limits of detection.

Additional means of reducing corrosion were the use of prepared **steel laths**, which were introduced into the FW system and would preferentially rust, leaving boiler tubes unscathed. **Sacrificial zinc sheet anodes** also were employed, but neither method ensured complete protection of the overall boiler system, and *uniform general corrosion* was often replaced by insidious *localized corrosion.*

Antifoams to reduce the risk of carryover employed emulsions of **castor oil** and similar substances. *Caustic embrittlement* was avoided by the use of **quebracho tannins, chile niter** *(sodium nitrate),* and **salt cake** (sodium sulfate), which was later discredited as an inhibitor.

Typically, chemical formulations were supplied as balls or briquets and dispensed through bypass feeders or hanging baskets. Alternatively, pulverized or powdered treatments were dissolved in water and pumped to FW tanks or added via drip-feed arrangements.

Two examples of powdered products used in riveted boilers are:

Navy Boiler Compound Formulation	***Ingredient by weight***
Secondary sodium phosphate	47%
Soda ash	44%
Cornstarch	9%
	100%

Lancashire Boiler Compound Formulation	***Ingredient by weight***
Quebracho tannin	20%
Hagan phosphate	23%
Soda ash	47%
Chile niter	2%
Sodium lignosulfonate	8%
	100%

10.2 ANODIC INHIBITOR CHEMISTRIES

The potential for electrochemical corrosion in a boiler results from an inherent thermodynamic instability, with the most common corrosion processes occurring at the boiler metal surface and the metal–BW interface (**Helmholtz double layer**). These processes may be controlled relatively easily in smaller and simpler design boilers (such as *dual-temperature, LPHW heating,* and *LP steam boiler systems*) by the use of various anodic inhibitors.

Anodic inhibitor programs are generally single-drum, multifunctional products and commonly include **nitrite** and **molybdate** in addition to other inhibitors and ingredients. The inhibitors provide a corrosion stifling effect resulting from a buildup of corrosion products and by-products on the metal surface.

NOTE: ***Dual-temperature systems*** *provide both HW and chilled water functions and employ common piping for much of the system. Water temperatures range from 34 °F/1.1 °C up to perhaps 250 °F/121.1 °C.*

Low-temperature and low-pressure hot water ***(LTHW/LPHW) systems*** *operate below 250 °F/121.1 °C (equivalent to 29.8 psia/15.1 psig). This is approximately the same as LP steam systems, which operate below a MAWP of 15 psig/29.7 psia (equivalent to 249.8 °F/121 °C).*

Anodic programs *without* a separate oxygen scavenging function are entirely suitable for all these system types, provided makeup (MU) requirements remain consistently low. Where MU water volumes are too high, the risk of oxygen corrosion processes is also high. Classically, this is evidenced by rapid pitting corrosion in boiler tubes.

NOTE: Where MU requirements exceed 5 to 10% of LTHW system volume per month, or 5% of the steam output of LP steam boilers, a separate oxygen scavenger is required. This usually is ***tannin, diethylhydroxylamine (DEHA),*** *or* ***erythorbic acid (isoascorbic acid).***

As MTHW and HTHW system temperatures and pressures rise, so the need to provide softened or deionized FW becomes increasingly necessary, although there is not always a clear cut-off point. Where these systems are supplied with higher quality water, traditional, inorganic *anodic inhibitor chemistries* tend to be replaced by **all-polymer**, **all-organic**, or **all-volatile chemistries** to keep measurable TDS to a

minimum and reduce the risk of unfavorable waterside surface deposits.

Effective metal waterside surface passivation (using **hydrazine, DEHA, tannin,** or similar products) remains an essential requirement of higher temperature or pressure system programs.

Anodic inhibitor programs are not employed for steam boilers operating at over 15 psig. Above this pressure, more comprehensive and problem-specific programs are employed.

*NOTE: **Medium-temperature** and **medium-pressure hot water (MTHW/MPHW) systems** typically operate above 250 °F and below 350 °F/176.7 °C, whereas **HTHW/HPHW systems** may be described as operating above 350 °F and below, say, 450 °F/232.2 °C.*

Apart from *nitrite* and *molybdate,* silicate is commonly employed in anodic inhibitor programs, although seldom as the primary inhibitor. Both silicates and molybdates provide benefits of synergistic inhibition and also help to reduce corrosion risks through softer waters and multimetal systems.

Benzoate can be used as an anodic inhibitor and is effective at preventing waterline attack. **Phosphate** is also sometimes included. **Sodium borate** *(borax)* is usually added to the formulation to provide an alkalinity reserve buffer. Typically, a copper inhibitor such as **benzotriazole** (BTA) or **tolyltriazole** (TTA) also forms part of a formulation and is used to provide *yellow metal* (copper and brasses) protection.

10.2.1 Nitrites

Nitrite-based formulations are available either as 100% powdered or granular products, or as liquids varying from 20 to 40% available sodium nitrite. **Sodium nitrite** ($NaNO_2$) is most commonly used and acts as an **anodic inhibitor** and **passivator**.

Nitrite formulations are employed for both hot and cold water closed loops (and also occasionally for open cooling systems). Unfortunately, nitrite is easily oxidized to nitrate and is very susceptible to microbiological attack (by ***Nitrobacter agilis*** and other microorganisms). Nevertheless, it is a good low-cost passivating inhibitor.

Nitrite-based programs require a relatively high application rate to ensure that all anodic areas within the system are fully protected from the risk of pitting corrosion. Undertreatment exposes anodic areas, which are subject to localized pitting as a result of the concentrating power from surrounding cathodic sites.

As an *anodic passivating agent,* nitrite enhances the formation of magnetite film and produces reducing conditions. It is simple to detect and test, but the high feed level and reserve requirement limit this product to small LPHW and LP steam boiler heating systems.

The specific nitrite reserve required depends on the *system design, cleanliness, metallurgy, leaks, water chemistry,* and *LPHW temperature.* The application rate must be increased when high **chlorides** or **sulfates** are present and further increased with a rise in HW temperature.

- **Dual-temperature** and simple LPHW heating systems typically require 1,000 to 1,300 ppm as NO_2 (1,500–2,000 ppm as $NaNO_2$) when a standard **nitrite/borate/TTA** formulation is employed. (This is about twice the level required for cold and chilled water closed loop systems.)
- LP steam and higher temperature HW heating systems typically require 1,300 to 1,600 ppm as NO_2 (2,000– 2,500 ppm as $NaNO_2$).
- Where *nitrite/molybdate* programs are employed, the nitrite reserve falls to 250 to 350 ppm as NO_2 in simpler systems and 350 to 650 ppm as NO_2 for higher temperature systems.
- Where chlorides and/or sulfates are present, the nitrite reserve (as NO_2) should be six to eight times the chloride (Cl) level and four times the sulfate (SO_4) level.

To obtain optimum results with nitrite in HW heating systems, it is necessary to take precautions, including:

- Good precleaning of the system to expose anodes and provide the opportunity for good initial passivation.
- Inspection of the system to ensure that no regular ingress of oxygen takes place. Use an oxygen scavenger if necessary.

NOTE: Do NOT use oxygen scavengers based on sodium bisulfite or other acid producers with programs containing nitrite because they are incompatible and may present a danger.

- Calculation of system volume to ensure adequate nitrite reserve and, for lower temperature systems, the use of a microbiocide.

NOTE: When feeding to a closed loop HW system, it is always preferable to add product at the highest rate possible to ensure complete passivation,

to make allowances for larger than anticipated system volumes, and to reduce the frequency of further product addition. Some limited overdosing is not detrimental to the system, but underdosing may be disastrous. With very small LP steam systems (which often employ cast iron boilers because of the flexibility in boiler sizing and construction), there is a very real risk that the high reserve of nitrite required will rapidly produce priming and result in BW carryover.

10.2.2 Molybdates

Typically, molybdate-based formulations are liquids having approximately 10% **sodium molybdate** ($Na_2MoO_4 \cdot 2H_2O$) combined with either a lower percentage of *silicate* or a higher percentage of *nitrite.* Sodium molybdate is commercially available as a 41% solution or 100% crystalline powder. Potassium molybdate (K_2MoO_4) is also available.

Molybdate acts as an anodic inhibitor and forms a passivating film composed of a *ferrous-ferric-Mooxides complex,* in the presence of some oxygen. Its use in formulations rapidly increased in the 1970s and 1980s, as that of **chromate** began to decrease, and it is now widely used in both open and closed cooling circuits as well as in HW and LP steam heating systems. However, molybdenum is expensive, and despite the fact that it is a very low toxicity metal (unlike many other *transition metals*), some negative publicity concerning U.S. environmental acceptability in recent years (mostly ill-founded) has done little to improve its image or reduce its price.

Molybdate is not a particularly strong passivator, but it is involved in the active-to-passive state **ferrous transition process** by adsorbing on the oxide layer (which is typically about 0.1 mm in thickness) and preventing the passage of other anions such as chlorides and sulfates. Thus, in high chloride waters, molybdate-containing programs often provide superior results compared to nitrite or borate programs.

Molybdate is always used in conjunction with other anion inhibitors, not only to reduce the cost of the inhibitor program, but also because, through synergism, much-improved **barrier films** are produced when coupled with nitrite or silicate.

Molybdate also functions as an effective inhibitor by slowing down pitting corrosion through a mechanism of adsorption onto the pit wall.

- Where *molybdate/nitrite* programs are employed in dual-temperature and simple HW heating systems, they typically require 150 to

250 ppm as MoO_4 and the same level of NO_2. Alternative formulations reduce the molybdate level to perhaps 100 to 150 ppm and increase the nitrite level to 250 to 350 ppm. (This is about twice the level required for cold and chilled water closed loop systems.) Where *molybdate/silicate* programs are used, the silicate level is generally about one-third of the molybdate level.

- Where *molybdate/nitrite* programs are employed in LP steam and higher temperature HW heating systems, they typically require 250 to 350 ppm as MoO_4 and the same level of NO_2. Alternatives reduce the molybdate level to perhaps 150 to 250 ppm and increase the nitrite level to 500 to 600 ppm. Where *molybdate/silicate* programs are used, the silica level is again, about one-third of the molybdate level.

10.2.3 Silicates

Orthosilicates are not suitable for corrosion inhibitor purposes, and **metasilicates** are not generally used because they tend to increase the caustic alkalinity too much, leading to the potential for caustic-induced problems. However, **glassy polysilicates** are widely used. They have inhibition properties similar to those of *polyphosphates* and also have an indefinite crystalline structure.

Polysilicates are effective in potable HW systems and provide **threshold effect** protection against *hardness destabilization* and *"red water."* They also function by laying down a protective calcium silicate film. Polysilicates used for this type of application typically require a dose rate of 8 to 15 ppm SiO_2 above that of the natural **orthosilicate** found in the MU water. Where polysilicates are employed for dual-temperature and LPHW systems, however, the silicate reserve required is higher and ranges from 50 to 150 ppm.

Commercially, the selection of a suitable polysilicate treatment depends to some extent on the pH level of the water but also on the temperatures involved. (The polysilicate Na_2O:SiO_3 ratio required tends to be around 1:2 at pH 7.0, rising to 1:4 at a pH level of 9.0.)

For larger, more complex LPHW systems and for LP steam heating systems, silicates are seldom used alone but are formulated with nitrite or molybdate inhibitors to provide synergistic corrosion protection.

Both **sodium** and **potassium polysilicates** are used in formulations of these types, and it is critical that products containing two (or slightly more) molecules of **silica** to every one molecule of **sodium oxide** are obtained to ensure adequate long-term inhibitor effectiveness.

Typically, either liquid sodium salts of 60 °Bé are employed (18% Na_2O, 36% SiO_2) or alternatively, potassium salts of 40.75 °Bé (12.6% K_2O, 26.8% SiO_2).

10.2.4 Borates

Borate is usually added to nitrite-based formulations to provide an alkalinity reserve buffer, ensuring that the system water pH level is maintained within the range of 7.5 to 9.5 (or greater).

Steel-based closed loop HW systems are usually maintained toward the higher pH level (9.0–9.5), but the pH level is reduced a little where copper and copper alloys are included (8.5–9.2). The pH level tends toward the lower level where aluminum is present (7.5–8.0).

Commercially, **sodium tetraborate decahydrate** or **borax** ($Na_2B_4O_7 \cdot 10H_2O$) is usually employed, although **sodium metaborate hydrate** ($NaBO_2 \cdot xH_2O$) may be used.

10.2.5 Anodic and Cathodic Phosphate Inhibitors

There is a wide variety of phosphates available and they are commonly produced in glassy, crystalline, amorphous powder and liquid forms. Figure 10.1 shows two common phosphate types.

They are used only sparingly in anodic inhibitor formulations, but the chemistry remains important. However, phosphates are extensively employed in other boiler chemical products for such purposes as *hard-*

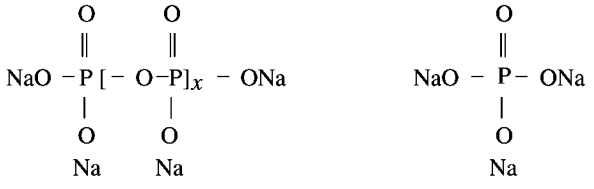


Figure 10.1 Types of phosphate structures. (a) Where x = 12 to 14, the structure represents **sodium polyphosphate**, a phosphate typically used in HW heating and industrial steam boiler formulations. The structure is ill defined and described as "glassy" rather than crystalline. Where x = 2, it represents **sodium tripolyphosphate**. (b) This is the structure where effectively, x = 0, and represents **trisodium phosphate** (*sodium orthophosphate*), which is commonly supplied in either crystalline or anhydrous powder form and used as an alkalinity booster, boiler boil-out cleaner, and metal surfaces passivator.

ness precipitation, cleaning, and *passivation programs.* These other applications are described elsewhere in this book.

With regard to the use of phosphates as anodic (and cathodic) inhibitors, **polyphosphates** are **cathodic polarizers** and form a durable, corrosion-inhibiting film that includes adsorbed calcium. In addition, they are **anodic inhibitors**, depositing *iron metaphosphate,* and forming gamma ferric ocxide (γ-Fe_2O_3), thus stifling the anodic reaction. As such, polyphosphates have been used as corrosion inhibitors for a very long time and are sometimes incorporated into anodic inhibitor formulations. Unfortunately, they suffer from a lack of thermal stability and reversion *(hydrolysis)* to **orthophosphate** occurs, which limits their potential for heavy duty application.

Although orthophosphates are themselves *passivating, anodic inhibitors* (and also *cathodic inhibitors,* forming a calcium phosphate barrier film), the film strength is weak, even in simple HW systems and they are not used for this purpose. Nevertheless, despite the thermal instability of **sodium hexametaphosphate** and other polyphosphates, phosphates in general have several important properties that make them useful in boiler plant operations. These properties include:

- **Hardness precipitation and deposit control**, functioning at a stoichiometric level. *Phosphate precipitation programs* utilize this function.
- **Hardness stabilization**, functioning at substoichiometric levels by crystal growth retardation, **(threshold effect)**. This attribute is useful in low heat-flux HW applications.
- **Calcium carbonate crystal distortion.**
- **Corrosion inhibition**, by mechanical deposition of crystalline or amorphous films on a metal surface.
- **Passivation**, by anodic polarization.
- **Metal surface cleaning**, by virtue of (limited) sequestration, dispersing, surface-acting, and detergent properties.

10.2.6 Azoles

Azoles provide effective corrosion inhibition primarily by **chemisorption** of the molecule on the metal substrate. Several different types of azoles are available for incorporation into formulations used for the corrosion inhibition of closed loop LPHW heating and low MU requirement, LP steam heating systems.

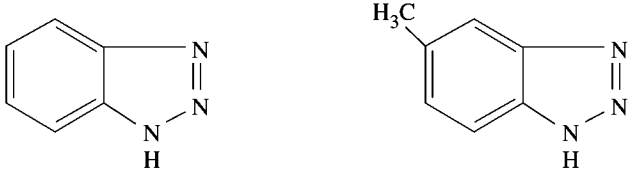
Azoles include the *sodium* and *potassium* salts of **mercaptobenzothiazole** (MBT), **benzotriazole** (BZT, BTZ, BTA), and **tolyltriazole** (TTA). The latter two azoles are most commonly found in formulations today and are shown in Figure 10.2.

Azoles are not very soluble at acidic pH levels (less than 0.5 % solubility) but are increasingly so under alkaline pH conditions. These products usually are supplied as the sodium salt. For example, TTA is available as a 50% sodium salt solution under the trade name **Cobratec® TT-100/T-50-S** from PMC Specialties, Inc. It is also available as a powder and 80% strength product under the names **Belclene®511** and **512** from BioLabs/Great Lakes Chemical Corp. (The brand originally was held by Ciba-Geigy, then FMC, and now BioLabs/GLC.)

NOTE: Strongly alkaline, closed loop LPHW system formulations, such as nitrite/borates, typically include an azole product at about 4 to 5% (50% solution). Lower alkalinity products (often the molybdates) have significantly less, perhaps only 0.5%. For comparison, open cooling water and chilled water system formulations typically contain about 2 to 3 % (50% solution) azole.

Although azoles are commonly thought of as only yellow metal inhibitors, they are, in fact, used for corrosion inhibition in a wider range of metals such as steel and aluminum. They also are often incorporated in molybdate-based programs to both provide some synergism and reduce the level of molybdate required. Azoles also are employed in many types of organic-based formulations, where they improve the overall protection of steel and reduce the risk of corrosion of yellow metals due to the corrosive action of some common phosphonates.

- Mercaptobenzothiazole (MBT) is often employed in formulations for nonaerated, multimetal systems (Cu, brass, Fe, Al, Sn, Pb, etc.),



a **b**

Figure 10.2 (a) benzotriazole and (b) tolyltriazole.

such as diesel engine generator cooling systems, and in systems in which **ethylene glycol antifreezes** are required. MBT is less effective then BTA and TTA at higher pH levels.

*NOTE: An alternative to MBT-based inhibitors for glycol are phosphate-based formulations. An example is based on 30% **dipotassium phosphate** and 5% TTA, used at 2,000 ppm product.*

*Where low-toxicity, **propylene glycol** is employed (rather than the more common ethylene glycol), the inhibitor is more usually simply 30% **dipotassium phosphate** (K_2HPO_4), so as to maintain the low-toxicity feature, and is then used at 3,000 ppm product. This same inhibitor is employed in the food industry in "sweet water" systems.*

- Benzotriazole (BTA) is very effective as a corrosion inhibitor for steel and **gray cast iron** within the pH range of 7.5 to 9.5 and for **copper** and **copper-steel couples** at lower pH ranges.
- Tolyltriazole (TTA) is most useful for partnering with molybdates and phosphonates in both aerated and nonaerated systems.

10.2.7 Anodic Inhibitor Programs

There is a wide range of metals commonly employed in the construction of HW closed loop circuits and LP steam heating systems, and every individual system design has particular characteristics that require specific corrosion controls.

As a consequence, it is not possible to devise a single class of anodic inhibitor formulation that satisfies all water treatment requirements. Rather, there several types of formulations, and some formulators may offer each of these products in different strengths, with or without oxygen scavengers and indicator dyes in their blends. As examples, a **nitrite/silicate formulation** and a **molybdate/nitrite formulation** are provided here:

Basic Formulation Materials	*Nitrite/Silicate Formulation*
NaOH, commercial solution	15.0%
Borax	6.0%
Sodium silicate 41 °Bé	8.0%
Sodium nitrite	30.0%
Polyacrylate (PAA)	3.0%
TTA commercial solution	2.0%
Water	36.0%
	100.0%

Basic Formulation Materials	*Molybdate/Nitrite Formulation*
NaOH, commercial solution	1.0%
Sodium molybdate dihydrate (41%)	10.0%
Sodium nitrite	13.0%
TTA commercial solution	0.5%
PAA	4.0%
Water	71.5%
	100.0%

Both of these formulations are suitable for closed loop, steel HW heating circuits and low MU, LP steam heating systems.

Where glycols are added to both hot and cold water systems, it is common for the glycol to be supplied "neat," preinhibited and buffered (although the glycol also may be supplied in a diluted and ready-to-use form). This formulation is an example of a type produced as an glycol inhibitor-pack concentrate:

Basic Formulation Materials	*Glycol Inhibitor Formulation*
NaOH commercial solution	3.0%
Sodium nitrite	3.0%
Sodium molybdate dihydrate	6.0%
Sodium tetraborate pentahydrate	10.0%
Sodium silicate 41 °Bé	4.0%
H_3PO_4 commercial solution	4.0%
MBT	11.0%
TTA	6.0%
Stabilizer/block copolymer/dye	3.0%
Water	50.0%
	100.0%

The inhibitor-pack is added to the neat glycol for use in multimetal systems. The glycol-inhibitor product is then supplied as 95% glycol and 5% inhibitor. Assuming that the glycol is present at, say, 20% strength in the HW system, the inhibitor concentration in the system is accordingly 1.0% (0.5% "actives"), equivalent to 10,000 ppm (5,000 ppm "actives").

10.3 TANNIN PROGRAMS

Tannins are water-soluble vegetable products, usually blends of natural extracts from certain trees (similar to **lignins** and their derivatives

lignisulfonates, which are also used in BW formulations), although other plants may be used and *synthetic tannins* are also available. (For BW purposes, synthetic tannins generally are not suitable. Only *natural tannins* should be used.) Very many different organic compounds are found in tannin blends; some are extremely complex, but all are primarily based on *phenolic* and *sugar molecules.*

They typically are supplied as single-tannin raw materials, either as spray-dried powders or 30 to 50% liquids. Fifty percent liquid products are extremely viscous and may need to be innoculated with a small dose of microbiocide (1–1.5%) to protect against microbial infection that leads to gas production, the swelling of plastic drums, and eventual product spoilage. Organisms attacking tannins include *Aspergillus niger* and *Pencillium glaucum.* Typical microbiocides employed (depending on local pesticide regulations) include **isothiazolines (Kathon® from Rohm and Haas Company)** and **Nipacide® chlorophenols** *(dichlorophen)* from **Nipa Laboratories** (U.K.).

Tannins make excellent BW inhibitors. They are multifunctional, possessing several characteristics that make them entirely suitable for the treatment of HW heating and LP steam boilers. They also are generally suitable for use in industrial and process WT boilers at pressures of up to 650 or even 950 psig.

Specifically, tannins as a class of chemical treatments are:

- **Oxygen scavengers**
- **Metal passivators**
- **Sludge conditioners**

Tannins have been available for over 100 years (since about 1880), although even today their chemistry is still imperfectly understood. Moreover, they have been seriously *undervalued* within the global BW treatment marketplace, except by a few noteworthy water treatment chemical and service companies.

NOTE: The British Standards Institution provided only a cursory mention of tannins in BS 2486:1978 (Treatment of Water for Land Boilers), but the 1997 revision (Treatment of Water for Steam Boilers and Water Heaters) refers quite extensively to tannins and their usefulness.

Although tannins are almost always formulated as a blend of raw materials, some knowledge of tannin chemistry is required because certain tannin constituents are useless in BW formulations and others lack

any meaningful oxygen-scavenging capability. Tannins for the leather industry, for example, are *not* suitable for BW treatment.

Formulated products usually are of two basic types:

1. **Tannin blend concentrates** primarily intended for *oxygen-scavenging duty* in steam boilers. They generally are offered as dark-brown to black, blended products of 25 to 50% active strength. Here, tannins provide an additional benefit of *sludge conditioning* at no extra cost.
2. **Multiblended inhibitors based on tannins,** for use in either closed loop HW systems or steam raising boiler plants. Tannin-based multiblends are often offered as an alternative to *sulfite-based* multiblends.

Tannins typically are available from service companies in several formulated options, containing, say, 10 to 15% of a tannin blend and with various ratios of phosphate and/or alkalinity provider, depending on the particular FW water quality to be treated.

10.3.1 Tannin Chemistries

Tannins comprise various **polyhydroxyphenols** and **polysaccharides (polysaccharoses),** which are complex carbohydrates **(polyhydroxy aldehydes** or **ketones)** and include starches and cellulose, and their derivatives.

Tannin vegetable extracts are obtained from plant galls [producing **gallotannin** ($C_{116}H_{88}O_{71}$)]; the fruits of *Terminalla chebula* (**myrobalans,** which produce **ellagitannins**); the bark of trees such as **chestnut** and **oak** *(querqus sp.)*; and the heartwood of **wattle** (*acacia*) and **quebracho** (*schinopsis).* Quebracho is the single most important source of beneficial tannins in BW programs.

Tannin chemistry is extremely complex, but the individual components may be classified in two primary groups:

- **Hydrolyzable tannins.** This group is readily oxidizable under boiler heat conditions, particularly in the presence of alkali. These tannins primarily produce the sodium salts of **tannic acid, ellagic acid, gallic acid** *(3,4,5 trihydroxybenzoic acid),* and **quinic acid** [*1,3,4,5 tetrahydroxycyclohexane-carboxylic acid,* $(HO)_4C_6H_7COOH$], as well as sugars (especially **D-glucose**) and *sugar-phenols.* In turn, *gallic acid,* for example, produces **pyrogallol** *(pyrogallic acid* or

1,2,3,trihydroxybenzene), which has been used as an *oxygen scavenger* in **Orsat gas analysis** work for many years. *Quinic acid* produces **hydroquinone** [C_6H_4-1,4-$(OH)_2$], which is a well-known photographic reducing agent and a "modern" oxygen-scavenging alternative to hydrazine. **Catechol** [*pyrocatechol* C_6H_4-1,2-$(OH)_2$], another oxygen absorber, is also produced. Further oxidation produces *cyclic diketones* and eventually simple *carboxylic acids* and their salts.

The *sodium carboxylates* resulting from the hydrolyable tannins are similar to the **gluconates** and **sarcosinates,** which are commonly employed as *iron chelants.* The result is that they combine at higher pH values with the waterside surface iron oxides to produce an adherent, passive **iron tannate** complex containing principally **gamma ferric oxide** (γ-Fe_2O_3), and tannin derivatives, especially **ellagotannin.** At higher pressures (over 450 psig, 31 bar) the *gamma iron oxide–tannin complex* is gradually replaced by **magnetite,** which is particularly stable and equally protective. Tannins also aid the stability of copper and copper alloy passive films.

- **Nonhydrolyzable tannins (condensed tannins, flavotannins)** are complex molecules (including polymerized *flavon-3-ols* and *flavon-3,4-diols*) with significant bond strength due to hydrogen bonding. Under conditions of boiler heat, they produce **otho-, meta-,** and **para-**isomers of **dihydroxy flavonoids** (colored compounds consisting of two six-carbon rings joined by a three-carbon link and found in plants, where they produce the pigmentation of flowers and leaves).

  These condensed tannins and their derivatives, all of high molecular weight, function as *anionic polyelectrolyte* sludge conditioners, tending to sequester hardness salts and hinder their precipitation as crystalline scales. In addition, when precipitation does occur, the condensed tannins coagulate the particles, resulting in a mobile sludge that can be easily blown down.

  The tannins influence *calcium salt* crystal structures to produce the easily dispersible **calcite** (cubic structure) rather than the scale-forming **aragonite** (rhombic structure).

10.3.2 Tannin Application Notes

- In theory, tannins are added based on the oxygen demand, with 10 ppm of 100% tannin blend being required per 1 ppm of oxygen (O_2). In practice, unless the MU water is particularly cold (i.e., high in dissolved oxygen), the tannin requirement is simply calculated on

the basis of a tannin reserve, irrespective of the oxygen content. The reserve typically maintained is in the range of 100 to 160 ppm (**tannin index value** of 10–16) for general commercial and industrial boilers of up to 435 psig (30 bar). Small boilers may maintain a tannin reserve of 200 ppm, or slightly more.

- Above 435 psig, tannins may still be used because, although the condensed tannin polymers begin to thermally breakdown, they are essentially *nonvolatile* until pressures of 1,000 psig (69 bar) are reached, when free carbon dioxide begins to be detected. Depending on the particular tannin source and other treatment or contaminant constituents, small levels of ammonia may begin to be detected (1–2 ppm NH_3) at this pressure. There is no precise tannin suitability cutoff point, however, because it depends on the blend of tannins used and the consistency of the blend. Between approximately 450 and 1,000 psig the composition of the *iron tannate* film gradually changes, as the tannin provides a greater role as a reducing agent and a lesser role as a film former. The *gamma iron oxide* (γ Fe_2O_3) is eventually totally reduced to a dark brown-black film of passive *magnetite* (Fe_3O_4).
- Tannins do begin to lose effectiveness at elevated temperatures and pressures because of oxidation of nonhydrolyzable polymer functional groups, which results in a reduced charge. However, even where some breakdown begins, this does not affect the oxygen-scavenging or metal-passivating properties of tannins. The addition of a high-temperature stable, **phosphinocarboxylic acid** (PCA) sludge dispersant supplement, such as **phosphino-** or **acrylic acid,** overcomes this problem.

NOTE: Tannin chemistry has been used very successfully for many years in Africa and in Central and South America, in sugar refinery boilers operating at 650 psig and higher, without any measurable breakdown in performance or detectable contamination of steam from volatiles.

- The resistance of BW tannins (**sodium tannates**) to thermal breakdown is aided by the presence of sufficient alkali, and optimum stability is conferred at an **alkalinity:tannin ratio** of 2:1.
- As boiler pressures increase, FW quality also tends to improve and is more than likely to be almost fully deaerated at higher pressure. Consequently, tannin reserves and residuals may be reduced accordingly. Also, because there is likely to be *lower* alkalinity reserves at *higher* boiler pressures, the tannin reserve *must* be lowered if insol-

uble tannin deposits are to be avoided. Unless the boiler is highly rated, there is no need to differentiate between FT and WT boilers. A suitable guide to tannin residuals in BW is provided in Table 10.1.

- The hydrolysis products of the hydrolyzable tannins are not dissimilar to some of the novel oxygen scavengers developed to replace hydrazine. Oxygen reaction rates and application rates are also similar. The oxygen reaction time for tannin blends varies with pH levels and temperature but at 45 °C (113 °F) is on the order of 75% complete within 5 seconds and 90% complete within 10 seconds.
- Tannins outperform sulfites where oxygen scavenging demands are high (where, for example, boiler MU water requirements are also high, or where the MU water is cold) because of the benefit of *metal passivation,* which provides short-term protection against oxygen pitting, even if the tannin reserve is temporarily lost.
- The 50%-strength liquid tannin products are particularly viscous, and some sediment is to be expected because of limited solubility of certain constituents at high strength *(ellagic acid?).* Tannins stored in drums should be mixed before use or before transfer into a day tank.
- Tannin-based multiblends cannot incorporate amines directly into their formulations (unlike sulfite-based multiblends). The neutralizing amine component must be added separately when using tannin multiblends.
- Tannins are often viewed as being "old-fashioned" and possibly unsuitable in certain boilers because they impart a tea-brown color to the BW.

*NOTE: Tea is brown because of the tannin present in the shoots of the tea bush (*Camellia sinensis*).*

The charge of being old-fashioned is correct, but this is no different from phosphate, which has been continuously used in boiler plants for perhaps just as long. The fact is that there is no other BW

Table 10.1 A Guide to Tannin Residuals in BW

Boiler Pressure		*Tannin Reserve*	*Tannin Index/*
psig	*bar*	*ppm*	*Value*
0 to 15	0 to 1	150 to 200	15 to 20
15 to 217	1 to 15	100 to 150	10 to 15
217 to 435	15 to 30	50 to 100	5 to 10
435 to 650	30 to 45	20 to 50	2 to 5

formulation ingredient that can beat tannin chemistry in a cost-benefit analysis exercise.

The problem of **color due to tannin** can be annoying, although not insurmountable. For small, simple boiler plants, the presence of color is, in fact, a benefit, as the depth of color is more or less related to the inhibitor concentration and the BW conductivity and TDS levels. Where multiblended formulations are employed, if the color is within range, then other parameters are also likely to be acceptable. Also, electrical conductivity is unaffected by color, and tannins do not appreciably add to the measurable TDS of the BW.

For larger and more complex boiler plants, where spectrophotometric tests are the norm, the presence of a brown color may cause interference, but these normally are dealt with quite easily.

The real problem lies in the middle-sized industrial boilers, where testing still may rely on the use of wet chemistry titrations, and the detection of color change is critical. Under these circumstances, trying to accurately measure chloride, hardness, or alkalinity levels is genuinely difficult.

Again, there are remedies, as the color interference may be removed before conducting the test. If this is unsuccessful, the method of testing must be changed.

When testing for a tannin reserve or tannin index, the presence of natural color aids detection. Testing for tannin is simple and relatively accurate using either a *permanganate reduction test* (development of permanent purple color) or *lignin/tannic acid polymer test* (tungstate blue color).

- Under poor operational conditions, tannin chemistry is a particularly "forgiving" form of internal treatment because it tolerates FW with significant variations in quality. It is capable of delivering clean, corrosion-free waterside surfaces in many types of boilers, despite low FW temperatures, high oxygen levels, and hardness ingress. It is especially suitable for use in smaller facilities that do not have the benefit of full-time, trained operators, and under on-off, batch process, or permanent low-fire circumstances.

10.3.3 Tannin Program Formulations

The starting point for tannin-based formulations is generally the provision of a tannin concentrate blend that eiether may be employed as a stand-alone oxygen scavenger, passivsator, and sludge conditioner, or may serve as a component of a multiblend program. The blend may

vary a little, as may the active tannin strength, depending on the source of the raw materials. Today, quebracho and some other important BW tannin raw materials originate mostly in South America.

Tannin Concentrate Formulation	*Materials*
Quebracho tannin 40% liquid	33%
Mimosa tannin 40% liquid	33%
Chestnut tannin 40% liquid	33%
Biocide	1%
	100%

If the tannin blend is made from spray-dried powders, the dilution water must be heated to 160 to 180 °F and the biocide only added when the temperature has cooled below 140 °F.

The *tannin-based, multiblend formula* shown here is designed for steam-raising boiler plants operating at up to 200 to 220 psig (say, 15 bar).

Tannin-Based Programs Materials	*Multiblend Formulation (for moderate alkalinity MU)*	*Closed-Loop Formulation (for black-iron system)*
Tannin blend 40%	14.0%	30.0%
NaOH commercial solution	8.0%	5.0%
PAA	6.0%	10.0%
SHMP commercial solution	13.0%	—
SSMA	3.0%	—
Synthetic antifoam	0.1%	0.1%
TTA commercial solution	—	0.5%
Water	55.9%	54.4%
	100.0.%	100.0%

NOTE: PAA = Polyacrylic acid or sodium salt; SHMP = Sodium hexametaphosphate; SSMA = Sulfonated styrene maleic anhydride

Tannin reserve to be maintained at 100 to 150 ppm, other parameters as per standard recommendations. The *tannin-based closed-loop formula,* also shown, is designed for use at 1,500 to 2,000 ppm product in the system, which provides approximately 180 to 240 ppm tannin reserve. Various modifications to these formulations exist; for example, 0.5 to 1.0% **diethylhydroxylamine** (DEHA) may be added to improve passivation when used in simple HW heating systems.

10.4 COAGULATION AND PRECIPITATION PROGRAM CHEMISTRIES

Coagulation and precipitation programs, designed to provide control over the deposition of scales resulting from the ingress of small amounts of FW hardness, are very widely used in all manner of industrial boilers operating within the range of, say, 50 to 950 psig. Alternative technologies tend to be **all-polymer programs** (especially at lower pressure ratings) and **chelant programs** (especially at upper pressure ratings).

Today, almost all internal programs of this type employ a combination of some type of *phosphate* plus *caustic soda,* although *sodium carbonate* (plus caustic) is still occasionally employed for smaller process boilers receiving poorer quality, hard water MU.

Soda ash (sodium carbonate) is less expensive than phosphate and so tends to be used as a BW treatment in some developing countries for basic industrial processes such as mashing of farm products for animal foods, palm oil extraction, rendering plants, tanneries, and textile washing and dyeing. Often there is little or no condensate return.

Before the advent of sophisticated polymer technology, *sodium aluminate* and *sodium silicates* (plus caustic) were sometimes used in both external and internal coagulation processes.

10.4.1 Alkaline Aluminate and Silicate-Based Boiler Compounds

Boiler compound formulations containing *aluminate, silicate,* and *carbonate* ingredients have commonly utilized various ratios of some or all of these constituents, together with caustic soda (for alkalinity control), sodium nitrate or sulfate (to prevent caustic embrittlement), sodium lignosulfonate (sludge conditioner), and other compounds.

The coagulant **sodium aluminate** ($NaAlO_2$) is strongly caustic (contributing hydroxide alkalinity to the BW) and reacts with calcium and magnesium salts and any silica present to form a *zeolite sludge* of **calcium-magnesium-aluminum silcate.**

Several different possible zeolite structures may result, and if the sodium content is too high, calcium and magnesium are excluded and a hard *zeolite scale* of **sodium-aluminum silicate** preferentially forms. If only *calcium* is present, **calcium-aluminum silicate** zeolite forms, also as a hard scale. If only *magnesium* is present in solution, it forms the flocculant **magnesium aluminate,** $MgAl_2O_4$.

If both *silica* and *magnesium* are present, they mutually precipitate; thus, salts of either mineral may be added to the BW to provide a balance and ensure coprecipitation as **serpentine**:

$$\underset{\text{silica}}{2SiO_2} + \underset{\substack{\text{magnesium}\\\text{chloride}}}{3MgCl_2} + \underset{\substack{\text{caustic}\\\text{soda}}}{6NaOH} \rightarrow \underset{\text{serpentine}}{3MgO{\cdot}2SiO_2{\cdot}2H_2O} + \underset{\substack{\text{sodium}\\\text{chloride}}}{6NaCl} + \underset{\text{water}}{H_2O}$$

Where only *silica* is present, it can be removed by absorption into added **ferric** or **magnesium hydroxide.** The resulting sludge is removed by BD.

When using programs based on these types of formulatory ingredients, obviously considerable care must be taken to fully understand the nature and amounts of FW mineral constituents and to properly balance the requirements for hydroxide alkalinity, aluminate, and silicates with the alkaline earth metal content of the FW to avoid the development of hard BW scales. Similarly, the sourcing of appropriate raw materials is equally important. As with polysilicates for HW and LP steam heating systems, commercial sodium and **potassium polysilicates** are used in these types of boiler compounds, and it is again critical that products contain approximately two molecules of silica to every one molecule of sodium oxide. Where the $Na_2O{:}SiO_2$ ratio approaches 1:3, the formation of calcium silicate scale preferentially tends to develop. Under these circumstances, phosphate is required to remove the calcium.

NOTE: Because silica and magnesium are mutual precipitants, in low heat-flux FT boilers operating below 250 psig without a softener or other effective FW hardness salt removal treatment, it is useful to try to balance the levels of each radical in the boiler. Thus, if magnesium levels are high and phosphate programs are employed, it is preferable to reduce the phosphate level and add sodium or potassium polysilicate to produce magnesium silicate sludge, rather than permit sticky magnesium phosphate to develop. Sodium silicates decrease in solubility with increase in temperature (and therefore steam pressure), and at pressures over 250 psig it is preferable to use potassium salt because it does not possess this reverse solubility function. For low heat-flux boilers silicates may be successfully employed at up to perhaps 650 psig.

This form of internal softening is not recommended in higher heat-flux boilers, however, because the risk of ***complex silicate scales*** *is inevitable. The risk of such scales is further increased by the presence of either* ***iron*** *or* ***aluminum****, and* ***analcite****,* ***acmite****, or similar minerals may result. Under*

these conditions, it is preferable to employ external conditioning to remove both hardness salts and silica (in addition to Fe and Al).

Where silicate levels are high (say, close to or above 150 ppm as SiO_2), the caustic alkalinity level must be ***at least*** *2.5* times the silica. At this level of alkalinity, any magnesium present will precipitate as a magnesium hydroxide sludge. Maintaining a high pH level also raises the solubility threshold level of silica.

10.4.2 Carbonate-Cycle Boiler Programs

The most popular form of *internal treatment* for many years dates from the nineteenth century and is based on a combination of *soda ash* and *caustic*. This traditional program, the so-called **carbonate-cycle** or **carbonate treatment**, utilizes the addition of *sodium carbonate* to the BW to deliberately form carbonate sludges that can be removed by BD, rather than permit sulfate scales to develop. If sulfate scales do form in the boiler, the removal process is difficult and very time-consuming, and obviously, boiler operating efficiency will continue to decrease as the sulfate scale increases in thickness.

In addition to the formation of calcium carbonate sludge, some of the carbonate decomposes giving sodium hydroxide, which precipitates magnesium bicarbonate, and chloride, etc. as the hydroxide and is then incorporated into the carbonate sludge. Silicates are also often removed in the process as **serpentine**. Additional caustic may also need to be added, depending on the natural alkalinity present in the MU water.

Sludge conditioners are required. Originally these were based on starches and lignins, but modern carbonate cycle treatments use **carbonate-polymer programs,** where the polymer (such as a **phosphinocarboxylic acid**) provides a combination of *threshold effect, crystal distortion,* and *sludge dispersion* to minimize scaling and prevent sludge deposition.

With high-hardness waters, the **carbonate-cycle** form of precipitation treatment is often preferred to the **phosphate-cycle** because it forms a less bulky and less dense sludge. The disadvantages of **hard-water carbonate-cycle** precipitation treatments include:

1. The limitations of modern boilers to accept the volumes of sludge produced because of the limited internal water space available.
2 An unacceptably high level of scaling and sludge deposition risk, especially in highly rated boilers.

3. The inability of the program to manage the diversity of other scale-forming ions that may be present.
4. The corrosion risks to the steam-condensate system resulting from the decomposition of carbonates and the subsequent formation of carbonic acid.

The principal carbon-cycle reaction chemistries are shown in the following equations, together with reactant molecular weights.

$Ca(HCO_3)_2$	→	$CaCO_3$	+	CO_2	+	H_2O
calcium bicarbonate	***boiler heat***	calcium carbonate		carbon dioxide		water
162		100		44		18

NOTE: Sludge becomes adherent limescale if not properly conditioned.

Na_2CO_3	+	H_2O	→	2NaOH	+	CO_2
soda ash		water		sodium hydroxide		carbon dioxide
106		18		80		44

$Ca(HCO_3)_2$	+	2NaOH	→	$CaCO_3$	+	Na_2CO_3	+	$2H_2O$
calcium bicarbonate		caustic soda		calcium carbonate		sodium carbonate		water
162		80		100		106		36

$CaSO_4$	+	Na_2CO_3	→	$CaCO_3$	+	Na_2SO_4
calcium sulfate		soda ash		calcium carbonate		sodium sulfate
136		106		100		142

$Mg(HCO_3)_2$	+	4NaOH	→	$Mg(OH)_2$	+	$2Na_2CO_3$	+	$2H_2O$
magnesium bicarbonate		caustic soda		magnesium hydroxide		sodium carbonate		water
146		160		58		212		36

$2SiO_2$	+	$3Mg(HCO_3)_2$	+	4NaOH	→
silica		magnesium bicarbonate		caustic soda	
92		146		80	

$3MgO{\cdot}2SiO_2{\cdot}2H_2O$	+	$2Na_2CO_3$	+	$2H_2O$
serpentine		sodium carbonate		water
248		212		36

If undesirable sulfate scale is to be avoided, a relatively high concentration of carbonate must be maintained as a BW reserve. The quantity of BW carbonate reserve required depends on the level of sulfates present in the BW and the boiler gauge pressure, as indicated in Table 10.2.

NOTE: The table is based on a paper by R.E. Hall, Carl Fisher, and George W. Smith. "The Prevention of Scale Formation by Boiler-Water Conditioning," Iron and Steel Engineer, *June 1924.*

This table provides a useful starting point for establishing a carbonate BW reserve, but fails to properly address the problem of rapid carbonate breakdown at increasingly higher pressures, such that the desired carbonate residual may never be reached.

Feedwater alkalinity requirements using 100% soda ash can be calculated using the formula on the next page.

Table 10.2 Carbonate-Cycle Program. BW Carbonate Reserve Requirements by Pressure and Sulfate Concentration

Pressure	***100 psig***	***200 psig***	***300 psig***	***400 psig***
Sulfate $(SO_4)^{2-}$ Concentration	***Carbonate $(CO_3)^{2-}$ Reserve***	***Carbonate $(CO_3)^{2-}$ Reserve***	***Carbonate $(CO_3)^{2-}$ Reserve***	***Carbonate $(CO_3)^{2-}$ Reserve***
100 ppm	5	15	30	45
200 ppm	10	30	55	90
300 ppm	15	45	80	135
400 ppm	20	60	110	185
500 ppm	25	75	140	235
1000 ppm	45	145	280	
1500 ppm	65	210		
2000 ppm	90	285		
2500 ppm	115	350		
3000 ppm	140			
3500 ppm	160			
4000 ppm	180			

$$[0.75 \times FWTH + (\underline{RBWMA} - FWMA)]$$
$$COC$$

= lb of product required, per 1×10^6 lb of boiler FW

Where:
FWTH = FW total hardness, in mg/l (ppm) $CaCO_3$
FWMA = FW methyl orange/total alkalinity, in mg/l $CaCO_3$
RBWMA = Required BW methyl orange alkalinity, in mg/l $CaCO_3$
COC = Cycles of FW concentration present or desired in the BW

In summary, the carbonate-cycle program provides preferred precipitation and coagulation reactions to prevent hard scale from forming. Key functions are:

- Calcium hardness precipitates as calcium carbonate sludge
- Magnesium salts precipitate as hydroxide or silicate
- Calcium sulfate deposition is inhibited by the addition of sufficient soda ash.

Sludge and other precipitated salts must be fluidized or mobilized (conditioned), so that they remains free-flowing and nonadherent, so sludge conditioners are essential.

Measurement and control of the BW "P" alkalinity is an essential indicator in applying this program.

NOTE: P alkalinity = OH alkalinity + $\frac{1}{2}$ CO_3 alkalinity.

- P alkalinity must be maintained between 150 to 500 ppm as $CaCO_3$. If this falls below 150 ppm, the reactions will not proceed to completion.
- Specific alkalinity ranges should be selected for individual boiler applications and maintained within an 80 ppm range (such as 240–300 ppm).
- P alkalinity must be maintained higher in high sulfate waters. However, if the P alkalinity reading is much over 500 ppm, coagulation will deteriorate.
- If correctly conditioned, the BW should filter easily, producing a very clear water (some color is permitted).
- For hard FW, limit the TDS, suspended solids, and silica (SiO_2) to a maximum of 2,000 ppm, 300 ppm, and 100 ppm, respectively (up

to 150 psig, 10.3 bar); 1,750/250/60 ppm (up to 250 psig, 17.2 bar). For higher pressures, or if the FW silica is too high, use a *phosphate-cycle program.*

For more details on carbonate-cycle control limits, see Table 10.3. These control limits are for non–highly rated boilers and assume that modern *polymeric sludge conditioners* are employed (i.e., not starches, agar, etc., which tend to form colloidal suspensions and may be difficult to remove by BD).

Despite its limitations, the carbonate-cycle program is nevertheless an important program type as it was the first stochiometric type of BW program. Results have always been marginal, although the more modern **carbonate-polymer programs** are better; where used today, this low-cost program ideally should be limited to low heat-flux rated boilers, operating at below 250 psig.

An example of a modern carbonate-cycle formulation is shown below. This formulation is designed for FT boilers operating within the pressure range of 50 to 125 psig, using untreated FW. The maximum BW silica permitted is 250 ppm SiO_2. This BW compound requires the separate addition of a **sulfite** oxygen scavenger and a **neutralizing amine** for control of carbonic acid production.

Table 10.3 Carbonate-Cycle Coagulation and Precipitation Program. Recommended BW Control Limits for Non-Highly-Rated FT Boilers Employing Hard or Partially Softened FW

FW hardness, ppm $CaCO_3$	*40 to 50*		*5 to 10*	
Pressure, psig/bar max. (approximate)	150/10	250/17	150/10	250/17
BW chemistry control limits				
TDS, ppm max.	2000	1750	2500	2000
Silica, ppm SiO_2 max.	100	100	100	100
Suspended solids, ppm max.	300	250	200	150
P Alk., ppm $CaCO_3$	30 to 150 in all cases			

NOTE: This chart assumes oxygen scavenger, polymer, and other necessary water chemistry controls are in place. If the FW is fully softened, there is no benefit in using this program. Employ a phosphate-cycle or alternative program.

Carbonate-Cycle Formulation	*Materials*
Soda ash (sodium carbonate)	10%
Caustic soda (sodium hydroxide) 50%	10%
Sodium lignosulfonate (sludge conditioner)	20%
Phosphino polycarboxylic acid (PCA:16) 35%	10%
Soft water	50%
	100%

Phosphate-cycle programs, which first became available at the turn of the twentieth century and were researched and formalized in the 1920s, have gradually replaced the carbonate-cycle programs. Formulation developments include **combined phosphate–carbonate cycle programs,** which incorporate the best of both basic programs while minimizing the problems associated with carbonate breakdown.

An example of a fairly complex, **combined phosphate-carbonate cycle,** liquid, multiblend formulation dating from the 1970s is provided below.

Combined Phosphate–Carbonate Cycle, Multiblend Formulation	*Materials*
Potash (potassium carbonate)	4.0%
Soda ash (sodium carbonate)	10.0%
DSP (Disodium phosphate)	3.0%
STTP (Sodium tripolyphosphate)	5.0%
Caustic soda (sodium hydroxide)	5.0%
Sodium sulfite (oxygen scavenger)	5.0%
DEAE (diethylaminoethanol, oxygen scavenger and Steam-condensate line corrosion inhibitor)	4.8%
Sodium lignosulfonate (sludge conditioner)	10.0%
PAGMBE (polyalkyleneglycol monobutylether, antifoam)	0.2%
Water	53.0%
	100%

This formulation is designed as a single-drum treatment for boilers operating at up to 300 psig and with a total hardness (TH) in the FW of up to 30 ppm $CaCO_3$. Initial feed is 15 ppm product per 1 ppm TH (as $CaCO_3$) in the FW. Control is based on maintaining 200 to 300 ppm hydroxide (OH) alkalinity and a maximum of 3,000 ppm total dissolved solids (TDS) in the BW.

10.4.3 Phosphate-Cycle Boiler Programs

Phosphates are perhaps the most versatile class of chemicals used in the treatment of boilers. They are widely employed in *boil-out, cleaning, lay-up,* and *passivation products* because of their functional properties, which include **hardness stabilization, crystal distortion, sequestration, buffering, deflocculation,** and **synergism** (with *detergents, wetting agents, emulsifers, and dispersants*). They also act as **corrosion inhibitors** (as described in Section 10.2.5). This section deals with phosphates functioning as **precipitation agents** in *phosphate-cycle programs.* On a global basis, phosphate-cycle programs probably continue to be the most commonly encountered form of internal BW treatment, although (similar to the cooling water treatment market), **all-polymer** and **all-organic programs** are slowly overhauling most other chemistries.

Related programs, such as **phosphate-chelant** and **phosphate-polymer**, are simply modifications of the basic phosphate-cycle, and they still rely on the precipitation of calcium (or other metal ions) as dispersible phosphate sludge.

10.4.3.1 Phosphate Product Selection

Several different types of phosphates may be employed:

- **Orthophosphate** (PO_4^{3-})
- **Metaphosphate** (PO_3^-)
- **Pyrophosphate** ($P_2O_7^{4-}$)

Some phosphates are simple **orthophosphates**, whereas others are **condensed phosphates**. Polymeric forms are also available; these are *complex* **condensed polyphosphates**, all of which may be present in *hydrogen, sodium, potassium,* or even *ammonium* form.

- **Orthophosphates** are derived from the *tribasic* **orthophosphoric acid** (H_3PO_4).
- **Condensed phosphates** are indirectly manufactured derivatives of phosphorous acids, having less water than orthophosphoric acid (two molecules of phosphoric can be written $P_2O_5 \cdot 3H_2O$, which indicates the source of the condensation reaction). Condensed phosphates are typically available in either crystalline or glassy forms.

The choice of phosphate is inextricably linked to the FW alkalinity in order to control the precipitation process. A minimum BW **hydroxide alkalinity** (hydroxyl, OH, O, or P_2 alkalinity) must be maintained. A maximum **total alkalinity** (M or T alkalinity), as well as a control range for **phosphate** (usually given as ppm or mg/l PO_4) also must be maintained. These various control parameters change not only with the level of FW hardness, but also with boiler pressure.

Consequently, all water treatment service companies provide several phosphate-based formulations in their product range, from which a particular phosphate-alkalinity combination can be selected. These formulations typically employ one of the following phosphate types:

- **Acid phosphates** (e.g., orthophosphates) such as *phosphoric acid* or *sodium dihydrogen phosphate*)
- **Neutral phosphates** such as *sodium hexametaphosphate* (SHMP)
- **Alkaline phosphates** such as *trisodium phosphate,* or phosphate-alkali mixtures containing various percentages of caustic soda

NOTE: Acid phosphates and SHMP may attack chemical tanks and associated equipment, so acid-resistant equipment should be specified. Alternatively, the addition of caustic up to a pH level of 8.2 to 8.3 (the production of a pink color when tested with phenolphthalein) provides adequate protection. A further alternative is to add neutralizing amine to the tank.

Dozens of phosphates are commercially available, supplied as anhydrous materials or with varying levels of water of crystallization, although only a limited number are employed for BW precipitating treatment programs.

Commodity products tend to be supplied in either powdered or crystalline form, whereas specialty products and blends were originally supplied pulverized, or as balls, but now are available as easier-to-handle liquids.

Some of the more common phosphates (with typical analyses) employed are:

- **Phosphoric acid** (orthophosphoric acid, H_3PO_4). Supplied commercially as > 98% crystals, or more usually as a 75% or 85% strength (by weight) liquid. MW = 98. As 100% material, P_2O_5 = 72.4%, PO_4 = 96.9%.

- **(Anhydrous) sodium dihydrogen phosphate** (MSP, acid or monobasic sodium orthophosphate, NaH_2PO_4). MW = 120.0, P_2O_5 = 58.9%, PO_4 = 79.1%, approximate solubility = 90% w/w at 75 °F/24 °C, 170% w/w at 150 °F/65 °C, approximate pH level of 1% solution = 4.6 to 4.8.
- **(Crystalline) sodium dihydrogen phosphate** (Crystalline or monohydrate MSP, $NaH_2PO_4 \cdot H_2O$). MW = 138, P_2O_5 = 51.4%, PO_4 = 68.8%, approximate solubility = 108% w/w at 75 °F/24 °C, 215% w/w at 150 °F/65 °C, approximate pH level of 1% solution = 4.6 to 4.8.
- **(Anhydrous) disodium hydrogen phosphate** (DSP, secondary or dibasic sodium orthophosphate, phosphate of soda, Na_2HPO_4). MW = 142, P_2O_5 = 49.7%, PO_4 = 66.9%, approximate solubility = 10% w/w at 75 °F/24 °C, 21% w/w at 150 °F/65 °C, approximate pH level of 1% solution = 8.8 to 8.9.
- **(Crystalline) disodium hydrogen phosphate** (Crystalline DSP, DSP dodecahydrate, $Na_2HPO_4 \cdot 12H_2O$). MW = 358, P_2O_5 = 19.8%, PO_4 = 26.5%, approximate solubility = 20% w/w at 75 °F/24 °C, 110% w/w at 150 °F/65 °C, approximate pH level of 1% solution = 8.8 to 8.9.
- **(Anhydrous) trisodium phosphate** (TSP, tribasic sodium orthophosphate, Na_3PO_4). MW = 164, P_2O_5 = 43.0%, PO_4 = 57.9%, approximate solubility = 16% w/w at 75 °F/24 °C, 54% w/w at 150 °F/65 °C, approximate pH level of 1% solution = 11.8.
- **(Monohydrate) trisodium phosphate** (Mono TSP, tribasic sodium orthophosphate monohydrate, $Na_3PO_4 \cdot H_2O$). MW =182, P_2O_5 = 39.0%, PO_4 = 52.1%, approximate solubility = 19% w/w at 75 °F/24 °C, 65% w/w at 150 °F/65 °C, approximate pH level of 1% solution = 12.0.
- **(Crystalline) trisodium phosphate** (Crystalline TSP, tribasic sodium orthophosphate dodecahydrate, $Na_3PO_4 \cdot 12H_2O$). MW = 380, P_2O_5 = 18.6%, PO_4 = 25.0%, approximate solubility = 33% w/w at 75 °F/24 °C, 375% w/w at 150 °F/65 °C, approximate pH level of 1% solution = 12.0. Some manufacturers provide crystalline TSP that incorporates 3 NaOH, which increases the MW to 390.
- **Sodium trimetaphosphate** [STMP, $Na_3P_3O_9$ or $(NaPO_4)_n$ where n = 3]. MW = 221.9, P_2O_5 = 63.8%, PO_4 = 42.8%, approximate solubility = 16% w/w at 75 °F/24 °C, 30% w/w at 150 °F/65 °C, approximate pH level of 1% solution = 6.8 to 7.2.

- **Sodium hexametaphosphate** [SHMP, glassy sodium polyphosphate, **Calgon®**, **Hexaphos®**, **Polyphos®**, **Sodaphos®**, etc., of variable composition by individual manufacturers representing their products by formulae such as $Na_n+2P_nO_{3n+1}$ and $(NaPO_3)_n$, where n = 6 to 21, although n typical = 13]. MW = 1387 to 1897, P_2O_5 = 61 to 69%, PO_4 = 65 to 89%, approximate solubility = >150% w/w at 75 °F/24 °C, >200% w/w at 150 °F/65 °C, approximate pH level of 1% solution = 6.7 to 7.0.
- **(Anhydrous) sodium tripolyphosphate** (STPP, $Na_5P_3O_{10}$). MW = 367.9, P_2O_5 = 57.9%, PO_4 = 77.4%, approximate solubility = 15% at 75 °F/24 °C, 21% at 150 °F/65 °C, approximate pH level of 1% solution = 9.7 to 10.1.
- [a] **(Crystalline) sodium tripolyphosphate** (Crystalline STPP, $Na_5P_3O_{10}\cdot 6H_2O$). MW = 475.9, P_2O_5 = 44.7%, PO_4 = 59.9%, approximate solubility = 22% at 75 °F/24 °C, 29% at 150 °F/65 °C, approximate pH level of 1% solution = 9.7 to 10.1.
- **(Anhydrous) tetrasodiumpyrophosphate** (TSPP, normal sodium pyrophosphate $Na_4P_2O_7$). MW = 265.9, P_2O_5 = 53.4%, PO_4 = 71.4%, approximate solubility = 6% at 75 °F/24 °C, 30% at 150 °F/65 °C, approximate pH level of 1% solution = 10.3.

10.4.3.2 Phosphate-Cycle Reactions

The **calcium phosphate solubility constant** *[$KCa_3(PO_4)_2$]* is extremely small and phosphate quickly reacts with calcium when present in warm to hot, alkaline BW in the *ortho-* form. This reaction is complete and superior to the soda ash precipitation reaction. In addition, calcium phosphate is stable and does not decompose.

Some phosphate-cycle reactions are shown below, and, although for the sake of simplicity only calcium phosphate is shown as a precipitant, depending on the operational circumstances, the reaction produces either *tricalcium phosphate, hydroxyapatite,* or a combination of both salts.

The formula for **tricalcium phosphate** is $Ca_3(PO_4)_2$ and that of **hydroxyapatite** (which is a complex, composed of a *mixed phosphate* and *hydroxide*) is variously written as:

- $Ca_{10}(OH)_2(PO_4)_6$
- $3Ca_3(PO_4)_2\cdot Ca(OH)_2$
- $10CaO\cdot 3P_2O_5\cdot H_2O$

$$\underset{\text{MSP}}{2NaH_2PO_4} + \underset{\substack{\text{calcium}\\\text{carbonate}}}{3CaCO_3} + \underset{\substack{\text{caustic}\\\text{soda}}}{4NaOH} \rightarrow \underset{\substack{\text{calcium}\\\text{phosphate}}}{Ca_3(PO_4)_2} + \underset{\substack{\text{sodium}\\\text{carbonate}}}{3Na_2CO_3} + \underset{\text{water}}{4H_2O}$$

$$\underset{\text{MSP}}{2NaH_2PO_4} + \underset{\substack{\text{calcium}\\\text{sulfate}}}{3CaSO_4} + \underset{\substack{\text{caustic}\\\text{soda}}}{4NaOH} \rightarrow \underset{\substack{\text{calcium}\\\text{phosphate}}}{Ca_3(PO_4)_2} + \underset{\substack{\text{sodium}\\\text{sulfate}}}{3Na_2SO_4} + \underset{\text{water}}{4H_2O}$$

$$\underset{\text{DSP}}{2Na_2HPO_4} + \underset{\substack{\text{calcium}\\\text{carbonate}}}{3CaCO_3} + \underset{\substack{\text{caustic}\\\text{soda}}}{2NaOH} \rightarrow \underset{\substack{\text{calcium}\\\text{phosphate}}}{Ca_3(PO_4)_2} + \underset{\substack{\text{sodium}\\\text{carbonate}}}{3Na_2CO_3} + \underset{\text{water}}{2H_2O}$$

$$\underset{\text{DSP}}{2Na_2HPO_4} + \underset{\substack{\text{calcium}\\\text{sulfate}}}{3CaSO_4} + \underset{\substack{\text{caustic}\\\text{soda}}}{2NaOH} \rightarrow \underset{\substack{\text{calcium}\\\text{phosphate}}}{Ca_3(PO_4)_2} + \underset{\substack{\text{sodium}\\\text{sulfate}}}{3Na_2SO_4} + \underset{\text{water}}{2H_2O}$$

$$\underset{\text{TSP}}{2Na_3PO_4} + \underset{\substack{\text{calcium}\\\text{carbonate}}}{3CaCO_3} \rightarrow \underset{\substack{\text{calcium}\\\text{phosphate}}}{Ca_3(PO_4)_2} + \underset{\substack{\text{sodium}\\\text{carbonate}}}{3Na_2CO_3}$$

$$\underset{\text{TSP}}{2Na_3PO_4} + \underset{\substack{\text{calcium}\\\text{sulfate}}}{3CaSO_4} \rightarrow \underset{\substack{\text{calcium}\\\text{phosphate}}}{Ca_3(PO_4)_2} + \underset{\substack{\text{sodium}\\\text{sulfate}}}{3Na_2SO_4}$$

It can be seen from these reactions that the requirement for caustic (or carbonate, which breaks down to form caustic) is high for MSP, less for DSP, and not required for TSP.

NOTE: Sufficient caustic is still required to maintain a suitable OH alkalinity reserve. Tests to confirm the presence of adequate alkalinity and a permanent phosphate reserve should be conducted frequently, normally at least once per day.

Hydroxyapatite produces a soft sludge that is not as sticky as *tricalcium phosphate* and can be more easily managed (dispersed) by a (polymeric) sludge conditioner.

The BW pH level should be above 10.2 to ensure that hydroxyapatite preferentially precipitates. Also, where magnesium is present, the pH level should be above 10.5 so that *magnesium hydroxide* [**brucite,** $Mg(OH)_2$] precipitates, rather than the stickier and more adherent **magnesium phosphate** [$Mg_3(PO_4)_2$]. In any event, where possible, it is

preferable to work with a BW pH of close to 11.0 because this is an optimum passivation pH level for steel.

NOTE: As the reaction between calcium and orthophosphate is rapid, it is not generally advisable to add phosphate to the feedline at any great distance from the boiler because the precipitation of phosphate sludge may foul the line quickly and eventually cause a complete blockage.

Phosphate should ideally be added continuously, direct to the boiler shell or steam drum, and in proportion to FW consumption. Where this is not possible and the phosphate is added to the feedline, several program options exist to minimize the potential for feedline blockage. The use of an alternate strategy is particularly important where an economizer is present. Options include:

1. *The use of a* ***polyphosphate,*** *first required to revert (thermally degrade) to the* ***orthophosphate*** *before the precipitation process begins.*
2. *Alternatively,* ***sodium metaphosphate*** *(an orthophosphate that has been "molecularly dehydrated" by the removal of a molecule of water) may be employed because this must regain the lost water molecule before reacting with calcium as the orthophosphate. This delay may provide the time necessary to ensure that the precipitation reaction takes place solely within the confines of the bulk BW.*
3. *Where direct addition to the boiler is possible, use a combined* ***phosphate-chelant program*** *because solubilization of hardness salts will occur; this limits the potential for adherence to metal surfaces.*
4. *A* ***phosphate-sludge conditioner blend*** *may be employed because the deposit control agent or sludge conditioner limits and controls crystal formation (threshold and crystal distortion effects) and ensures particle fluidization (dispersion effect).*

The phosphate requirement is primarily based on the FW hardness, so the lower the hardness, the lower the phosphate demand. Where hardness levels are continuously low, the phosphate reserve should be maintained closer to the minimum of the specified range (typically 30–60 ppm PO_4 for FT boilers operating up to 30 bar, 435 psig). Conversely, the phosphate reserve should be higher with variable or higher FW hardness levels. If higher phosphate reserves are required, the hydroxide alkalinity should be increased accordingly.

NOTE: Higher incoming hardness ultimately results in a reduction in BW alkalinity because the various hardness and phosphate reactions consume alkalinity in the production of tricalcium phosphate and hydroxyapatite.

Normally, the minimum BW hydroxide alkalinity required is approximately 200 to 300 ppm (as $CaCO_3$) for boilers under 300 to 400 psig. If this level is allowed to drop significantly, hard, dense, and adherent phosphate scale will likely form in the boiler.

Phosphate and caustic may be mixed together (most formulations provide for this) in the same day tank.

The chemical feed pump should be wired into the boiler FW pump, so that when the boiler calls for water, both phosphate and alkali are added in proportion to the FW volume and the hardness it contains.

To ensure adequate fluidity of the phosphate sludge, polymer also may be added to the same day tank, although it is often added to the FW tank or feed line.

10.4.3.3 Phosphate-Cycle Requirement Calculations

For **precipitating phosphate programs** it is necessary to ensure adequate BW alkalinity in addition to the phosphate reserve. *Sodium hydroxide should be used.* The **alkalinity feed-rate** is based on FW consumption and calculated as follows:

$$[0.67 \times FWCaH + (FWMgH - FWMA + \underline{RBWPA})] \times \frac{100}{\%\ \text{NaOH in product}}$$
$$COC$$

$$= \text{lb of product required, per } 1 \times 10^6 \text{ lb of boiler FW}$$

Where:
FWCaH = FW calcium hardness, in mg/l (ppm) $CaCO_3$
FWMgH = FW magnesium hardness, in mg/l $CaCO_3$
FWMA = FW methyl orange/total alkalinity, in mg/l $CaCO_3$
RBWPA = Required BW phenolphthalein alkalinity, in mg/l $CaCO_3$
COC = Cycles of FW concentration required in the BW

Factor 0.67 above originates from the phosphate to calcium ratio, i.e., $2(PO_4^{3-}) + 3(Ca^{2+}) \rightarrow Ca_3(PO_4)^2$, $^2/_3 = 0.67$.

Example:

Boiler steam production = 250,000 lb/day

Condensate return (CR) = 75% (assume clean CR—no contaminants)

MU water Ca hardness = 8 mg/l $CaCO_3$

MU water Mg hardness = 4 mg/l $CaCO_3$
MU water M alkalinity = 60 mg/l $CaCO_3$
RBWPA = 500 mg/l $CaCO_3$
COC = 25x
Alkalinity-furnishing product contains 15% NaOH

Therefore:
FWCaH = 2 (8 x 25%)
FWMgH = 1 (4 x 25%)
FWMA = 15 (60 x 25%)
RPBWA = 500
COC = 25
% NaOH = 15

Substituting:

$$[0.67 \times 2 + (1 - 15 + \frac{500}{25})] \times \frac{100}{30}$$

= 24.4 lb of product required, per 1×10^6 lb. of boiler FW

This approximates to, say, 24 lb. per 1×10^6 lb, or 6 lb of alkalinity-furnishing product per day.

NOTE: If the value within brackets is negative, adequate free alkalinity exists in the FW and the addition of supplementary alkalinity is not required.

Additionally, the **phosphate feed-rate requirement** for FW must be calculated. The following formula will suffice:

$$[0.67 \times FWCaH + (\frac{RBWPO_4}{COC})] \times \frac{100}{\%\ PO_4\ \text{in product}}$$

= lb of product required, per 1×10^6 lb of boiler FW

Where:
FWCaH = FW calcium hardness, in mg/l (ppm) $CaCO_3$
$RBWPO_4$ = Required BW phosphate reserve in mg/l PO_4
COC = Cycles of FW concentration present or desired in the BW

Typically, for FT boilers operating phosphate-cycles programs at pressures below 435 psig (30 bar):

- Maintain BW total (M) alkalinity at 350 to 700 ppm CaCO3.
- M alkalinity should generally not exceed 20% of the TDS.
- Maintain OH alkalinity at a minimum reserve level of 350 ppm $CaCO_3$.
- Maintain phosphate reserve at 30 to 60 ppm PO_4 (50 to 100 ppm Na_3PO_4).
- If maintaining phosphate reserves toward the upper end of the range, ensure caustic alkalinity is also high. Try to ensure an OH:PO_4 ratio of 10 or 12 to 1.

NOTE: All these recommended values relate to moderately rated FT boilers. Where highly rated FT boilers are concerned, values should be maintained at perhaps 10 to 20 % of the above. This may require higher quality FW.

Where phosphate-cycle chemistry is employed in WT boilers, a different set of rules apply. However, for *non–highly rated boilers,* phosphate-cycle programs normally may be employed up to 1,200 psig (82 bar), and phosphate itself is generally satisfactory in industrial applications up to at least 1,885 psig (130 bar), or for any specific boiler application up to the **phosphate hideout point.**

NOTE: Phosphate is employed in utility boilers at pressures up to 2,750 psig (190 bar, 360 °C/680 °F).

In practice today, coagulation and precipitation chemistries using phosphate-cycle programs employing a *free-caustic reserve* are widely employed in boilers operating at up to 950 psig (65.5 bar). This is, however, only for conventional, non–highly rated, nonriveted, stress-relieved,welded industrial boilers. For higher pressure, nonconventional, or highly rated industrial or power boilers, coordinated phosphate or other, more appropriate, programs tend to be employed.

Tables 10.4 and 10.5 set out phosphate-cycle control limits. These control limits are for non–highly rated, FT and WT boilers and assume that modern *polymeric sludge conditioners* are employed (i.e., not starches, lignosulphonates, etc.).

10.4.3.4 Phosphate-Cycle Benefits and Formulations

Phosphate-cycle programs are a relatively low-cost, well-established technology that provides good, well-proven results in variable and

Table 10.4 Phosphate-Cycle Coagulation and Precipitation Program. Recommended BW Control Limits for Non-Highly-Rated FT Boilers Employing Hard, Partially Softened, or Fully Softened FW.

FW hardness, ppm $CaCO_3$	***40 to 50***		***5 to 10***		***1 to 2***
Pressure, psig/bar max. (approximate	150/10	250/17	150/10	250/17	350/25
BW chemistry control limits					
BW TDS, ppm max.	2000	1750	2500	2000	3500
Silica, ppm SiO_2 max.	140	140	140	140	175
S/Solids, ppm max.	300	250	200	150	50
T Alk., ppm $CaCO_3$ max.	700	600	900	700	1200
OH Alk., ppm $CaCO_3$	In all cases this should be 350 min.				
Phosphate, ppm PO_4	In all cases this should be 30 to 60				

NOTE: This chart assumes oxygen scavenger, polymer, and other necessary water chemistry controls are in place.

higher hardness FW. They are safe, are noncorrosive, and have a high tolerance for excursions in FW quality, provided that an adequate OH alkalinity and phosphate reserve is available.

The drawback is that the precipitation chemistry results in suspended solids that must be fluidized and removed from the boiler by BD, so a *polymeric sludge conditioner (dispersant, deposit control agent)* product and additional BD is required. The higher the FW hardness, the more BD is required because of the buildup of suspended solids, so there is a trade-off in terms of operating with lower quality FW and the resulting reduced efficiency.

Two examples of typical phosphate-cycle formulations are shown here.

Phosphate-Cycle Formulation for Simple Systems with Adequate FW Alkalinity	***Materials***
Caustic soda	4.0%
SHMP	25.0%
PAA	10.0%
PAGMBE	0.2%
Water	60.8%
	100.0%

Table 10.5 Phosphate-Cycle Coagulation and Precipitation Program. Recommended BW Control Limits for Non-Highly-Rated WT Boilers Employing Hard, Partially Softened, or Fully Softened FW.

Pressure, psig/bar max. (approx.)	350/25	650/45	950/65
FW hardness, ppm, $CaCO_3$	**40 to 50**	**10 to 20**	**5 to 10**
BW chemistry control limits			
TDS, ppm max.	2000	2000	1500
Silica, ppm SiO_2 max.	0.4*x* OH alkalinity	0.4*x* OH alkalinity	0.4*x* OH alkalinity
Suspended solids, ppm max.	300	200	100
T Alk., ppm $CaCO_3$ max.	700	600	500
OH Alk., ppm $CaCO_3$ min.	350	300	250
Phosphate, ppm PO_4	30 to 60	30 to 50	20 to 40
Pressure, psig/bar max. (approx.)	350/25	650/45	950/65
FW hardness, ppm, $CaCO_3$	**1 to 2**	**<1.0**	**<0.5**
BW chemistry control limits			
TDS, ppm max.	2500	1500	1000
Silica, ppm SiO_2 max. alkalinity	0.4*x* OH alkalinity	0.4*x* OH alkalinity	0.4*x* OH
Suspended solids, ppm max.	50	20	5
T Alk., ppm $CaCO_3$ max.	600	500	300
OH Alk., ppm $CaCO_3$ min.	300	150	60
Phosphate, ppm PO_4	30 to 60	20 to 40	15 to 30

NOTE: This chart assumes oxygen scavenger, polymer, and other necessary water chemistry controls are in place. If determining TDS via a conductivity meter, use an un-neutralized sample.

Phosphate-Cycle Formulation for Systems with Moderate Alkalinity, Higher Hardness FW	***Materials***
Caustic soda	13.0%
STPP	13.0%
PAA	6.0%
Sodium lignosulfonate	9.0%
PAGMBE	0.2%
Water	58.8%
	100.0%

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NOTE: The first formulation operates under a control limit of 20x COC. The second formulation offers the benefit of additional on-line chelating and cleaning power through use of STPP. A limit of 10 to 12x COC would typically apply.

Because all phosphate-cycle programs employ polymers, the distinction between **simple phosphate programs** and **phosphate-polymer programs** is blurred. A subtle distinction is that simple phosphate programs were essentially designed to provide alternatives to the carbonate-cycle as a means of internally treating FW with up to perhaps 40 to 50 ppm total hardness, whereas more modern phosphate-polymer programs strive for low hardness FW, with the phosphate acting as a "reserve" and providing an easy means of testing.

10.5 CHELANT PROGRAM CHEMISTRIES

Chelant programs are **solubilizing programs** and are commonly prescribed for both FT and WT boilers either as replacements for, or used in combination with, **phosphate precipitation programs**.

Chelants are relatively high molecular weight compounds and react stoichiometrically with cations. In higher hardness waters the consumption of chelant-based programs may be both excessive and expensive; consequently, they are not normally employed with high hardness FW sources.

Chelants tend to be used in the following types of situations:

1. **In low-hardness FW hardness boilers**, where very clean waterside surfaces are needed to maximize heat transfer. Here the formulation may be essentially a *"straight" chelant* with minimal additional ingredients, or it may be a *balanced chelant-polymer program.*
2. **As a continuous support to an existing program** that is struggling to maintain overall effectiveness. Here a straight chelant formulation may be used.
3. **Under variable FW conditions,** where waterside fouling has occurred and on-line cleaning is needed. In this situation, the initial cleaning phase may use a high-chelant formulation (e.g., *chelant-phosphonate program*), following which a low-chelant formulation may be employed (e.g., a *phosphate-chelant program*).

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NOTE: All chelant formulations should be manufactured using high-quality water because any residual hardness will be complexed and reduce the active strength of the chelant.

10.5.1 Chelant Basics

(Chelant: from *Chela,* the claw of a crab, lobster, or scorpion, and, in this context, meaning to **hold apart**).

Chelants, or **chelating agents**, typically are organic chemicals (although inorganic chelants exist) that react with polyvalent metal ions to form stable ring structures that incorporate the metal ion within the molecule. Chelants *tie up* metals and deactivate them.

The mechanism of chelation involves the donation of a pair of electrons to a substrate species (such as *iron, copper, calcium,* or *magnesium*) and a reconfiguration of the shape of the new molecule to provide a minimum of bond strain. The chelant or **ligand** "bites" the substrate at several points, forming a stable, but not necessarily particularly strong, coordinate bond.

Ligands "bite" at one or more points. Chelants bite at two or more points, so all ligands are not necessarily chelants. Chelants forming water-soluble complexes with metal ions are called **sequestrants** (but not all sequestrants are chelants). The most commonly employed BW chelant, **ethylenediaminetetraacetic acid** (EDTA) produces coordination complexes with four points of attachment and is termed a *tetradentate ligand.*

The size of the EDTA ring structure complex (not too big or too small), plus the multiple points of attachment, provides a very stable complex (high stability constant) that overcomes reaction tendencies to reach equilibrium via the lowest possible energy state or maximum state of disorder **(entropy)**.

The affinity of chelants for particular substrates differs, but copper, chromium, and iron are more attracted than calcium or magnesium. Chelation is also affected by pH levels and other conditions, so it is necessary when formulating BW compounds to ensure that the correct chelant is selected for the particular purpose.

Apart from the primary purposes of tying up alkaline earth metals to reduce waterside fouling and solubilizing old, formed deposits, formulators have also long used chelants because of their buffering, product stability, and oxidation-reduction control effects.

The most common chelants employed for boiler deposit control, solubilization, and cleaning duty include:

- **EDTA** and especially its tetrasodium, dihydrate salt, $NaO_2CCH_2N(CH_2CO_2Na)CH_2{\cdot}CH_2N(CH_2CO_2Na)CH_2CO_2Na{\cdot}2H_2O$. EDTA is an aminopolycarboxylic acid. Others include **N-hydroxyethylenediaminetriacetic acid** (HEDTA) and **diethylenetriaminepentaacetic acid** (DTPA). The primary manufacturers of EDTA and related chemistries are the Hampshire Chemical Division of W.R. Grace, Inc. (**Hampene®**) and DOW Chemical Company, Inc. (**Versene®**). Anhydrous EDTA has a MW of 380. It is generally supplied for incorporation into formulations as 38% EDTA (41.6% EDTA $Na_4{\cdot}2H_2O$), (Hampene 100/Versene 100) specifically because its chelating activity at a pH level of 11 is 100 mg $CaCO_3$ per gram of chelant. That is, 10 ppm of chelant will sequester 1 ppm of calcium hardness.
- **Nitrilotriacetic acid** (NTA) and especially its trisodium, monohydrate salt, $N(CHCOONa)_3{\cdot}H_2O$. NTA is primarily manufactured by Monsanto Chemical Company, Inc. and Hampshire Chemical. Anhydrous NTA has a MW of 257. It is generally supplied for incorporation into formulations as 40% NTA (42.8% NTA $Na_3{\cdot}H_2O$), (**Hampene 150**). Its chelating activity at a pH level of 11 is 156 mg $CaCO_3$ per gram of chelant. That is, 10 ppm of chelant will sequester 1.56 ppm of calcium hardness.
- **Diethanolglycine** (DEG), **ethanoldiglycine** (EDG), and their salts, which are used for the control of iron in alkaline solutions (DEG at a pH level of 9.5 to 12.5 and EDG at 6.5 to 9.5).
- **Citric acid** and other *hydroxycarboxylic acids,* such as **gluconic acid.** Also, derivatives such as **sodium gluconate** (D-gluconic acid, sodium salt), $HOCH_2[CH(OH)]_4\ COONa$.
- **Sodium glucoheptonate** (sodium heptonate), which has the formula, $HOCH_2[CH(OH)]_5COONa$. Glucoheptonate shows a greater stability than sodium gluconate and retains the ability to chelate ions effectively in high pH water, which citrates and EDTA do not do so well. Because of the ability of glucoheptonates to chelate calcium and iron, and to dissolve rust films without attacking the bare metal (in the pH range of 5 to 9), it is very useful in boiler cleaning operations.
- **Phosphonates,** especially **aminotri(methylenephosphonic acid)** (ATMP) and **1-hydroxyethylidene-1,1-diphosphonic acid** (HEDP). Organophosphonates have the ability to control both scaling and corrosion by a combination of chelation and crystal nuclei growth supression (**threshold**) mechanisms; they also provide scale control by crystal distortion.

- **Polyphosphates,** including **SHMP, TKPP,** and **STPP.**
- **Lignin sulfonates** (lignosulfonates), which are also sludge conditioners.

10.5.2 Practical Application of Chelants

EDTA and NTA are essentially the only two chelants formulated into BW deposit control programs. The rationale for selection of one product over another is often a point of contention. Looking first at the relative **chelation stability constants** (chelate log values, Ks):

- For Fe^{3+}, this is 25.1 for EDTA and 15.9 for NTA
- For Cu^{2+}, this is 18.8 for EDTA and 12.7 for NTA
- For Fe^{2+}, this is 14.3 for EDTA and 8.8 for NTA
- For Ca^{2+}, this is 10.6 for EDTA and 6.4 for NTA
- For Mg^{2+}, this is 8.7 for EDTA and 5.4 for NTA

This clearly shows that EDTA forms a stronger complex than NTA for all common BW contaminants.

*NOTE: It is also apparent that the **ferric ion** (Fe^{3+}) should chelate most readily. In practice, however, under strongly alkaline conditions, the preferred reaction is to instantaneously form **ferrous hydroxide** and then to slowly revert to **ferric hydroxide** (**competing anion effect**).*

The **order of chelation** under most boiler conditions is: calcium > magnesium > iron > copper.

NOTE: If the BW contains phosphate, the preferred reaction is for calcium to precipitate as hydroxyapatite, rather than to chelate with EDTA or NTA (a further competing anion effect). Consequently, there would seem to be no valid reason to produce combined phosphate-chelant programs, with the chelant acting as a "reserve" against unforeseen hardness incursions caused by a softener leakage, or other source. In practice, the chelant acts to solubilize existing deposits, producing a very clean boiler.

Looking next at the thermal and hydrolytic stability:

- NTA is stable up to 900 psig (530 °F, 62 bar, 222 °C) and then rapidly hydrolyzes. It is fully broken down at 1,000 psig.

- EDTA begins to decompose at only 400 psig (441 °F, 27.5 bar, 227 °C). However, the initial decomposition products are weaker chelants, **hydroxyethyliminodiacetic acid** (HEIDA) and **iminodiacetic acid** (IDA), so chelation still takes place. (Hydrolysis of HEIDA then continues at a much slower rate to produce more IDA and ethylene glycol.) Despite this reversion problem, EDTA is effective and, in practice, is employed at up to 1,200 psig (82.7 bar) and up to 1,500 psig (103.4 bar) when employed as an **overlay product**.

Finally, when comparing the relative cost and consumption of NTA and EDTA. It is a fact, that NTA is considerably less expensive than EDTA (about 60% of the cost of EDTA, depending on specific market conditions). However, this gain may easily be lost, depending on the relative cost impact of other formulatory ingredients. Also, the selling price of most boiler compounds is normally several times the raw materials and blending or drumming cost (to pay for technical support and other customer services), so that any cost benefit gains are further diluted.

Where NTA does provide a benefit over EDTA is in the area of **chelant demand**. NTA has a smaller molecule and does not require as much product to form the **chelonate** (see Table 10.6).

In larger boiler plants, the 99 to 100% versions of NTA are sometimes employed, also EDTA disodium salt (see Table 10.6), and more recently, HEDTA.

Table 10.6 Chelant demand (ppm product) per 1 ppm substrate

Substrate	*38% EDTA*	*Hampene Na_2*	*40% NTA*
Chelant molecular weight	380	372	257
Hardness, ppm $CaCO_3$	10.0	3.7	6.5
Calcium, ppm Ca	25.0	9.3	17.3
Magnesium, ppm Mg	41.0	15.5	28.3
Iron, ppm Fe	17.9	6.6	12.3
Copper, as ppm Cu	15.7	5.8	10.8
Aluminum, as ppm Al	37.1	13.7	25.5

*NOTE: **38% EDTA** = 41.6% EDTA Na_4•$2H_2O$, Hampene or Versene 100 (100 mg $CaCO_3$/g). Typically supplied as a 40% w/w product. **Hampene Na_2** = 99% EDTA Na_2•$2H_2O$, (267 mg $CaCO_3$/g). **40% NTA** = 42.8% NTA Na_3•H_2O, Hampene 150 (156 mg $CaCO_3$/g). Typically supplied as a 43% w/w product.*

HEDTA has been widely used as a boiler cleaning compound, but has proved useful for iron control at elevated temperatures. HEDTA is supplied as 98% $Na_3 \cdot 2H_2O$ (MW 380) and has a chelating activity of 258 mg $CaCO_3$/g at a pH level of 11.

NOTE: Although control over transported iron is critical in larger power boilers, as discussed earlier, control by the chelation of ferric iron is not possible (because of the competing anion effect). Consequently, Fe_2O_3 and Fe_3O_4 are essentially unaffected by chelants. However, it is well known that where an iron chelate (chelonate) is formed, it is stable and will not be destroyed by hydrolysis at high temperature.

Chelant demand can be calculated by referring to Table 10.6 and the formula below.

$$\textbf{FW chelant demand (ppm)} = (A + B + C) + \frac{\text{BW chelant residual}}{\text{COC}}$$

Where:

$(A + B + C)$ = sum of individual FW contaminant substrates × respective chelant demand for specific chelant employed

BW chelant residual = typically 3 to 5 ppm

COC = Cycles of FW concentration present or desired in the BW

NOTE: If the chelant forms only part of the formulated product, the ppm of product required in the FW is determined by dividing the total chelant demand by the percentage chelant in the product.

The most reliable way to control the chelant program is to base it on FW chelant demand, rather than to aim at maintaining a **chelant residual** in the boiler. The fact is that most chelant residual tests in the field are widely inaccurate, and EDTA begins to break down at pressures over 400 psig. Nevertheless, it is useful to conduct these tests on a purely qualitative basis, simply to gain some confidence that a small residual exists. Consequently, recommended chelant residuals are provided in the appropriate tables. Needless to say, it is imperative that the chelant demand is made on a truly representative FW sample or series of samples.

Chelant programs offer a number of benefits over phosphate programs, primarily:

1. Hardness is controlled as a soluble complex rather than being precipitated.

2. Boiler surfaces tend to be cleaner with little or no suspended solids or sludge present, resulting in improved heat transfer.
3. The lack of sludge reduces the need for BD, which further improves efficiency.

An issue with chelants, and especially EDTA as the most widely used chelant, is the risk of corrosion to the feed equipment, feed injection points, and ultraclean boiler surfaces. This issue is generally associated with a lack of **oxygen control** in some way or other.

High temperature hydrolysis of EDTA is accelerated by the presence of oxygen, and **chelant corrosion** may take place in the presence of oxygen and a chelant overfeed. (See Section 7.4.1 for more details). Key points are:

1. Chelant corrosion only takes place when a number of unfavorable boiler operating factors are collectively present, including an overfeed of chelant *and* the presence of DO.
2. High levels of chelant or *oxygen* affect the **redox** tendencies of iron-oxygen reactions and permit the liberation of Fe^{2+} ions (corrosion) from a metal surface and their subsequent chelation, thus preventing the formation or repair of blanketing ferric oxides, hydroxides, or a passivated magnetite film.
3. Under normal conditions, the magnetite film is not disrupted by the presence of chelant.
4. Where chelant corrosion does occur, attack may take place either at the *chelant entry point* (resulting in rapid thinning of the metal in the immediate vicinity) or at several possible *boiler surface* locations (resulting in **thinning wastage** and **"comet tails"**).
5. Extremely good control over oxygen levels is critical when using chelants. The injection point of chelant should be into the boiler FW as far downsteam as possible from the deaerator and chemical oxygen scavenging point to permit sufficient time for effective oxygen removal to take place. Typically, the injection point is the high-pressure side of the FW pump. This serves to dilute the chelant before it enters the boiler drum and provides for low-temperature complexing so that hydrolytic breakdown is minimized.
6. Where good control over oxygen and overfeed is exercised, boilers are always clean and the rate of internal corrosion is limited (certainly no worse than for other types of programs).

Further chelant program control notes are:

- Only low total hardness levels can be tolerated (the ceiling is 0.5–3.0 ppm $CaCO_3$) or the program becomes too expensive. Chelant programs work particularly well with good quality FW.
- Boiler water chelant reserves are minimal, so that any change in FW substrate contaminants demands additional chelant, unlike phosphate-cycle programs, which carry a much higher reserve and can manage occasional incursions without any change in product feed.
- Optimum chelation pH level is 11.0 to 11.2. This corresponds to a P alkalinity in the boiler of approximately 300 to 500 ppm $CaCO_3$. The lowest practical caustic alkalinity is 100 ppm.
- If the alkalinity is too low, iron corrosion may take place. If the alkalinity is too high, there is a further competing anion effect, with magnesium precipitated as $Mg(OH)_2$, rather than chelated.
- Silica control requirements are the same as for phosphate-cycle programs.
- Where oil is present in the FW, special precautions must be taken when using chelant programs. Under coagulation and precipitation programs, any oil is partially absorbed on the precipitate and the problem is minimized. However, because no sludge is present in chelant programs, the oil problem is magnified. Use antifoams and increase BD.
- Chelants should not be used downstream of hot process or hot lime soda softening MU water treatment.
- Chelants should not be used in the presence of of high iron and copper content or in boiler systems with either very high or very low velocities because corrosion rates may be enhanced.
- Chelants should not be used where the design is particularly sensitive to corrosive conditions (e.g., certain economizer systems).
- The simplest type of **chelant formulation** is standard industrial-strength liquid EDTA (38% w/w Hampene 100 or competitive equivalent).

10.6 ALL-POLYMER/ALL-ORGANIC PROGRAMS

NOTE: This section discusses organic BW treatment inhibitors and conditioners but is not concerned with those classes of organics used for oxygen

scavenging or steam-condensate line corrosion control. Rather, it is primarily intended to examine modern sludge conditioners and deposit control agents (DCAs) as both overlays and complete replacements for conventional programs.

As in cooling water (CW) inhibitor formulation chemistries today, a significant proportion of any BW chemical program is now invariably organic based and often polymeric. *Sludge conditioners* have always been of organic origin (generally natural organics). Many of these functional chemicals have been employed for more than 50 years and remain in useful service to this day. They include **carboxy-methylcellulose** (CMC), **tannins, hydrolyzed starches,** and **lignins** (as **lignosulfonates**). However, these materials usually are consigned to the smaller and relatively lower pressure end of the BW treatment market.

- *CMC (sodium salt)* is useful for internal precipitation programs with high sludge volumes because it acts as a **protective colloid** (a colloid that prevents the precipitation or coagulation of another colloid).
- *Tannins,* as DCAs, are particularly effective in conditioning carbonate-cycle sludges.
- *Starches* continue to be useful in cases of continuous oil contamination and with high-silica FWs where silicate sludges are produced.
- *Lignins,* as DCAs, are excellent for phosphate-cycle sludges in FT boilers where FW hardness may vary and also where iron oxides are present.

In the pursuit of enhanced water treatment performance (and higher profitability), various novel organic chemistries have periodically been introduced into the marketplace over the years, including **polyacrylates**, **polymethacrylates**, **polyacrylamides**, **phosphonates**, and **maleates.** The trend in recent years, however, has been for major international chemical companies to significantly increase the rate of development and marketing of new chemistries or modifications of existing chemistries. The resulting products tend to be branded and heavily promoted; they are extremely effective as replacements for traditional *sludge-conditioning additives* But in addition, they also support, enhance, or even totally replace several of the existing mainstream BW *scale* and *corrosion control technologies,* including **anodic inhibitors**, **tannins**, **carbonates**, **phosphates**, and **EDTA/NTA chelants**.

Some of these newer chemistries (those possessing the highest thermal stability) are suitable for application in industrial WT steam generators and power boilers operating at pressures of 1,500 psig and possibly higher.

These novel organic polymers were not developed solely for the CW or BW treatment market but are for much wider application. These same value-adding process additives are regularly incorporated into products for *industrial and domestic cleaning, concrete, pulp and paper, metal finishing, paints and surface coatings, wastewater, seawater distillation, drilling muds, secondary oil-recovery, plastics extrusion, fibers, rubbers,* and a host of other areas.

Many of these newer chemistries compete with each other in specific application areas, and for any particular chemistry to succeed, it is necessary for the technologist to know under what operational conditions it may add value to the process and how best to apply and control the product.

This is precisely the position in the BW treatment marketplace because, although there are several different basic organic chemistries readily available and literally hundreds of branded, organic raw materials around the globe for the formulator to choose from, the necessary information regarding in-field applications and practical operating expertise is more difficult to obtain.

This position is made even more difficult because most available technical information concerning these novel chemistries is for the pure polymer; almost without exception, formulators will employ at least two or three classes of organic materials (all of different chemistries) in each BW *sludge conditioning and deposit control program.* This practice is designed to obtain synergistic program benefits while keeping raw material ingredient costs down to a minimum (polymers are expensive). Thus, to obtain optimum in-field results, it is also necessary to understand the compatabilities, synergies, and limitations of each class of polymer or organic.

There are many types of **all-polymer/all-organic programs** on the market today, and with the ready availability of both broad-spectrum and highly specialized polymeric ingredients, these programs are commonly proposed for application in almost every shape, size, and pressure of boiler plant, from the smallest to the largest.

NOTE: Although this class of program is usually called "all-polymer," this is incorrect because other types of organic DCAs are usually present. The term "all-organic" is preferred.

Also, these programs seldom contain only organic ingredients, as sodium or potassium hydroxide usually is present, and some multifunctional programs contain sulfite as an oxygen scavenger.

All-polymer/all-organic programs are relatively thermally stable and multifunctional. Typically, they replace **coagulation and precipitation programs**, **flocculation improvers**, **deflocculators**, and **sludge conditioners** and also provide control over very specific and troublesome BW problems, such as **silica scaling** and **iron transport**.

- Because of their high degree of hydrolytic stability and the extended abilities and effectiveness of these novel chemistries, wherever *phosphate-cycle* or *chelant programs* are employed, the circumstances generally permit all-polymer/all-organic programs to be used as technically and economically viable alternatives.
- The essential quality of *all-polymer/all-organic programs* is their high-efficiency operating performance and ability to produce ultraclean waterside surfaces. As a consequence, to obtain maximum beneficial effect from these programs, FW quality should be very good. Either use fully softened MU water or, if boiler pressure demands it, MU water of demineralized or equivalent quality.

All-polymer/all-organic programs enjoy significant growth in an otherwise mature and largely static marketplace. They possess a degree of novelty and a "high-tech" status, but are more expensive than traditional programs. Despite their popularity, they are not without some inherent problems:

1. There is wide variation in the activity, specificity, compatibility, and mode of action of the many individual raw material organics used in product formulations. The quality of some raw materials, and ultimately supplier formulations, may be suspect. Not all competitive polymers or formulated products provide equal performance for an equivalent price.
2. For any specific BW treatment application, determining the types and concentrations of polymers that are likely to prove the most successful remains a difficult task. There are few design rules, the in-field application and control processes are still more art than dependable science, and the various reaction mechanisms are not

stoichiometric. Too much or too little polymer in the BW, and the results are likely to be both unpredictable and unsuccessful.

NOTE: Despite these applications technology "negatives," all-polymer/all-organic programs are essentially safe materials and generally work incredibly well, providing very clean, corrosion-free boilers. Their ability to perform under widely variable and difficult operating circumstances, and limited polymer-control conditions, is often outstanding.

1. The provision of simple, low-cost but accurate means of the in-field testing of polymers or other organic ingredients is a notorious dilemma. Consequently, the downstream chain of confirming BW product reserves and identifying optimum courses of action to forestall potential future waterside deposit problems, also may be a problem.

*NOTE: Although polymer **tagging methods** such as **TRASAR®** from **ONDEO Nalco** (now part of Suez-Lyonnaise) has been available for quite some time, it is not necessarily simple, low-cost, or commonly available. Also, the use of lower-key, specialty polymer tagging and accompanying immunoassay field-testing methods, such as **Optidose®** from **Rohm and Haas Company** and **Bel-Trak™** from **Bio-Labs/Great Lakes Chemical Company** (previously Ciba-Geigy then FMC Corporation) have not yet been fully accepted by mainstream water treaters. The range of tagged polymers available for incorporation into formulations may gradually expand in time, and presumably, increased competition will help reduce the costs of these polymers. However, if users are determined in their search to find ways to easily and accurately measure polymer reserves, it is likely that they also will demand some form of on-line, real-time measurement, rather than an after-the-fact monitoring system.*

A further complication is that even if acceptable, simple, low-cost, but accurate methods of polymer detection existed, the level of product reserve in the bulk water often has little relevance to the reactions taking place at the metal-water interface and boundary layers.

NOTE: Compare this with similar problems in CW systems—those of easily and accurately (and at low-cost) determining levels of microbiological contamination. In most CW systems, apart from a general maintenance quality indicator, the levels of bulk water planktonic organisms tend to have little relevance to sessile organism-biofilm reactions occurring at the metal-water interface.

10.6.1 Functional Attributes of All-Polymer/ All-Organic Chemistries

Each of the many different types of polymers and related organic ingredients employed in BW products today tend to have several functional attributes that warrant their potential selection in particular formulations. When two or more materials are blended together, each may provide some degree of overlapping functionality and, ideally (if formulated correctly), these will provide a degree of synergism that confers additional technical and value-adding benefit to the finished product.

Polymer technology has progressed very rapidly in recent years, and it is now common research and development practice to design polymers with specific, marketable functions by varying chain lengths, structural composition, and functional positioning.

When the same **monomer** is used to build up a polymer, it is termed a **homopolymer**. **Copolymers** have two different monomers or functional groups, and **terpolymers** have three groups. There are even tetrapolymers available. These polymers may be further classified, for example, as *random, graft,* or *block copolymers.* **Block copolymers,** which have alternating sections of specific molecular chains, are used in BW formulations (but are more commonly found in CW programs).

As a generality, most foulants tend to have a slightly *negative* surface charge, Consequently, those polymers with *dispersing* and *scale-inhibiting* functions tend to have *weakly anionic* sulfonate groups, which adds to the foulants' total negative surface-charge and thus increases the *repelling (dispersing) action.*

The stronger **carboxylate groups** (such as **polyacrylates** and **maleates**) provide a coordinate bond that aids *solubilizing* and *descaling actions* and prevents sludge particles sticking onto waterside surfaces *(sludge conditioning function).*

Nonionic functional groups provide *steric repulsion* and *improved particulate adsorption.* Each of the various polymers, phosphonates, and other organics employed have combinations of functions. The overall molecules may act as:

- **Deposit control agents** (DCAs) or **antiscalents** to inhibit the deposition of $CaCO_3$ and other alkaline earth salts.
- **Chelants** or **sequestrants** to provide a metal complexing and solubilizing action.
- **Dispersants, antifoulants,** or **sludge fluidizers** to control the physical adherence of insoluble salts, corrosion products, oils, fats, and

process contaminants onto heat-transfer and other water-wetted boiler surfaces.

- **Stabilizers, transport agents,** or **problem-specific polymers** to either inhibit, transport, or otherwise control the specific deposition of *sulfates, phosphates, carbonates, silicates, barium, iron, aluminum,* and other "difficult" metals and their salts in the BW. In reality, these specialist polymers are DCAs that act as **solubilizers, threshold agents,** or **dispersants** and **deflocculators** for precipitated salts and particulate and colloidal metals.
- **Antifoulants** or **metal surface cleaners** to reduce the risk of pitting corrosion and other forms of concentration cell corrosion initiated at the metal surface by shielding effects from inorganic deposits. These could also be called *deposit control agents.*

Essentially, most novel BW polymers, phosphonates, and related organics are employed as DCAs. Apart from dispersion, the commonest mechanisms employed include:

- **Hardness stabilization,** whereby the molecule functions at *substoichiometric levels* by **crystal growth retardation (threshold effect).**
- **Calcium carbonate crystal distortion** or **crystal modification,** which prevents the agglomeration of crystals to form heat transfer–resisting scales.

In addition, the molecules may also exhibit additional beneficial effects, these include:

- **Corrosion inhibition,** by mechanical deposition of crystalline or amorphous films on a metal surface.
- **Anodic polarization.**

10.6.2 Types of BW All-Polymer/All-Organic Chemistries and Products

Common chemistries include **tannins** and **lignins** but also more modern **polyacrylates** and derivatives, which often act as carriers for specific functional groups and provide novel chemistry molecules. The polyacrylates may also be *copolymerized,* perhaps with **maleates** *[maleic anhydride, cis-butenedioic anhydride* (OCOCH:CHCO) is the usual starting point material], **styrene** (*vinylbenzene, phenylethylene,*

$C_6H_5CH{:}CH_2$), or the unsaturated monovalent **vinyl** radical ($CH_2{:}CH–$) and then *sulfonated.*

Other common chemistries includes **phosphonates, polymaleates,** and **phosphono-** and **phosphinopolycarboxylates.**

Many sludge conditioner and DCA chemistries are acceptable by various national governments for use as safe BW additives where steam may contact food (although under certain strict conditions and concentration levels). In the United States, for example, these conditions are contained in the *Code of Federal Regulations (CFR) 21 §173.310 Boiler water additives.*

Acceptable chemistries include:

- **Sodium carboxy-methylcellulose**
- **Sodium lignosulfonate**
- **Tannins** including *quebracho*
- **Sodium humate**
- **Sodium alginates**
- **Polyacrylates**
- **Polymethacrylates**
- **Acrylate/acrylamide copolymer**
- **Acrylic acid/2-acrylamido-2-methyl propane sulfonic acid copolymer** (AA/AMPS)
- **Phosphinopolycarboxylic acid** (PCA type 16)
- **Polymaleic acid** (PMA)
- **Polyethylene glycol** (PEG).

10.6.2.1 Tannins and Lignin-Based Sludge Dispersants

Although tannins and lignins have been available for well over 50 years (and perhaps twice as long), they remain very useful as low-cost, general-purpose particulate-matter dispersants. Both tannins and lignins are coproducts of the wood pulping process

Tannin chemistry is complex and tannin blends (composed of single-tree species tannins mixed together) offer a number of useful water treatment functions. Apart from *oxygen-scavenging abilities,* they act as *passivating agents, film-formers, sequestrants,* and *polymeric sludge dispersants* (for more details, see Section 10.3).

The *sodium carboxylates* resulting from **hydrolyzable tannins** are similar to the **gluconates** and **sarcosinates** commonly employed as

iron chelants. They also produce an adherent, passive **iron tannate** complex and aid the stability of copper and copper alloy passive films.

The **nonhydrolyzable** *(condensed)* **tannins** and their derivatives have significant bond strength due to *hydrogen bonding.* They are all of high MW and function as *anionic polyelectrolyte* sludge conditioners, tending to sequester hardness salts and hinder their precipitation as crystalline scales. In addition, when precipitation does occur, the condensed tannins coagulate the particles, resulting in a mobile sludge that is easily blown down.

In the United States, *spray-dried tannins* are available from chemical distributors such as **American Industrial Chemical Corporation, Inc.** or as *liquid single-tannins* (40% w/w) from **Tannin Corporation** (Peabody, MA).

Lignins are most usually employed as various types of **sodium lignosulfonate** and are products of *sulfite pulping.* (**Kraft lignins** from the *Kraft pulping process* are also available.) They are used as *dispersants, binders, sequestrants,* and *emulsifiers.* Sodium lignosulfonate product variables include color, MW, and the degree of carboxylation and sulfonation on the lignin backbone.

Similar to tannins, the polycarboxylic acid group provides a *chelating function* that ties up metal ions. The anionic sulfonate group functionality confers both *solubility* and *dispersing capability* for multivalent cations (calcium, iron, etc.).

Kelig® 100 is a sodium lignosulfonate with a high degree of sulfonation and excellent sequestering properties, and it is compatible with almost all types of formulations.

Maracel® XE is a general-purpose BW lignosulfonate that imparts a darker color to the finished product than, say, the **Marasperse®** products (which are often used in CW formulations).

Neither tannins nor lignins steam distill.

10.6.2.2 Polyacrylates and Related Carboxylates

A wide range of **polyacrylic acids** (PAAs), **polymethacrylic acids** (PMAAs), **polyacrylamides** (PAMs), their *salts* and *homo-, co-,* and *terpolymer derivatives are* available from a great many manufacturers around the world today. *Polyacrylates* especially are a backbone of BW chemical formulations and are manufactured with an almost infinite variety of average molecular weights (MWs), MW distributions, activity strengths, and other characteristics.

The base materials include **acrylic acid** (*ethylenecarboxylic acid, propenoic acid, vinylformic acid,* CH_2:CHCOOH) and its sodium salt, **methacrylic acid** [*2-methylpropenoic acid,* CH_2•C(CH_3)COOH], **acrylamide** (*acrylic amide, propenamide,* CH_2:CH-$CONH_2$), and **methacrylamide**.

- Polyacrylates are anionic in character, and those with a MW of approximately 1,500 to 2,000 are useful as *calcium carbonate anti-scalents* under severe operating conditions. An example is **Polacryl® A30-43**.
- PAAs with a MW of approximately 2,000 to 3,000 are useful as *general-purpose antiscalents.* Examples include **Polacryl® A40-43, Good-Rite® K-752, Acumer® 1000, Aquatreat® AR-900**, and **Sokalan®PA20**.
- PAAs with a MW of approximately 4,000 to 6,000 are useful as *general-purpose dispersants.* Examples include **Polacryl® A50-43, Good-Rite® K732, Acumer® 1100, Aquatreat® AR-602, Sokalan®PA25**, and **BSI® 89**.
- PAAs are also recognized as useful DCAs for *calcium sulfate.* A typical MW is approximately 2,000 to 3,000.
- **Sodium polymethacrylates** are also anionic and are useful as *iron oxide dispersants* and *iron stabilizers.* Typical MWs range from 6,000 to 20,000. Examples include **Polacryl® F70-40S, Tamol® 850, Tamol® 960**, and **Aquatreat® AR-232**.
- **Polyacrylamides** are nonionic polymers, usually with much higher molecular weights (MW from 100,000 up to 12 or 15 M). They often are copolymerized with polyacrylates. Depending on the MW ratios employed, they may act as *colloidal dispersants, sludge conditioners,* or *flocculants.* Nonionics such as *polyacrylamides* (and *isobutylenes*) are particularly useful at dispersing uncharged particles.
- All of these various *homopolymeric carboxylates* may form soluble complexes with hardness salts in BW, similar to EDTA and NTA. However, using polyacrylates in dirty boilers with a considerable excess of *iron* or *calcium* may cause **metal acrylate deposition**.
- PAA, PMAA, and PAM are all useful, low-cost DCAs. They show good thermal stability well in excess of 250 °C/482 °F (600 psig/42 bar) and, despite gradual thermal breakdown at higher pressures, have been reported to still function properly at 330 °C/625 °F (1,800 psig/124 bar). Nevertheless, they exhibit only perhaps 30 to

40% of the iron oxide–dispersing capability of acrylic acid–based co- and terpolymers (such as **acrylic acid/vinylsulfonate copolymer**), which effectively confines them to simple dispersion duties in limited stress, lower pressure systems. Alternatively, they may be blended with higher efficiency polymers to gain a balance between performance and cost.

10.6.2.3 Polyacrylate Backbone, Co- and Terpolymers

For the most part, it is the provision of specific functional groups into certain positions on a backbone molecule, and its subsequent polymerization to form chains of particular molecular weight ranges, that gives the novel chemistry co- and terpolymers their beneficial and sometimes unique properties. Polyacrylates are commonly employed as backbone molecules.

- Some **acrylic acid copolymers** are promoted as having a very wide range of functions that permit them to act as *calcium phosphate DCAs, barium sulfate antiprecipitants, particulate iron oxides dispersants,* and *colloidal iron stabilizers.* One such popular copolymer is **acrylic acid/sulfonic acid** (or **acrylic acid/ 2-acrylamido-methylpropane sulfonic acid,** AA/SA, AA/AMPS). Examples of this chemistry include **Acumer® 2000** (4,500 MW) **2100** (11,000 MW) **Belclene® 400**, **Acrysol® QR-1086**, **TRC®-233**, and **Polycol®43**.
- Other chemistries include **acrylic acid/sodium 3-allyloxy-2-hydroxypropane sulfonate** (AA/COPS), such as **Aquatreat® AR-540**; and its newer derivative, having a higher degree of sulfonation, **acrylic acid/non-ionic aromatic and linear sulfonate** (AA/NI-AS-LS), **Aquatreat® AR-550**.
- **Acrylic acid terpolymers** have appeared on the market in recent years. With their broad spectrum of functions, they offer the potential for excellent waterside conditions. In particular, the terpolymers have proved to be very effective *particulate iron oxides dispersants* and *colloidal iron stabilizers.* Examples include **acrylic acid/sulfonic acid/sodium styrene sulfonate** (AA/SA/SSS), such as **Good-Rite® K781**, **K797**, **K798**. A further example is **acrylic acid/ sulfonic acid/substituted acrylamide** (AA/SA/NI), such as **Acumer® 3100**.
- Although the **terpolymers** have the widest possible range of functions, providing not only *basic calcium carbonate control,* but also *high-stress capability and dispersion of colloids, plus iron, phos-*

phate, and *silica control,* they are also the most expensive of the "designer" polymers. It is probable that for many types of commercial or industrial FT boiler operating below 350 psig, this cost is simply not justified. However, where difficult and intractable *iron transport* or *silica control* problems exist, the terpolymers come into their own. Even when thermal breakdown begins to occur, the degradation products generally continue to exhibit significant scale inhibition and other functional properties.

- Another excellent but expensive *acrylic acid terpolymer* is **Acumer® 5000**, a silica and magnesium silicate dispersant. Although this polymer remains effective well above 600 psig (42 bar), it is recommended that at or above this pressure, FW silica should be removed at source, using DI or some other appropriate external treatment process.

10.6.2.4 Phosphonates

Phosphonates are **organic phosphates** characterized by a C–P–O bond, which is much more resistant to hydrolysis than the **polyphosphate bond** (O–P–O) or the **phosphate ester bond** (C–O–P), making them suitable for many types of BW treatment formulation. Phosphonates were originally developed for the industrial and institutional (I&I) cleaning market in the 1960s, but are commonly employed in a myriad of applications.

Phosphonates exhibit all the properties of polyphosphates, such as *threshold effect, crystal distortion,* and *sequestration,* but are superior in their effectiveness. They provide good *chelates* for calcium, magnesium, iron, and copper and are commonly used where iron fouling is a problem. Their sequestering properties are generally superior to other common chelants, such as **EDTA** and **NTA**.

They also provide useful corrosion inhibition by the adsorption of calcium phosphonate onto iron oxide corrosion products, thus reducing the ferrous metal corrosion rate. Phosphonates can be described as **cathanodic** corrosion inhibitors.

However, some of the most widely used phosphonates tend to be poor calcium sulfate inhibitors, and they may **adversely affect the corrosion of copper in the boiler**, so care in formulation design and product application is very important.

There are several phosphonates commonly employed in BW compounds, as shown below. These are usually supplied as either the acid or sodium salt.

- **Aminotri(methylenephosphonic acid)** [ATMP or AMP] is the least expensive phosphonate. It is a good, general-purpose, cost-effective scale inhibitor; an effective *chelant;* and the most thermally stable of all the common phosphonates. It is satisfactory up to at least 700 psia. However, if fed as a concentrate ATMP may easily form insoluble calcium phosphonate and it may also affect copper. ATMP has a sequestration value of 870 mg $CaCO_3$/g product at a pH level of 11 and for iron, a sequestration value of 150 mg Fe/g product at a pH level of 10. The pentasodium salt has a MW of 409. Examples include **Dequest® 2000/2006, Mayoquest® 1230, Phos® -2, Briquest® 301-50A, Unihib® 305**, and **Codex®8503**.

- **1-Hydroxyethylidene-1,1-diphosphonic acid** (HEDP) is an excellent calcium carbonate scale inhibitor and is less likely to form calcium phosphonate sludge than ATMP. It is the *only* phosphonate approved under the U.S. CFR 21,§173.310. However, it is the *least* thermally stable of all the common phosphonates (90% scale inhibition loss at 450 °F/232 °C) *and is not suitable for use above 400 psia.*

  In addition, the sodium salts are metastable at best, producing white precipitates unpredictably and thus making formulatory work difficult. (It is also more expensive than ATMP.) HEDP has a sequestration value of 843 mg $CaCO_3$/g product at a pH level of 11. The tetrasodium salt has a MW of 294. Examples include **Dequest® 2010/2016, Mayoquest1500, Phos®-6, Briquest® ADPA 60A, Unihib® 106**, and **Sequacel® HD**.

- **2-Phosphonobutane-1,2,4-tricarboxylic acid** (PBTC) is the most expensive of the commonly used phosphonates. However it is excellent at providing calcium carbonate control under highly stressed operating conditions. It is most resistant to the problem of calcium phosphonate precipitation and, from an environmental position, has the lowest phosphorus content of the common phosphonates. The acid material has a MW of 270. PBTC has a sequestration value of 280 mg $CaCO_3$/g product at a pH level of 11. It is very stable and can operate under very high pH conditions. However, it may also attack copper. Examples include **Bayhibit ®AM, Mayoquest® 2100, Phos®-9**, and **Codex® 551**.

- **Hexamethylenediaminetetra (methylene phosphonic acid)** [HMDTMP] is an excellent DCA for calcium sulfate, but a relatively poor sequestrant compared to other phosphonates (although still satisfactory compared to EDTA and NTA, which have similar

sequestration values). HMDTMP has a sequestration value of 300 mg $CaCO_3$/g product at a pH level of 11. The hexapotassium salt has a MW of 721. Examples include **Dequest® 2054** and **Mayoquest® 1635**.

- **Diethylenetriaminepenta (methylene phosphonic acid)** [DETPMP] is the most effective sequestrant for barium sulfate. DETPMP has a sequestration value of 820 mg $CaCO_3$/g product at pH 11. The hexasodium salt has MW of 705. Examples include **Dequest® 2066** and **Mayoquest® 1860**.

10.6.2.5 Polymaleates

Maleate chemistry has proved to be an enduring mainstay of many water treatment formulations, primarily as non–phosphate-containing *calcium carbonate scale inhibitors.* For most water treatment applications, *polymaleic acid* and its derivatives offer a good alternative to phosphonate chemistries, when required.

- The *homopolymer* **polymaleic acid** (PMA) is made from the polymerization of **maleic anhydride**, which is subsequently hydrolyzed. PMA is a straight chain polymer and has the general formula $(C_4H_4O_4)_x$, where x is between 4 and 8, giving a MW of 500 to 1,000. PMA is also available as a neutralized salt and is marketed in several grades (often neutralized and with precise molecular weight distributions) for very specific water treatment and process applications. PMA is a particularly effective DCA for *calcium carbonate* scale under extreme stress conditions. It can provide excellent control over *calcium carbonate* scaling under high temperature, alkalinity, and pH conditions, and it exhibits perhaps the best *crystal-distorting* properties of all the commonly available scale inhibitors.

  PMA is useful as a *calcium sulfate* inhibitor and more recently has been promoted as an antiscalent for control of *high-silica* waters, countering newer silica control terpolymers (such as Acumer 5000).

  PMA may require support from a copper corrosion inhibitor under some circumstances **because it can adversely affect the corrosion of copper**.

  PMA does not exhibit particularly good dispersion properties and under difficult conditions should be blended with a contaminant-

specific dispersant. However, it is particularly thermally stable and can be used at pressures up to 572 °F/300 °C (1,300 psig/ 90 bar).

Examples of PMA include **Belclene® 200**, **Mayoquest® 3000**, **Acumer® 4210**, and **Polycol® 100**.

- The maleic copolymer, **sulfonated styrene maleic anhydride** (SS/MA) is a popular inhibitor for *calcium phosphate* control in phosphate-cycle and coordinated phosphate programs. As such, it competes with other *calcium phosphate* control technologies, such as AA/AMPS (AA/SA). SS/MA is an excellent calcium phosphate inhibitor when *soluble iron* is absent and can perform better than AA/AMPS. In practice, however, the ranking may change when soluble iron is present. It is nevertheless a very good *iron oxide* dispersant. In general, SS/MA and the other *calcium phosphate* inhibitors are not as good at inhibiting *calcium carbonate* scale as, say, PMA or HEDP. SS/MA is not as good at inhibiting *calcium sulfate* scale as PMA and 2,000 MW PAA.

  SS/MA may be structured in different ratios of **sulfonated styrene** to **maleic anhydride.** Typically, it is 3:1 (20,000 MW) or 1:1 (15,000 MW). The application rates of all *calcium phosphate scale/sludge inhibitors* or *"stabilizers"* vary, based on the amount of *calcium* present in the cooling system, with increased calcium hardness leading to higher levels of polymer required.

  SS/MA is very useful in cleaning boilers on-line that have been fouled as a result of out-of-control phosphate programs. It is a first-class polymer for operating phosphate programs with high FW hardness and voluminous amounts of sludge in the bulk BW.

  SS/MA examples include **Versa® TL-3**, **TL-4**, **TL-7**.

10.6.2.6 Phosphino Polycarboxylic Acids

Various **phospono-** and **phosphinopolycarboxylic acids** (PCAs) are available in the market. These polymers are similar to phosphonates and some actually are phosphonates. They tend to exhibit varying degrees of both deposit control and corrosion control properties. For BW applications, the **acrylic acid/organic phosphate polymer** (PCA type 16) is the only important *phosphinopolycarboxylic* and has a C–P–C bond (phosphonates have a C–P–O bond).

The PCAs tend to exhibit good performance as *iron dispersants, phosphate stabilizers,* and *corrosion inhibitors,* with additional good thermal and hydrolytic stability.

- **PCA:16** is available as **Belclene® 161/164** (50/35% w/w solids), **Acumer® 4161** (50%), and **Polysperse®** (50%). These are low-phosphorus content materials that have found application in boiler FW formulations because of excellent sludge conditioning and particulate dispersion properties. The number 16 represents a 16:1 w/w ratio of **acrylic acid** and **sodium hypophosphite,** giving PCA:16 a MW range of 3,300 to 3,900. PCA:16 is particularly effective for the control of *calcium carbonate* and *sulfate* deposition. It is usually incorporated with other polymers in formulations and is approved for use under U.S. CFR 21, §173.310.

  A general application guideline is that 1.75 to 3.5 ppm PCA:16 (50% w/w product) is required in the BW for every 10 ppm phosphate sludge generated. For 50% w/w material, typical the BW reserves are 25 to 30 ppm PCA for 0 to 200 psig boilers, 20 to 25 ppm for 200 to 400 psig boilers, and 12 to 15 ppm for 400 to 600 psig boilers. PCA begins to thermally degrade above 200 °C/392 °F, but does not lose effectiveness at this temperature. It is suitable up to 1,000 psig.

Some structures of polymers and phosponates are shown in Figure 10.3.

Popular PCAs include:

Acumer®	is a trademark of the Rohm & Haas Company
Aquatreat®	is a trademark of ICI PLC (National Starch/ALCO Chemical Div.)
Bayhibit®	is a trademark of the Bayer Corporation
Belclene®	is a trademark of Great Lakes Chemical Corp. (previously FMC and Ciba-Geigy)
Briquest®	is a trademark of Rhodia (Albright & Wilson Div.)
BSI®	is a trademark of Buckman Laboratories, Inc.
Cobratec®	is a trademark of PMC Specialties Group, Inc.
Codex®	is a trademark of Excel Industries Ltd., India
Dequest®	is a trademark of the Monsanto Chemical Company
Good-Rite®	is a trademark of Noveon, Inc. (formerly BF Goodrich Company)
Kelig®	is a trademark of Orkla AS (Norway), (Borregaard LignoTech Group Div.)
Maracel®	is a trademark of Orkla AS (Norway), (Borregaard LignoTech Group Div.)
Marasperse®	is a trademark of Orkla AS (Norway), (Borregaard LignoTech Group Div.)

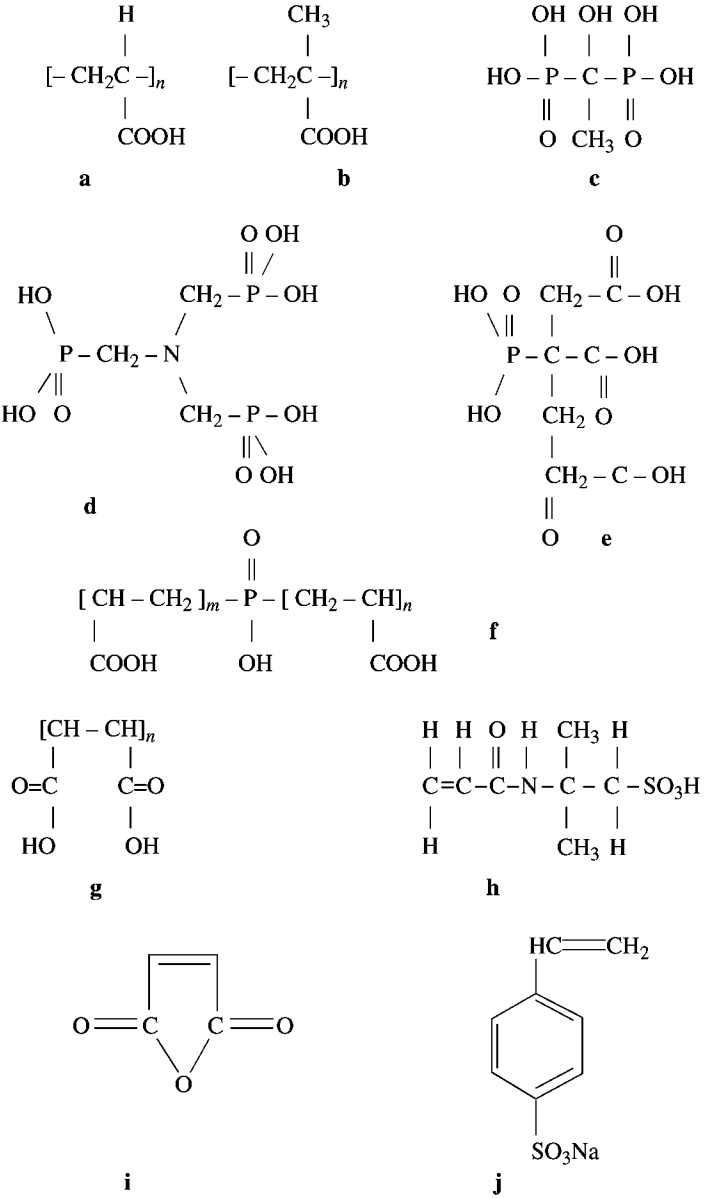


Figure 10.3 (a) PPA, (b) PMAA, (c) HEDP, (d) ATMP, (e) PBTC, (f) PCA:16 where $m + n = 16$, (g) PMA, (h) AMPS, (i) maleic anhydride, and (j) SSS.

Mayoquest®	is a trademark of Vulcan Chemicals (Calloway Chemical Div.)
Phos®	is a trademark of Buckman Laboratories, Inc.
Polycol®	is a trademark of Pacific Standard Specialities, Inc.
Polycryl®	is a trademark of Polycryl Corporation
Polysperse®	is a trademark of Pacific Standard Specialities, Inc.
Sequacel®	is a trademark of Excel Industries Ltd., India
Sokalan®	is a trademark of BASF AG
Tamol®	is a trademark of the Rohm & Haas Company
TRC®	is a trademark of the Calgon Corporation
Unihib®	is a trademark of Lonza Corporation
Versa®	is a trademark of ICI PLC (National Starch/ALCO Chemical Div.)

10.6.3 Designing and Operating All-Polymer/ All-Organic Programs

Apart from the materials described earlier, formulations usually include other organics, including *coupling agents, antifoams,* and *surfactants.* A commonly employed raw material is **polyethylene glycol** (PEG) in the form of perhaps **PEG-8 oleate** or **PEG-6 distearate**. This surfactant material is used as a *metal surface cleaner.* It prepares the metal surface to receive inhibitors and improve DCA surface mechanisms.

The evaluation of competing chemistries and subsequent product selection may be difficult, and feed rates for the wide array of available phosphonates and novel homo-, co-, and terpolymers available vary considerably. Polymers do not control all types of contaminants at an equal performance level, and product selection depends on the type, level, and ratios of contaminants present.

For any specific BW application, the boiler design, pressure-temperature, operation, and heat-flux rate are all contributing factors; these chemistries generally function at substoichiometric levels (the *coordinating* and *complexing* **polycarboxylic component** of polymers aside), so that the use of reliable, directly measurable relationships is not always possible. Nevertheless, some rules and recommendations do exist, a few of which are discussed later.

Combinations of polymers are widely used as **overlays** in phosphate or chelant programs, or as the primary ingredients in *all-polymer* and *mixed-organic/inorganic multifunctional program* product ranges. These combinations may offer new or additional technical benefits and are marketed as such.

A well-known example of such *all-polymer programs* in the industry is the well-marketed **Transport-Plus™** programs from the **ONDEO Nalco** division of **Degrémont/Suez-Lyonnaise**. The polymers used include **PMA**, as well as various combinations, such as **acrylate/acrylamide copolymer** (PAA/PAM) with **acrylic acid/vinyl sulfonate copolymer** (PAA/VS), and *acrylate/acrylamide copolymer* with **polyacrylate.** All larger water treatment companies (and most smaller regional businesses, no matter their global location) have a full complement of all-polymer products in their ranges, for similar types of applications. **Drew Industrial** (division of **Ashland Chemical Corporation**), for example, offers its innovative **Advantage™** deposit inhibitor programs.

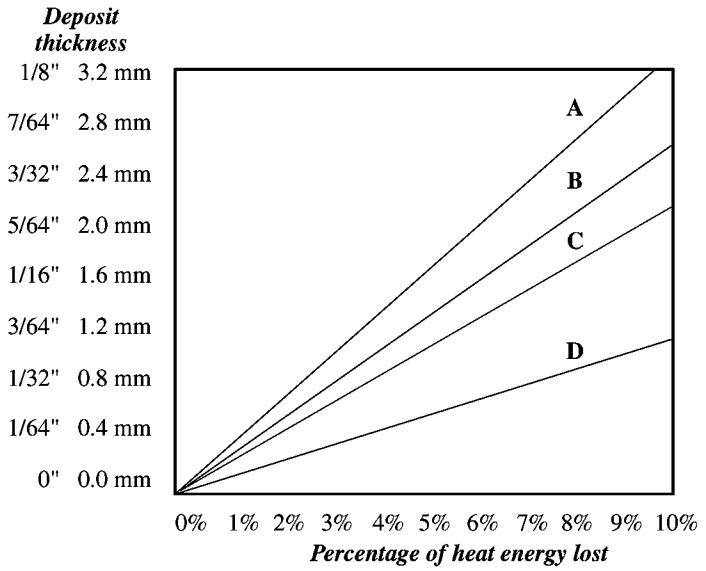
A further issue to consider is the effect of thermal and hydrolytic stability at high temperature and pressure. All polymers and other organics begin to fragment as temperatures increase, but this does not automatically mean an immediate loss of functionality. The recent **acrylic acid/nonionic aromatic and linear sulfonate** (AA/NI-AS-LS) product **Aquatreat AR-550®** from ALCO Chemical Company (Division of National Starch/ICI PLC) is a case in point. This product is designed as a high-temperature DCA for iron and, although fragmentation eventually begins to occur from the middle of the molecule, a very high degree of (aromatic and linear) sulfonation maintains functionality. This is not always the position with other copolymers.

10.6.3.1 Meeting Boiler Plant Operating Objectives with All-Polymer/All-Organics

Some basic BW treatment objectives include keeping *boiler surfaces* clean and corrosion-free to minimize fuel bills and managing variable quality FW smoothly and efficiently to limit upsets and other downstream problems. But the nature of potential boiler deposition problems changes with increases in pressure and, simply put, is primarily concerned with a reduction in *simple, hardness-related deposits* and an increase in *complex, iron oxide deposits.* The effect of dirty boilers on fuel costs can be seen in Figure 10.4.

The significance, therefore, of using all-polymer/all-organic programs as a mechanism for keeping boilers cleaner than may be otherwise generally possible with conventional phosphate, chelant and other programs should not be underestimated.

If novel chemistry polymer overlays or all-polymer programs are used to improve boiler cleanliness, technical support services should



Key: **A** = Typical $CaCO_3$ based boiler sludge
B = Typical deposit including 4 to 5% iron oxides
C = Typical deposit including 8 to 10% iron oxides
D = Typical deposit including 8 to 10% iron and silica

Figure 10.4 Heat energy losses in WT boiler due to deposition.

provide **energy balance summaries** linked to FW **contaminant mass balance summaries**.

Where the transport of contaminants (such as hardness salts and iron) through the boiler is 100% effective, no deposition is indicated and energy consumption per-unit-steam should remain constant (all other parameters being equal). However, if *boiler surfaces* are being cleaned on-line, existing deposits are gradually removed and contaminant transport through the boiler is effectively greater than 100%. Heat-transfer efficiency is consequently raised, and this improvement should be reflected in a more favorable energy balance summary report.

Eventual inspections of internal boiler components should reveal lower **dirt loading levels** in tubes and on all other *boiler surfaces,* in addition to well-passivated internals.

NOTE: For more information on dirt loading, refer to Section 4.8.3, "Limiting Deposition," and Table 4.2, "Boiler Heat Transfer Surface Cleanliness."

From the table it can be seen, for example, that a boiler operating within the pressure range of 300 to 1,500 psig is considered clean if the deposit thickness is within 1.5 to 3.0 mil. Given an average deposit density of 3.5 g/cm^3, this level of deposit thickness equates to a dirt loading of 14 to 28 g/ft^2.

Improvements in corrosion control should be reflected by *reduced iron in the BD, lower ppb values for hydrogen in steam,* and possibly *decreased corrosion rates at FW heaters,* and other components.

Additionally, if a selected polymeric DCA is properly matched to a particular boiler operating temperature and pressure, there should be no *increase* in the **total organic carbon** (TOC) level of the steam.

Consequently, when selecting and blending the various raw materials used in all-polymer/all-organic formulations, the questions of thermal and hydrolytic stability and ability to transport or otherwise control colloidal iron oxides (in addition to possible adverse effects such as copper corrosion) become increasingly important at higher boiler temperatures and pressures.

Some relevant points include:

- Tannin sludge conditioners are adversely affected by higher temperatures and, without the support of a supplemental PAA polymer, are limited to 350 psig. This probably is also true of lignosulfonates.
- PAA (for $CaCO_3$), PMA (for Fe), and PAM (for general sludge) are all excellent as low-cost, general-purpose DCAs. They also all have good thermal stability, but are relatively poor performers compared to co- and terpolymers under circumstances where more complex deposit control problems are involved. Limit these materials to boilers operating at up to 650 psig. (Possibly up to 950 psig if deposit control requirements appear straightforward).
- For iron transport and control problems at pressures of up to 1,500 or possibly as high as 1,800 psig, copolymers such as AA/VS or AA/NI-AS-LS, or terpolymers such as AA/SA/SSS should be used.
- For calcium carbonate or calcium sulfate control under high-stress conditions, use PMA. It is suitable for use at up to 1,300 psig.
- Where variable FW quality requires the benefit of additional chelation and EDTA and NTA are not appropriate, add ATMP to the formulation. It is suitable for up to 700 psig. However, where steam comes into contact with food only HEDP can be employed. The pressure limitation for HEDP is 400 psig.

NOTE: As a comparison, NTA is suitable for up to 900 psig, EDTA is suitable for up to 1,200 psig, or 1,500 psig if employed as an overlay to a polymer program.

- For **phosphate overlay programs,** PAA is generally satisfactory, but where good phosphate control is required or for on-line cleaning of fouled boilers using phosphate-cycle, SS/MA or AA/AMPS should be used. These products also perform in the presence of iron.

NOTE: Phosphate-cycle programs may be employed at up to 1,200 psig.

- For **chelant overlay programs** PAA/PMA (for Fe) blends are generally satisfactory, but where improved dispersion is required PCA:16 is recommended. PCA:16 is suitable for up to 1,000 psig.
- For optimum dispersion functionality in any type of all-polymer/all-organic program, use PCA:16 or AA/NI-AS-LS.
- For complex, wide-spectrum deposit problems, consider Acumer 3100 (high iron) at up to 900 psig, or 5,000 (high silica); if over 650 psig, remove silica at source. A**ll-polymer/all-organic product feed rates** vary, depending on these factors.
- Tannins are typically used in BW at 150 to 200 ppm active tannin product, but perhaps only a third of this is related to its polymeric sludge conditioning functionality.
- Programs containing lignins as the primary polymeric dispersant are generally formulated to provide 30 to 50 ppm of "active" lignin product in the BW.
- Where relatively expensive products such as terpolymers are employed in conventional programs, feed rates are not as high as, say, PAA, because of improved terpolymer performance. As an example, where a product such as **Acumer 3100** is employed in phosphate-cycle programs, typical BW polymer requirement is 10 to 15 × COC "active" product, with a phosphate reserve of 30 to 60 ppm and perhaps 10 to 15 × COC.
- Polymer feed rates can be calculated based on a 1:1 stoichiometric ratio with FW hardness or total metals (Ca/Mg/Fe/Cu/Al/Ni). If, for example, a boiler operates at 950 psig, runs at 50 × COC, and is supplied with FW containing 0.05 ppm total metals, this may require 0.05 × 50 = 2.5 ppm polymer "actives" in the BW.

Further feed-rate starting point guidelines are:

- 0 to 350 psig: 15 to 25 ppm polymer "actives" in the BW
- 350 to 650 psig: 10 to 15 ppm polymer "actives" in the BW
- 650 to 950 psig: 5 to 10 ppm polymer "actives" in the BW
- 950 to 1,250 psig: 2 to 5 ppm polymer "actives" in the BW
- 1250 to 1,550 psig: 2 to 3 ppm polymer "actives" in the BW

Table 10.7 EDTA Chelant or All-Polymer/All-Organic Program. Recommended BW Control Limits for Fired WT Boilers Employing Demineralized or Similar Quality FW

Pressure, psig/bar max. (approx.)	**350/25**	**650/45**	**950/65**
FW chemistry control limits			
Hardness, ppm $CaCO_3$ (max.)	2	1	0.2
Total Fe/Cu/Ni, ppm (max.)	0.05	0.05	0.03
BW chemistry control limits			
Conductivity, μS/cm/25°C max.	3000	2000	1000
Silica, ppm SiO_2 max.	0.4*x* OH alkalinity	0.4*x* OH alkalinity	0.4*x* OH alkalinity
OH Alk., ppm $CaCO_3$	50 to 250	50 to 100	20 to 50
Polymer, ppm "actives"	15 to 25	10 to 15	5 to 10
OR Chelant reserve, ppm $CaCO_3$	4 to 8	3 to 6	2 to 3
Pressure, psig/bar max. (approx.)	**1250/85**	**1550/105**	**1850/130**
FW chemistry control limits			
Hardness, ppm $CaCO_3$ (max.)	<0.05	ND	ND
Total Fe/Cu/Ni, ppm (max.)	0.02	0.02	0.02
BW chemistry control limits			
Conductivity, μS/cm/25°C max.	250	60 to 80	30 to 40
Silica, ppm SiO_2 max.	8	2.0	1.0
OH Alk., ppm $CaCO_3$	5 to 20	ND	ND
Polymer, ppm "actives"	2 to 5	2 to 3	1 to 2
OR Chelant reserve, ppm $CaCO_3$	1 to 2	unsuitable	unsuitable

NOTE: This chart assumes oxygen scavenger, FW pH, and other necessary water chemistry controls are in place.

FW total metals sampled from economizer outlet.

Conductivity test is on un-neutralized samples.

ND = not detected.

- 1550 to 1,800 psig: 1 to 2 ppm polymer "actives" in the BW

NOTE: All-polymer programs seldom contain more than 15 to 20% w/w organics, so that whole product reserves in the boiler may need to be five or six times the level indicated above.

Table 10.7 is an **all-polymer/all-organic program control chart** designed for WT boilers. This chart is also suitable for EDTA chelants (and NTA, but only up to 900 psig).

Where chelants or all-polymer/all-organics are employed in FT boilers the control limits shown for boilers up to 350 psig/25 bar are applicable as a starting point, although slightly higher conductivity levels and OH alkalinity reserves may be possible.

Where chelant or chelant/polymer programs are used, typically, instructions are given to maintain a specific chelant reserve. In practice, this is not always achievable because of test method limitations and internal water chemistry constraints.

Where **dual-chelant programs** are employed, they generally are designed with low NTA/EDTA content and have *no measurable chelant reserve.* There are several versions of these *dual-chelants,* including *phosphonate-NTA* (some early types were called **SCA programs**) and *gluconate-EDTA.* Polymers employed in these programs typically include combinations of *polyacrylate, polymethacrylate, polyacrylamide, vinylsulfonate,* or *polyphosphonocarboxylic acid.*

10.6.4 All-Polymer/All-Organic (AP/AO) Program Formulations

Some examples of all-polymer/all-organic (AP/AO) formulations are provided below.

1. ***Basic AP/AO formulation for use in plants requiring BW treatments with USDA/FDA approval (CFR 21 §173.310)***

   Materials

Caustic soda, commercial solution	12.0%
PAA, 2,000 MW (50%)	16.5%
HEDP (60%)	8.5%
PAGMBE	0.8%
Water	62.2%
	100.0%

   - Maintain 150 to 400 ppm product in the boiler

2. ***AP/AO alternative to phosphate-cycle program for commercial, HVAC and light industrial markets (15 to 150 psig)***

Materials

Caustic soda, commercial solution	10.0%
PMA (50%)	3.0%
PCA:16 (50%)	3.0%
PAA Na, 2,600 MW (43%)	3.0%
Sodium lignosulfonate	12.0%
PAGMBE	0.2%
Water	68.8%
	100.0%

- Maintain 200 to 600 ppm product in the boiler

3. ***Wide-spectrum AP/AO product for heavy industry, 650 psig WT boiler using softened FW (good iron transport required)***

Materials

Caustic soda, commercial solution	3.5%
PMAA (25%)	4.0%
PCA:16 (50%)	3.0%
SS/MA (50%)	12.0%
ATMP (50%)	4.0%
PAGMBE	0.4%
Water	73.1%
	100.0%

- Maintain 100 to 200 ppm product in the boiler

10.7 CHELANT-, PHOSPHATE-, OR POLYMER-BASED COMBINATION PROGRAMS

Every water treatment service company has several dual-function or multifunction programs in their BW product range based on *chelant, phosphate,* or *polymer.* Which of these particular chemistries takes the lead position depends on the type of waterside problems likely to be encountered (in some ways this is related to the particular market sector) and the positioning of the company within the overall BW treatment marketplace.

The various chemistry combinations, ratios employed, and activity-levels offered give rise to an enormous number of possible permutations. Some common formulation examples include:

- Chelant/phosphate
- Phosphate/polymer
- Chelant/polymer
- Alkali/phosphate
- Polymer/phosphate
- Chelant/polymer/phosphate
- Alkali/polymer/phosphate
- Chelant/phosphonate

Some examples of these combination programs follow.

1. ***Chelant/polymer formulation for heavy-duty application or clean-up and iron transport duty in large industrial boilers.***

   Materials

Caustic soda, commercial solution	4.0%
EDTA (38%)	30.0%
PAA, 2,000 MW (50%)	6.0%
PMAA (25%)	11.0%
ATMP (50%)	3.0%
PAGMBE	0.2%
Water	45.8%
	100.0%

   - Maintain adequate chelant reserve. Use sulfite or alternative oxygen scavenger, plus amine for program support.

2. ***Polymer/phosphate/chelant formulation. General purpose application, but good iron and phosphate dispersion.***

   Materials

PAA (4,500 MW) 50%	16.0%
SS/MA (50%)	16.0%
SHMP (33%)	35.0%
EDTA (38%)	5.0%
PAGMBE	0.3%
Water	27.7%
	100.0%

   - Control program on phosphate reserve

3. ***Alkali/polymer based multifunctional formulation for hard water MU (up to 50 ppm $CaCO_3$) in LP steam or light-industrial FT boilers. Includes a metal passivator.***

Materials	
Caustic soda, commercial solution	10.0%
Soda ash	5.0%
Sodium lignosulfonate	6.0%
PMA (50%)	1.5%
PCA:16 (50%)	1.5%
Sodium sulfite	9.0%
Sodium erythorbate	0.1%
PAGMBE	0.3%
Water	66.6%
	100.0%

- Maintain adequate sulfite reserve and use as product reserve indicator.

4. ***Phosphate/polymer based multifunctional formulation, with low alkalinity to phosphate ratio for use in high alkalinity water containing some hardness. Program has USDA/FDA approval (CFR 21 §173.310).***

Materials	
Caustic soda, commercial solution	5.0%
PCA:16 (50%)	2.0%
HEDP (60%)	1.0%
PAA (4,500 MW) 50%	4.0%
SHMP (33%)	17.0%
Sodium sulfite	6.0%
Morpholine (30%)	5.0%
PAGMBE	0.2%
Water	59.8%
	100.0%

- Control program on phosphate reserve (30–60 ppm PO_4), but also sulfite reserve (30–50 ppm SO_3) and P alkalinity (400–800 ppm as $CaCO_3$).

10.8 COORDINATED PHOSPHATE AND PROGRAM DERIVATIONS

Coordinated phosphate and phosphate-based derivations are designed for use with high-quality (demineralized or equivalent) FW in higher pressure WT boilers, for industrial, power, and cogeneration application.

The **coordinated phosphate program** *(captive alkalinity program)* was the first of a limited number of *pH buffering* or *controlled-pH programs* introduced since the early 1940s. This program was especially formulated and required careful control to ensure a sufficiently high pH level in the BW to prevent **general waterside corrosion** and yet avoid the formation of **free hydroxyl alkalinity** *(free caustic)* and the subsequent risks of severe, *caustic-based corrosion problems* linked to *porous waterside deposits.* The original intention of coordinated phosphate programs was to control the chemistry *under deposits.*

Over the years and around the world, the various incremental improvements in boiler design and changes in heat-flux ratings and operating pressures (and the introduction of nuclear-powered generating stations) have created new waterside chemistry challenges for chemists and engineers to overcome. These challenges have led to modifications in *coordinated phosphate chemistry* and the introduction of alternate programs, including **congruent, precision control, equilibrium, nonacid phosphate programs,** and non-phosphate, **all-volatile programs** *(AVP, vapor phase programs, zero solids programs).*

Today, because of the wide spectrum of higher pressure boiler designs and operating conditions, there is no single program type that outperforms all others, and, indeed, the original rationale of preventing free caustic in the BW appears to be no longer valid in certain cases.

For some boiler plant applications, the approach to internal treatment has turned full-circle and consequently, best-practice water conditioning may really only be established on a case-by-case basis.

However, the various national standards organizations, power boiler manufacturers associations and research institutes (such as the **Electric Power Research Institute** in the United States) do offer guidelines and recommendations for good waterside control and the avoidance (or at least the minimization) of the more exotic forms of waterside damage.

10.8.1 A Synopsis of Higher Pressure Boiler Waterside Problems and Controlled-pH Program Considerations

The high levels of alkalinity normally associated with *phosphate-cycle programs* do not present a problem until pressures of 850 to 900 psig are reached, at which point *caustic gouging corrosion, saline corrosion,* and other similar problems may start to develop. Consequently, boiler operations personnel typically consider the use of lower alkalinity, controlled pH *coordinated,* or *congruent phosphate programs* for steam generators having pressure ratings upward of 650 psig (although some opinions regard 950 psig or even 1,250 psig as a minimum pressure requirement).

Essentially, except for once-through boilers, steam generation primarily involves **two-phase nucleate boiling** and **convective boiling** mechanisms (see Section 1.1). Any deposition at the heat transfer surfaces may disturb the thermal gradient resulting from the initial conduction of heat from the metal surface to the adjacent layer of slower and more laminar flow, inner-wall water and on to the higher velocity and more turbulent flow bulk water.

As boiler design pressures (and therefore temperatures) rise, the formation of metal oxides, silica, or other mineral deposits (and there is always some level of deposition) significantly increases the risk of waterside problems in a chain of cause and effect, thus resulting in a **departure from nucleate boiling** (DNB) and severe boiler damage. Boiler tube failures are the commonest form of boiler damage in subcritical plants and result from a discontinuous but repetitive breakdown in the magnetite film and the development of *transgranular* cracks, generally in areas of tube attachment where stresses are high.

These problems are more acute in the power industry, where intermittently operated, *peaking steam generators* produce and collect significantly more iron oxides than *base load boilers.* Frequent startups of power boilers are very detrimental to their lifespan.

Boiler section problems include the following (see Chapter 7 and Tables 7.3 to 7.7 for more details):

1. **Caustic gouging corrosion** caused by localized high concentrations of caustic developing within and under porous surface deposits dissolving the protective magnetite film forming *ferrite* and *hypoferrite ions.*
2. **Saline corrosion,** which develops in a similar manner.

3. Various other forms of **concentration-cell corrosion.**
4. **Low pH localized corrosion** resulting from *acid phosphates.*
5. **Caustic embrittlement corrosion** *(caustic induced, stress corrosion cracking),* which occurs as an *intergranular* form of corrosion where localized stresses and strains are present (and some *silicate,* which acts as a general corrosion inhibitor that protects grains at the expense of the grain boundaries).
6. Various forms of **high temperature corrosion** including **long-term overheating, decarburization,** and **hydrogen embrittlement** *(hydrogen damage).*

The simple **orthophosphates** primarily employed as internal treatments are produced industrially by the selective reactions of phosphoric acid with caustic soda. Under BW hydrolyzing conditions, where MSP is employed, these specific reactions reverse, liberating *hydrogen phosphate ions* and some level of *sodium ions*, plus *hydrogen ions* (producing a tendency to lower the pH as in equation 1). Where DSP is employed, no *hydrogen ions* are liberated (producing a tendency to lower the pH as in eqution 2). Where TSP is employed, *hydroxyl ions* result (producing a tendency to raise the pH as in equation 3).

1. NaH_2PO_4 + H_2O → HPO_4^{2-} + H^+ + Na^+ + H_2O
   MSP water hydrogen phosphate ion hydrogen ion sodium ion water

2. Na_2HPO_4 + H_2O → HPO_4^{2-} + $2Na^+$ + H_2O
   DSP water hydrogen phosphate ion sodium ion water

3. Na_3PO_4 + H_2O → HPO_4^{2-} + $3Na^+$ + OH
   TSP water hydrogen phosphate ion sodium ion hydroxyl ion

From these and other related equations, it can be seen that, by using internal programs based on phosphate blends with specific sodium-to-phosphate ($Na:PO_4$) mole ratios, BW alkalinity may be controlled

while still providing the required pH buffering and hardness polishing function.

By maintaining a Na:PO_4 mole ratio at some suitable level below 3.0:1.0 (the ratio for TSP), the production of free caustic alkalinity is avoided.

Also, where free caustic alkalinity exists, the use of DSP "mops up" the caustic (as shown in equation 4) and thus reduces the risk of *caustic gouging corrosion.*

4.	Na_2HPO_4	+	NaOH	→	Na_3PO_4	+	H_2O
	DSP		caustic alkalinity		TSP		water

Consequently, it is possible to select an operating pH level high enough to ensure magnetite film stability, yet low enough to prevent the formation of free caustic, together with a Na:PO_4 ratio that provides the selected pH range and an adequate phosphate reserve.

The chosen coordinates defining minimum/maximum pH levels and minimum/maximum phosphate (as ppm PO_4) led to the production of various *coordinated phosphate program* control charts for different pressure ratings (maximum phosphate solubility is a function of pressure). The area within the coordinates providies a simple control box for BW testing purposes.

In practice, *coordinated phosphate programs* are held at a Na:PO_4 ratio below 3.0:1.0 (normally around 2.8 or 2.85:1.0) because, at the higher ratio any high-temperature crystallization of TSP leads also to some DSP and NaOH.

At later dates and as a result of specific water chemistry or new boiler design problems, various derivations of coordinated phosphate programs appeared. The basic philosophy relating to waterside control through the use of *coordinated treatment programs* still holds true today (albeit with modifications), and **controlled-pH phosphate programs** remain the principal choice for internal treatment of higher pressure boilers.

Nevertheless, the early programs were too simplistic and failed to take into account several important factors. Over time, and influenced by new boiler designs and polymer technologies, plus higher pressures, heat-flux ratings, and fuel costs, these factors have spurred the development of new and increasingly complex program derivations and methods of control.

Basic flaws in *coordinated phosphate program* control logic and other relevant issues include:

- The presence of *free caustic* does not automatically lead to caustic gouging corrosion, caustic embrittlement, or other related problems.
- Because thermal gradients vary considerably within boilers, a typical BW sample, which is essentially representative of average internal bulk water conditions, is unlikely to provide sufficient valid information necessary for the critical assessment of conditions at *boiler surfaces.* This makes fine-tune control of coordinated phosphate programs within the areas they are most needed very difficult, if not impossible, especially because caustic and saline concentrations may be much higher under deposits than in the bulk water as a result of localized effects.
- Coordinated phosphate control charts assume either that all contribution to pH level is derived from phosphate or that the buffering action of phosphate is sufficient to overcome the presence of other alkaline species, such as amines. Neither assumption is true. This may lead operators to conclude perhaps that a higher than anticipated bulk water pH level (caused by the presence of amine) should be rectified by the addition of MSP. This action may lower localized Na:PO_4 ratios below 2.2:1.0, producing **acid phosphate corrosion** *(phosphate wastage) and* resulting in tube thinning and ultimately tube failure.

  Corrosion may be especially rapid under existing deposits where amine is absent and the pH level is lower than that of the bulk water, as **incongruent phosphate effects** and *concentrating effects* further contribute to the problem.
- Perhaps the most important waterside problems relate to the likelihood of **boiler surface deposits** and their control. High concentrations of *caustic* or *salines* only occur if porous deposits are present. It is much better to remove the cause of deposition problems than to try to manage their effects, and modern *iron* and *silica transport polymers,* together with improved cleaning protocols, have done much to limit deposition in large boilers.

NOTE: The original rationale for using coordinated phosphate programs was to control under-deposit chemistry, not to minimize the presence of the deposits themselves.

- The introduction of modern, very high pressure or temperature boilers has led to water chemistry control problems and cause-and-effect corrosion problems due to **phosphate hideout**. Under

high-load conditions, BW phosphate reserves may "disappear," in effect temporarily depositing out because of localized supersaturation, thus permitting caustic and salines to concentrate and effect corrosion. Upon a reduction in load, the resolubilization and reemergence of phosphate takes place and, where MSP and DSP are used, the resulting acid phosphate may cause further under-deposit problems (together with hydrogen evolution as an indicator). Later versions of controlled pH programs have emphatically concentrated on avoiding *hideout* and the false conclusions and inappropriate actions that may stem from this problem.

- Additionally, the combination of high temperatures (over 600 to 610 °F/320 °C, 1,550 psia/107 bar) and acid phosphates has given rise to more pronounced **acid phosphate attack** of both magnetite and base metal, which in modern tube steel alloy compositions may produce esoteric corrosion products such as **maricite** ($NaFePO_4$). Secondary corrosion by *caustic gouging* (as similarly evidenced by hydrogen evolution) also occurs.

10.8.2 Types of Controlled-pH Phosphate Programs

All programs presuppose the provision of high-quality, fully deaerated FW, with a pH level of 8.5 to 9.5 and appropriately low levels of sodium, silica, copper, iron, nickel, and other contaminants. (Refer to Figure 10.5 for additional details. Also refer to Table 9.3 for MU water purity grades.)

10.8.2.1 Coordinated Phosphate Program (Captive Alkalinity Program)

This program was originally devised for non–highly rated boilers. It requires that the bulk BW $Na:PO_4$ ratio be permanently controlled below 3:1 and typically at a ratio of 2.85:1. The original recommendations for phosphate reserves have tended to move around a little in recent years.

Typically, for boilers using coordinated phosphate programs, operating in the range of 600 to 1,200 psig.

FW requirements are:

- Condensate pH level of 8.6 to 9.0
- No detectable suspended solids in the condensate

- Hydrazine after the last FW heater present at a positive residual of 0.01 to 0.05 ppm N_2H_2
- Iron at 0.2 ppm Fe maximum
- Copper at 0.02 ppm Cu maximum
- Oxygen at the deaerator outlet at 10 ppb O_2 maximum
- Ammonia at 0.5 ppm maximum

BW requirements are:

- Cycles of concentration may reach 130 to 150 times
- PO_4 reserves are maintained at 15 to 25 ppm
- pH level is maintained at 9.8 to 10.2
- P alkalinity is maintained at 12 to 22 ppm $CaCO_3$
- M alkalinity at 25 to 45 ppm
- Chlorides are maintained at 30 ppm Cl maximum
- Silica is 4 ppm SiO_2 maximum
- Unneutralized conductivity is maintained at 300 μS/cm
- Hydrazine is maintained at 0.01 to 0.1 ppm N_2H_2

For boilers in excess of 1,200 psig, the PO_4 reserves may be as low as 5 to 10 psig to avoid carryover.

10.8.2.2 Congruent Phosphate Program

Congruent phosphate programs are modifications of coordinated phosphate programs that operate at a Na:PO_4 ratio lower than the normal 2.8 or 2.85:1. Experience has demonstrated that (contrary to theory) **diminished phosphate salt solubility** *(phosphate hideout)* takes place under high-load conditions. This is in addition to the recognized problems of high-temperature crystallization of TSP at the higher ratio of 3:1 (with the formation of some DSP and free caustic).

Congruent phosphate programs are based on agreed upon congruent points favoring a maximum Na:PO_4 ratio of 2.6:1 and are probably the most usual type of *controlled-pH program* utilized by industrial and cogeneration boilers operating within the pressure range of approximately 950 to 1,500 psig.

- Boilers operating at 650 to 950 psig typically operate with a PO_4 reserve of 20 to 45 ppm and a pH range of 9.5 to 10.5.

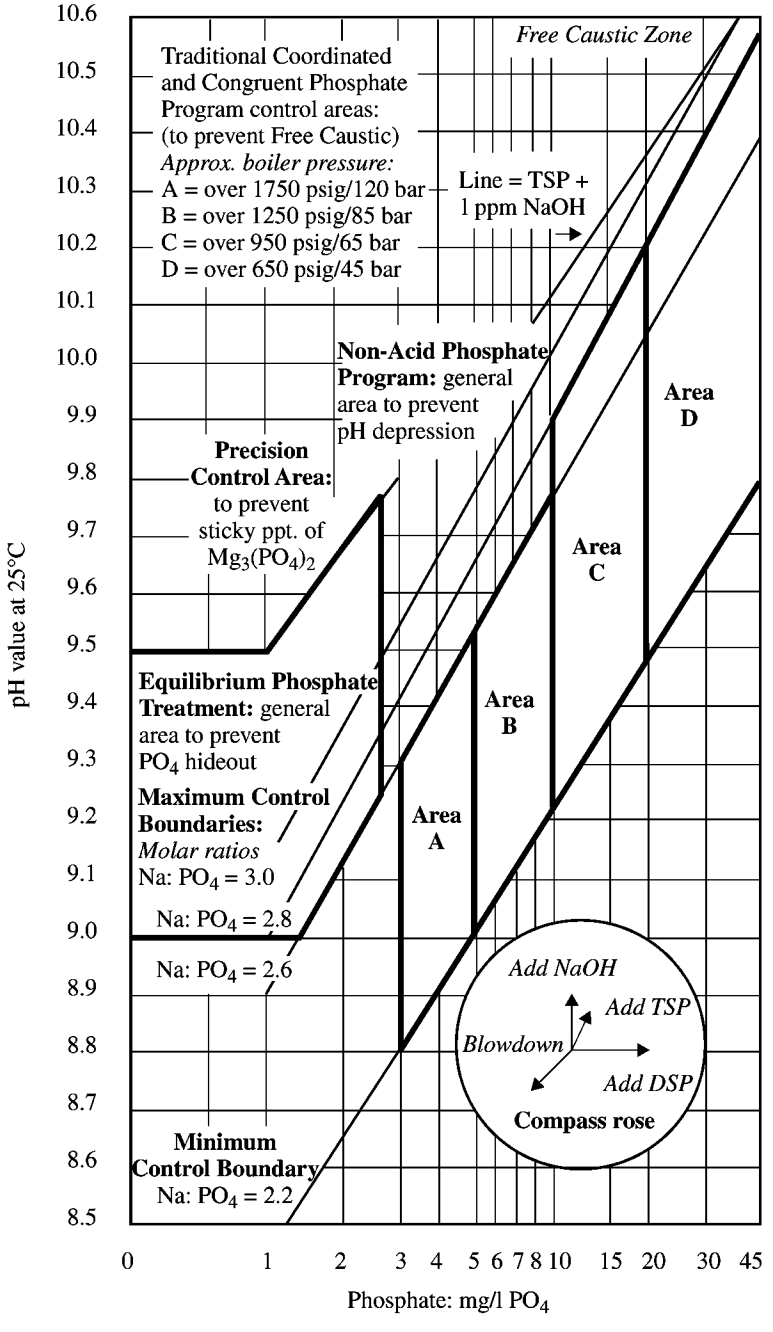


Figure 10.5 Coordinated, congruent, precision control, equilibrium and non-acid phosphate programs for higher-pressure WT boilers

- Boilers operating at 950 to 1,250 psig typically operate with a PO_4 reserve of 10 to 20 ppm and a pH range of 9.2 to 10.1.
- Boilers operating at 1,250 to 1,750 psig typically operate with a PO_4 reserve of 5 to 10 ppm and a pH range of 9.0 to 9.7. Tighter controls may require 4 to 6 ppm and a pH of 8.5 to 9.3 in boilers at the top end of the pressure range.
- Boilers operating at 1,750 to well over 2,000 or 2,500 psig typically operate with a PO_4 reserve of 3 to 5 ppm and a pH range of 8.7 to 9.5. Tighter controls may require 2 to 4 ppm PO_4 and a pH of 8.5 to 9.3 in boilers close to 3,000 psig.

NOTE: For pressure comparison purposes, critical pressure is 3,208.2 psia or 221.1 bar (374.15 °C/705.47 °F).

10.8.2.3 Precision Control Phosphate Program

This variation was designed for lower grade FW where the risk of hardness leakage may occur (e.g., in marine boilers). Under circumstances of minimal *reserve alkalinity* and a hardness leak, **magnesium hydroxide** does not develop; rather, the stickier **magnesium phosphate** [$Mg_3(PO_4)_2$] will precipitate in the boiler and has an unfortunate preponderance to adhere to hot boiler tubes.

To minimize this effect, the Na:PO_4 ratio is maintained at 2.8 to 2.6:1, phosphate is kept very low (at only 2–4 ppm PO_4), and M alkalinity is maintained at 15 to 50 ppm. The pH range is 9.2 to 9.5.

10.8.2.4 Equilibrium Phosphate Program

All preceding programs accept the conventional wisdom of operating within a control box of pH level and phosphate coordinates, despite the vagaries associated with BW sampling, amine contribution to pH and the omnipresent risk of hideout in utility boilers operating at high pressures.

Equilibrium phosphate concentration theory refutes the concept of blanket control determined by boiler pressure and operates each boiler system on a case-by-case basis. It seeks to strenuously avoid hideout-related problems and the subsequent risks of misdiagnosis. Operators are encouraged to explore the maximum operating tolerances before phosphate destabilization takes effect and hideout results, and to ensure

thereafter that water chemistry equilibrium is strictly maintained at a level below the hideout threshold.

The equilibrium phosphate program is confined to those utility boilers operating under knife-edge control, where any changes in heat and mass transfer patterns at boiler surfaces and other high-heat flux areas may exert significant ripple effects throughout the boiler plant.

For any specific boiler application, the general area of phosphate equilibrium concentration may produce phosphate reserves of below 1.0 ppm PO_4 and an operating pH level of around 9.0

Clearly, at this functional level of operation, there is little margin for error and this type of program probably will not tolerate the degree of *dirt loading* and other problems associated with frequent boiler startups.

10.8.2.5 Non-Acid Phosphate Programs

A non-acid phosphate program is more than just a further modification of coordinated phosphate program. Like equilibrium phosphate concentration programs, it is a further practical attempt to overcome the imposed constraints of operating a 60-year-old program in modern boilers, where new engineering design and chemistry technology have changed the rules.

Non-acid phosphate programs turn *controlled-pH programs* full circle by essentially using TSP as the only phosphate source and advocating that some free caustic (up to 1 ppm addition) is acceptable.

The background to this development is the knowledge that **corrosion fatigue cracking** is a primary source of boiler failure. This form of corrosion is more strongly influenced by the strain of startups and shutdowns and unstable water chemistry (including hideout problems) than by the presence of trace amounts of oxygen. It is also known that one of the most significant influences on water chemistry is the problem of low pH level conditions caused by the reemergence of acid phosphates following a period of hideout.

New guidelines therefore advocate the use of non-acid phosphates plus some caustic to avoid low pH level depressions. Nevertheless, this type of program is likely to achieve a good success rate in the long term under constant load conditions and careful attention to iron oxide transport and control.

10.8.3 Controlled-pH Formulations

Maintaining the correct BW Na:PO_4 ratio using a congruent phosphate program may be achieved by mixing individual ingredients into a day

tank or by using premixed blends. Important considerations are the potential variations in the percentage of available phosphate depending on the quality grade obtained, the absence or presence of *water of crystallization,* the limited solubility of some phosphate salts, and the need to use high-quality dilution water in the formulation mix.

Examples of controlled-pH formulations suitable for a 1250 psig industrial WT boiler are shown here:

Controlled-pH Formulations	**Formula A**	**Formula B**	**Formula C**
Na:PO_4 ratio	2.4:1	2.6:1	2.8:1
TSP	40%	60%	80%
DSP	60%	40%	20%
Materials			
TSP•12H_2O	7.58%	11.37%	15.16%
DSP anhydrous	4.91%	3.27%	1.64%
EDTA 38%	0.10%	0.10%	0.10%
AA/COPS	1.00%	1.00%	1.00%
PAGMBE	0.02%	0.02%	0.02%
Water	86.39%	84.24%	82.08%
	100%	100%	100%

10.9 ALL-VOLATILE TREATMENT PROGRAM CHEMISTRIES

All-volatile treatment (AVT) programs *(zero solids programs, vapor phase programs)* do not add any TDS to the FW cycle or the BW system. AVT programs provide an alternative technology to *controlled-pH programs.* They are suitable for use in industrial boilers operating at pressures of over 1,000 psig, but are generally only used in **once-through boilers, nuclear-powered steam generators,** and the highest pressure fossil-fuel utility boilers (i.e., boilers operating at over 2,500 psig, including supercritical boilers operating at up to 3,500 psig.).

Needless to say, there is little point contemplating this form of treatment unless the FW quality is of a consistently high purity and excellent control systems are in place. Also, there is no purpose in attempting to combine AVT with any other type of program; AVT combination programs do not work and the entire concept of AVT is lost.

All-volatile treatment essentially consists of adding a **volatile oxygen scavenger,** such as *hydrazine, diethylhydroxylamine* (DEHA), *car-*

bohydrazide, or *methylethylketoxime* (MEKO), plus a **volatile neutralizing amine**, such as *morpholine, cyclohexylamine,* and *diethylaminoethanol* DEAE).

- **Ammonia** is sometimes used to boost the pH but may be unsuitable where copper alloys are present. Hydrazine and the neutralizing amines produce ammonia as part of their breakdown process, so additional care is required here to minimize copper corrosion.
- Effective oxygen scavenging, down to *less* than 5 ppb is generally required, plus good pH control because the BW is unbuffered. Typically, the pH of the BD is slightly lower than that of the FW because some of the (alkaline) amine in the BW leaves with the steam.
- Measurement of the (limited) dissolved solids present in the BW is normally best achieved by means of electrical conductivity. Clearly, any rise in conductivity indicates that solids are entering with the FW.

Some FW controls for AVT treatment include:

- **Conductivity:** (Samples should be taken from the DI polisher or equivalent pretreatment equipment). 0.2 μS/cm maximum for once-through and sub- and supercritical boilers, 0.5 μS/cm maximum for industrial boilers.
- **Silica:** 0.02 ppm SiO_2 maximum for once-through and sub- and supercritical boilers, 0.2 ppm SiO_2 maximum for industrial boilers.
- **Iron:** 0.01 ppm Fe maximum for once-through and sub- and supercritical boilers, 0.1 ppm Fe maximum for industrial boilers.
- **Copper and nickel:** 0.005 ppm Cu/Ni total maximum for once-through and sub- and supercritical boilers, 0.1 ppm Cu/Ni maximum for industrial boilers.

NOTE: For supercritical boilers, particular care must be given to controlling copper (transported in the condensate and resulting from corrosion of condenser admiralty brass) because it tends to be very troublesome, laying down metal and oxides in the turbine.

- **pH:** 8.8 to 9.5, but restricted to 9.2 maximum if significant copper alloys are present.

For BW control using AVT:

- **Amine** addition should be controlled to provide a BW pH of 9.0 to 9.5.
- **Hydrazine** in the BW should be within the range 10 to 15 ppb N_2H_2 for once-through and sub- and supercritical boilers, 20 to 30 ppb N_2H_2 for industrial boilers.
- Ensure a maximum **total solids** of 20 ppb TDS (or equivalent conductivity) for once-through and sub- and supercritical boilers, 2 ppm TDS for industrial boilers.
- For supercritical boilers, additional BW controls are **ammonia:** 250 to 400 ppb NH_3, **silica:** 20 ppb SiO_2, **sodium:** 1 ppb Na, and **copper in steam:** 5 ppb Cu.

Feed points for AVT treatments vary, usually hydrazine is added to the base of the deaerator but it also can be added to the base of the condensate extraction pump. Ammonia (where used) or amine is injected into the suction side of the boiler feed pump.

10.10 MIXED TREATMENT AND ZERO SOLIDS TREATMENT

Mixed treatment (MT) is essentially an AVT program, sometimes used in very high pressure once-through utility boilers and nuclear-powered steam generators. This type of program is designed to ensure continuous FW purity by passing **full-flow condensate** through a deep mixed-bed ion-exchange polishing plant (FFCPP) and is recommended when there is any risk of SCC through **chloride in-leakage** through the condenser.

Zero solids treatment (ZST) is a further enhancement of AVT and MT programs and, as its name suggests, the program employs extensive pre- and post-treatment equipment to ensure the highest possible FW and BW purity. ZST has been employed in the secondary circuits of nuclear-powered SGs as an aid in the prevention of **SCC**, **crevice corrosion**, and **denting**, especially where condenser cooling is effected by the use of brackish or estuarine waters.

NOTE: Denting is a phenomenon affecting tubes and tube supports. It is caused by the buildup of voluminous metallic oxides (such as copper oxide from FW heaters and iron oxide from carbon steel components), plus chloride ions. The deposit buildup distorts equipment and causes dents.

10.11 AN OUTLINE OF WATER TREATMENT FOR NUCLEAR POWERED STEAM GENERATORS

10.11.1 Treatment of Primary Circuit Coolant Water

The current worldwide standard operating pH for PWR plant primary coolants is 6.9 to 7.4. (Twenty-five years ago the limits were much broader, perhaps 4.5 to 10, depending on the SG manufacturer.) This pH range is maintained by the buffering action of *lithium hydroxide,* which is present in the coolant to the extent of 1.0 to 2.2 ppm. At levels higher than 7.4 **fuel-cladding corrosion** may result, and although the low pH point is 6.9, if the pH level drops much below 7.2, corrosion of the primary piping may also occur.

Corrosion products include **iron oxide** (Fe_2O_3), **ferrosoferric oxide** (Fe_3O_4), **nickel oxide** (NiO), **cobalt oxide** (CoO), and complex Fe, Ni, and Co oxides. Cobalt in particular may present a problem (as **cobalt^{59}**, a naturally occurring isotope), and when present as a contaminant in nickel alloys (such as **Inconel 800**), may enhance the development of an outer-core radiation field (see Section 7.4.1).

Boric acid [$B(OH)_3$] is employed in primary coolant systems as a soluble, **core reactivity controlling agent (moderator)**. It has a *high capture cross-section* for neutrons and is typically present to the extent of perhaps 300 to 1,000 ppm (down from perhaps 500 to 2,500 ppm 25 years ago), depending on nuclear reactor plant design and the equilibrium concentration reached with lithium hydroxide. However, boric acid may be present to a maximum extent of 1,200 ppm product in *"hot power"* nuclear operations.

Boron is, in fact, present not merely as boric acid, but is also distributed as various **hydroxborates**, such as $B(OH)_4$, $B_2(OH)_7$, and $B_3(OH)_{10}$.

During startup and shutdown programs boric acid also is used in the primary coolant water at strengths of up to 1 to 1.2% as a **moderator** (or **soluble poison**) to keep the reactor subcritical. During startup the boron must ultimately be removed to permit the reactor to go critical. Boron removal is provided by initially flushing some of the primary coolant to a waste treatment plant and finally by using **nuclear grade anion exchange** when the boron levels falls to, say, 250 to 500 ppm.

Where continuous demineralization of reactor coolant is provided, premature degradation of the strong base anion (SBA) resins may occur. To avoid this, oxygen removal by use of anion resin in the sulfite form is employed.

Today, *all-membrane processes* are also employed to ensure the integrity of high-purity primary coolant water and the removal of *chlorides and fluorides.* **Crud** (iron/steel corrosion debris) is removed by filtration.

10.11.2 Treatment of Secondary Circuit Working Fluid

Various chemistries are employed in the secondary circuit, including **congruent phosphate**, **AVT**, **MT**, and **ZST**.

The precise chemistry selected depends on the system design and the propensity for corrosion problems such as **denting, tube or tube sheet crevice corrosion,** and *SCC* of stainless steel (by *chlorides*) and nickel-based alloys (by *lead*).

Today, AVT or better is the norm. Feedwater and BW control chemistries are described in Section 10.9.

11

ADJUNCTS AND CONJUCTIONAL TREATMENTS

Under almost all circumstances, the programs described in Chapter 10 rely on some level of support from additional treatments, inhibitors, or BW chemistry modifiers. These *program-support chemicals* tend to have specific functions and historically have been described as either *conjunctional treatments* or *adjuncts,* although over the years any distinctions have all but disappeared.

- **Conjunctional treatments**, meaning chemicals bound in close association or occurring only in combination.
- **Adjuncts**, meaning functional chemicals added to programs (as in multifunctional one-drum mixes) or together with BW programs, but not essentially part of them.

Alkalinity boosters, which are vitally necessary to enable carbonate, phosphate, **balanced polymer** (polymer plus phosphate or chelant), and some other program types to function, are perhaps best described as conjunctional treatments, whereas *oxygen scavengers, antifoams,* and *condensate line corrosion inhibitors* are adjuncts. Programs such as phosphate-tannin mixtures are sometimes described as **adjunct treatments**. The chemistries and applications of various types of conjunctional treatments and adjuncts are described in this chapter.

11.1 OXYGEN SCAVENGER CHEMISTRIES

As has been discussed at length in this book, it is almost always necessary to remove all traces of oxygen in the boiler plant system to protect

all water and steam surfaces from oxygen-induced corrosion damage, such as **pitting attack**.

Exceptions to this requirement include many HW heating systems, where there is minimal water loss and *sodium nitrite* or another strong reducing agent and passivator is employed as a corrosion inhibitor, and in some very high pressure utility boilers where **oxygenation treatment** practices may be employed. In this latter example, the prime purpose of the treatment is to control the residual oxygen within very tight and extremely low limits following deaeration. This permits some oxygen addition, rather than total eradication, to ensure the necessary repair and integrity of all waterside passivated surfaces.

Where oxygen removal is required, this includes the eradication of O_2 from:

- **Pre-boiler section** (*ecomomizer, FW tank, FW lines*, etc.)
- **Boiler section** (*boiler surfaces, steam drum*, etc.)
- **Post-boiler section** (*steam and condensate lines, superheaters*, etc.)

The level of DO in water is primarily a function of temperature and pressure, but salt concentration (or TDS) and some other parameters can influence oxygen solubility, and some variation may occur. Nevertheless, a good approximation is shown in Table 11.1.

Smaller or lower pressure boilers usually do not have mechanical deaeration and thus employ only a chemical reactant for DO removal, which can be expensive if the FW temperature is low and less than totally effective if the feedlines are very short. Treatment is by the direct injection of a suitable oxygen-scavenging chemical into the FW system. The feed rate requirement is based on combining a quantity proportional to the level of oxygen present, plus a further amount that contributes to a BW reserve.

Ideally, the oxygen scavenger is added continuously rather than periodically shot-dosed; where batch tanks are employed, there should not be more than one day's supply of oxygen scavenger in the tank. The tank contents should not be agitated any longer than necessary, to avoid aerating the mix.

Conversely, larger and higher pressure boilers tend to employ mechanical deaeration systems and supplement this by using a smaller quantity of oxygen-removing chemical as a true "scavenger." This is added to the base of the deaerator (the deaerator storage section).

The residual oxygen content remaining after deaeration varies depending on equipment design and operational efficiency, but suffice to say that, unless the deaerator is scrupulously well maintained, its per-

Table 11.1 Oxygen Solubility at Atmospheric Pressure

Temperature		*Oxygen solubility*	
°C	*°F*	*mg/l (ppm)*	*ml/l*
25	77	8.5	12.2
30	86	7.3	10.5
35	95	6.7	9.6
40	104	6.2	8.9
45	113	5.9	8.5
50	122	5.4	7.7
55	131	5.0	7.2
60	140	4.6	6.6
65	149	4.1	5.9
70	158	3.8	5.4
75	167	3.1	4.4
80	176	2.7	3.9
85	185	2.2	3.2
90	194	1.7	2.4
95	203	1.0	1.4
100	212	0.0	0.0

NOTE: 0.005 to 0.01 cc/l O_2 = 0.0072 to 0.0143 part per million (ppm), 0.0072 to 0.0143 milligram per liter [mg/l], or 7.2 to 14.3 parts per billion (ppb).

To convert DO in cc/l to mg/l, multiply by 1.433, for 0°C and 760 mm pressure.

Solubility corrections are needed for different temperatures, pressures and salt concentration, but can be ignored for the low levels of DO in deaerated water.

formance can deteriorate to a point significantly below design specifications. Typically, deaerator performance is on the order shown below.

- **DA manufacturer's typical performance claim:** < 0.005 cc/l, (0.005 ml/l, 7.2 ppb) O_2 and zero cc/l CO_2 at 227 °F (108.3 °C, 5 psig nominal).
- **HP utility power-generating stations, operational standards:** maximum DO level of 0.005 to 0.007 mg/l (5–7 ppb) O_2 at the economizer inlet, before the addition of chemical oxygen scavenger. This is a tough standard but usually is achievable.
- **Typical industrial DA system performance:** A more common FW DO performance standard achieved is 0.008 to 0.030 cc/l (0.008–0.030 ml/l, 0.011–0.043 mg/l, 11–43 ppb) O_2.

Oxygen scavengers are, by definition, **reducing agents** and particularly effective oxygen scavengers will create good reducing conditions at the metal surface. Within the correct pH range, these reducing conditions promote the development of a tough, adherent, dense **passivated film** and, given that the primary line of defense against boiler waterside corrosion is this passivated film, it is clearly at least as important that O_2 scavengers should also be strong passivators.

NOTE: Probably the most important function of "oxygen scavengers" is, in reality, the ability to passivate boiler steel. In recognition of this, today most novel oxygen scavenger trials try to identify, not merely comparative oxygen reaction rates, but more importantly, the reduction in iron and copper transport rates through the boiler system. In other words, they seek to optimize the passivation of boiler surfaces and other system components.

Most oxygen scavengers perform best within an alkaline pH range, usually around 9.5, as a result of the catalyst or scavenger *deprotonation step* before the actual oxygen scavenging reaction. Typically, the minimum reaction pH is 8.5 (hence, the general minimum recommendation for FW pH).

Certain types of oxygen scavenger have additional functions, such as pH neutralizing and metal chelating effects.

Apart from the primary requirements of a strong reducing action and good passivation ability (although not all oxygen scavengers are good passivators), it is additionally useful if oxygen scavengers meet certain other criteria, including:

- Low consumption rate relative to oxygen content (**combining ratio**)
- Rapid rate of reaction with oxygen
- Thermal stability and no charring
- Good compatibility with other chemicals
- Minimal contribution to BW TDS
- Zero inherent corrosion potential
- Noncorrosive reactants or decomposition products
- Safe handling and appropriate environmental acceptability
- No contribution to taste or smell and safe to use where steam comes into contact with air, food, surgical instruments, industrial process, etc.

- Sufficient volatility to remove oxygen from condensate return lines, where this is a problem (and this can often be a problem)
- Good aqueous solubility

Today there are many chemical oxygen scavengers available, both inorganic and organic, some of which are novel and patented for specific scavenging applications. (Some of these patents have now expired or are beginning to expire). However, there is no single product that meets all the criteria identified; consequently, the selection of an oxygen scavenger must be a compromise based on the most pressing needs for any particular application.

For HW, LP steam, and many lower pressure industrial operations, **sulfite** or **sulfite derivatives** have proved to be excellent scavengers and suitably cost-effective, provided the MU requirements are not too high and FW temperatures not too low. Alternatively, **tannin-based products** provide a similar degree of effectiveness without the contribution to TDS and, in practice, almost irrespective of FW oxygen content.

For higher pressure boilers, **hydrazine** remains the primary product employed on a global basis, although during the last 20 to 25 years a wide range of novel chemistry alternatives have been developed and promoted in the marketplace. For the most part, the chemistry is not new, merely the application.

For the very highest pressure boilers, the fastest reacting, **volatile organic scavengers** are perhaps the most useful because they also provide effective post-boiler protection.

Where **ammonia** or **amine** is also carried over (the ammonia often stems from some level of scavenger breakdown), protection against **carbonic acid corrosion** complements the oxygen-scavenging capability. As a result, merely to dismiss a volatile scavenger for any specific high-pressure application on the grounds that it will break down and liberate ammonia is short-sighted. Many of the more common oxygen scavengers are described in the following sections.

11.1.1 Sodium Sulfite

Anhydrous sodium sulfite (Na_2SO_3) has a MW of 126, purity of 98% or greater, and a specific gravity (sp. gr.) of 2.63. It is a white to tan or pink powder and is soluble to approximately 32% w/v. It is also available as crystalline hydrated sodium sulfite ($Na_2SO_3 \cdot 7H_2O$) with a sp. gr. of 1.56. The pH of a 5% solution is approximately 9.5. It is

approved under the U.S. **Code of Federal Regulations** (CFR) 21, §172.615 and §173.310. In the United States, Europe, Japan, and other countries, it also appears on **"Generally Recognized as Safe"** (GRAS) lists.

NOTE: In the United States the use of BW treatment chemicals in steam-raising systems where steam may come into contact with food and drugs is governed by ***Food and Drug Administration*** *(FDA) rules, which are laid out in 21CFR. Where compliance with* ***United States Department of Agriculture*** *(USDA) requirements is also required, the limits are defined under 21CFR §173.310 Specific Usage Additives, although sometimes with added restrictions. Compliance with USDA requirements is now administered by* ***NSF International****, a nonprofit company acting like a quasi-government agency and spun off from the* ***Environmental Protection Agency*** *(EPA). NSF International (www.nsf.org) is a food safety, public health, water quality, and environmental protection organization.*

Other agencies involved include the ***U.S. Department of Health****, through the* ***Occupational Safety and Health Administration*** *(OSHA), and the* ***Department of Transportation*** *(DOT).*

Sulfite was introduced in the 1920s but was not widely employed until the 1930s. It essentially replaced *quebracho* and *dried chestnut tannins* as an oxygen scavenger for general industrial boiler applications and, as pressure ratings steadily rose in the 1940s and 1950s, was itself replaced by *hydrazine* as the product of choice for utility boilers. Nevertheless, sulfite- or bisulfite-based products remain the most common oxygen scavengers used today, primarily because the greatest number of boilers around the world are lower pressure units without benefit of a deaerator, and they are tolerant of the sulfite or sulfate contribution to TDS (because they operate in the 2,500 to 5,000 ppm BW TDS range).

Sulfite reacts readily with oxygen, particularly under hot, alkaline conditions, but the reaction rate is slow in colder, neutral waters; thus complete FW deaeration cannot be guaranteed. Consequently, it is standard practice to add a small amount of catalyst to the sulfite. The catalyst is usually **cobalt sulfate** [more properly, **cobaltous sulfate** ($CoSO_4$) supplied as an *anhydrous, monohydrate,* or *heptahydrate* salt] or sometimes **cobaltous nitrate**. The catalyst is added to 100% sodium sulfite at a concentration level of 0.2 to 0.25%.

At FW temperatures and without a catalyst, the sodium sulfite reaction is only 50% complete after 45 seconds, but this rate increases to 100% complete after 10 seconds with cobalt sulfate.

Similarly, when catalyzed the reaction rate decreases significantly as a function of pH level. The optimum reaction pH level is approximately 9.5 to 10.5. Iron, and especially copper, in the boiler may act as **adventitious catalysts**. However, as *metal transport polymers* are frequently employed, iron, copper, or cobalt may be transported away from contact with sulfite, and thus are not available for catalysis. (This may be a serious problem in high-pressure units employing combinations of organic oxygen scavengers and metal ion catalysts.)

The basic oxygen scavenging reaction is as follows:

Na_2SO_3	+	$1/2\ O_2$	→	Na_2SO_4
sodium sulfite		oxygen	*Co*	sodium sulfate

During this reaction, *cobaltous sulfate* produces intermediates of **cobaltic sulfate** $[Co_2(SO_4)_3]$ and cobaltous hydroxide $[Co(OH)_2]$ before reforming as cobaltous sulfate.

Catalyzed sodium sulfite should be fed separately from other treatments and inhibitors (via a stainless steel injection quill) because the presence of other alkaline treatments causes the cobalt to precipitate as *cobaltous hydroxide* in the tank.

Where sodium sulfite is added as a component of multifunctional or one-drum products designed for smaller boilers, no cobalt catalyst is added because of the cobalt alkaline precipitation problem. Consequently, if the FW temperature is low this type of formulation is unsuitable because the sulfite requirement will be too high and the available reaction time too short. Probably a tannin-based, one-drum product would be more suitable (although here again there may be a problem because tannin-based products, unlike sulfite cannot be mixed with *amines*).

Commercial sodium sulfite is acceptable for food plants; higher grades are used for pharmaceutical and electronic chip manufacturing, but in these higher grades the catalyst is usually changed to **sodium erythorbate** (at a level of 0.05 to 0.1%, which also provides lower pressure and temperature passivation).

Sulfite-based formulations used in food handling applications may als incorporate **sodium lignosulfonate** as a *decharacterizer* to avoid changing the color of meats. Formulation difficulties here include the need to keep the product alkalinity low enough to prevent cobalt hydroxide precipitation, but high enough to retain the *lignin decharac-*

terizer solubility. Blending with bisulfite or replacing the *cobalt sulfate* with *erythorbate* may be useful. Under such circumstances, a typical formulation is:

Sulfite-Based Formulation to Meet FDA/USDA Requirements

Sodium sulfite, 32% commercial solution	50.00%
Sodium bisulfite, 40% commercial solution	5.00%
Sodium lignosulfonate powder	0.95%
Cobalt sulfate heptahydrate crystals	0.05%
Water	44.00%
	100.00%

Sulfite is not recommended above 850 to 900 psig because it decomposes to form corrosive sulfur compounds. In the absence of *erythorbate,* it begins to provide a **magnetite-passivation effect** above 300 to 325 psig; above 400 psig, it starts to break down in the boiler (see equation 1), although initially the level of decomposition is not particularly serious.

Nevertheless, as pressures increase, the steam and condensate pH levels begin to drop significantly. This pH depression is accelerated with higher BW sulfite levels. At 700 psig, with a BW sodium sulfite reserve of, say, 40 ppm, the condensate can dip to as low as pH 4.2. This ultimately produces a very corrosive situation caused by the production of **sulfur dioxide** gas (SO_2) and **hydrogen sulfide** gas (H_2S).

Additionally, sulfite may undergo simultaneous auto-oxidation and reduction reactions at higher pressures (see equation 2).

1. Na_2SO_3 + $2H_2O$ → 2NaOH + H_2SO_3
   sodium sulfite; water; caustic soda; sulfurous acid

2. $4Na_2SO_3$ → $3Na_2SO_4$ + Na_2S
   sodium sulfite; sodium sulfate; sodium sulfide

Some benefits of sulfite are:

- A fast reaction rate using the catalyzed product
- A low product cost
- Ease of handling

Its negative points include:

- A lack of passivating ability below 300 psig (425 °F)
- A high stoichiometric reaction relationship (hence high consumption)
- No volatility, thus no post-boiler section protection
- Addition of TDS to the boiler
- Unsuitablility for boilers operating above 850 to 900 psig because of the high corrosion potential from sulfur gases

11.1.1.1 Feeding Sodium Sulfite

The recommended sulfite reserve (as ppm Na_2SO_3) is typically:

- 0 to 300 psig (approximately 0–20 bar): 30 to 50 ppm
- 300 to 600 psig (approximately 20–40 bar): 20 to 40 ppm
- 600 to 900 psig (approximately 40–60 bar): 10 to 20 ppm
- To convert SO_3 to Na_2SO_3, multiply by 1.6
- The stoichiometric relationship for 100% sodium sulfite with oxygen (O_2) is 7.88: 1.0; in practice, 10:1 is commonly used

The feed rate for 100% sulfite is based on the oxygen content of the FW and the desired BW reserve, It can be calculated as:

$$\text{Sodium sulfite required} = (\text{FW } O_2 \text{ ppm} \times 10) + \frac{Na_2SO_3 \text{ BW residual}}{\text{COC}}$$

as lb dry sodium sulfite product, per 1 million lb FW

NOTE: Sulfite, bisulfite, and metabisulfite are commonly used as a reducing agent for chromate in industrial water and chlorine in potable water.

11.1.2 Sodium Bisulfite

Sodium acid sulfite or *sodium hydrogen sulfite* ($NaHSO_3$) has a MW of 104 and a sp. gr. of 1.48. It is a white, corrosive crystalline powder that is very soluble in hot or cold water. It is approved in the United States under 21CFR §173.310, GRAS. It is typically available as a 40% w/w

strongly acidic solution, or supplied as a variable mixture of sodium bisulfite and sodium metabisulfite ($Na_2S_2O_5$):

$2NaHSO_3$	$\leftrightarrow$	$Na_2S_2O_5$	+	H_2O
sodium bisulfite		sodium metabisulfite		water

Where the natural MU water alkalinity is particularly high, the overall FW alkalinity may be reduced somewhat by the use of *sodium bisulfite,* rather than sulfite. Combinations of sulfite and bisulfite (usually with some caustic) produce a range of concentrations and formulation pH levels, generally within the range of 4 to 9.

Where larger, semibulk quantities of sulfite-based oxygen scavengers are required, a 20 to 25% bisulfite solution is recommended. It is sufficiently concentrated to provide reasonable freeze protection. The overall oxygen scavenging reaction is:

$NaHSO_3$	+	$1/2\ O_2$	+	NaOH	$\rightarrow$	Na_2SO_4	+	H_2O
sodium bisulfite		oxygen		caustic soda		sodium sulfate		water

- To convert SO_3 to $NaHSO_3$, multiply by 1.3
- The stoichiometric relationship for 100% sodium bisulfite with oxygen (O_2) is 6.5:1.0. Typically, 7:1 is used.

11.1.3 Sodium Metabisulfite

Sodium pyrosulfite ($Na_2S_2O_5$) has a MW of 190.1 and a sp. gr. of 1.48. It is a colorless crystal or white to yellowish powder and is approved under 21CFR §173.310, GRAS.

Metabisulfite is moisture-sensitive, reverting to sodium bisulfite in the presence of water.

Where dry, catalyzed sodium sulfite is used as the scavenger source, the provision of 2 to 3% metabisulfite into the day-tank batch provides sufficient pH level reduction to ensure the cobalt catalyst does not precipitate. The overall oxygen scavenging reaction is as follows:

$Na_2S_2O_5$	+	O_2	+	2NaOH	$\rightarrow$	$2Na_2SO_4$	+	H_2O
sodium metabisulfite		oxygen		caustic soda		sodium sulfate		water

- To convert SO_3 to $Na_2S_2O_5$, multiply by 1.775
- The stoichiometric relationship for 100% sodium metabisulfite with oxygen (O_2) is 4.44:1.0. Typically, 5:1 is used.

11.1.4 Hydrazine

Diamine (N_2H_4) has a MW of 32 and a sp. gr. of 1.004. Under 21CFR §173.310, zero tolerance in steam is demanded because it is a suspected carcinogen. It is usually supplied as **hydrazine hydrate** ($N_2H_4 \cdot_x H_2O$) in solution strengths of 65%, 35%, and 15%.

A 35% solution is colorless, has a pH level of 10.0, and has no flash point or fire point **(important)**. A 65% hydrazine solution is approximately 100% hydrazine hydrate. Global producers include **Bayer A.G.**, **Elf Atochem S.A.**, and **Olin Mathieson Corporation**.

Hydrazine was first developed in Germany and became the international product of choice in the late 1940s, during World War II. It was first used in a public utility in the United States in 1950 (Duke Power Company, Charlotte, NC).

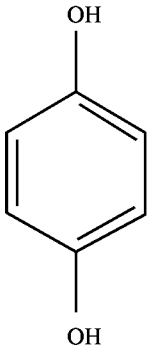
It has been used in the past in the form of **hydrazine sulfate**, but this tended to cause corrosive sulfur gases to form and it was quickly discontinued. It has been widely employed as a **volatile oxygen scavenger** (VOC) replacement for sulfite and tannins, and even used in low-pressure equipment such as apartment building heating systems and steam locomotives. Apart from being an effective oxygen scavenger, it is an excellent passivator and does not contribute to TDS.

Today, in many parts of the world, despite handling precautions and possible health-related problems, it remains the product of choice for high-pressure (say, over 950–1,250 psig) utility boiler plants because of its low FW requirements and low commodity price.

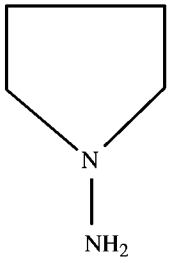
The hydrazine reaction with oxygen is slow, but with the advent of organic catalysts such as **hydroquinone** (which speeds up the reaction 50-fold or so), hydrazine is also the product of choice in medium-pressure (say, over 650 to 950 psig) industrial and cogeneration plants.

NOTE: Cupric copper (Cu^{2+}) is a catalyst for the hydrazine-oxygen reaction, as well as a catalyst for sulfite, DEHA, erythorbic acid, and hydroquinone. Cuprous copper (Cu^{+}) acts as a complexing agent in the desirable formation of protective, pasivated copper oxide films.

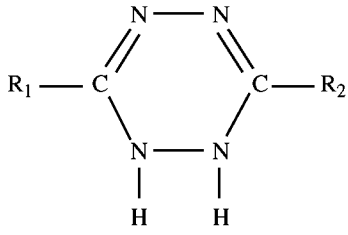
Furthermore, there are many lower-pressure industrial boiler plants around the world, typically operating within the range of 75 to 125 psig



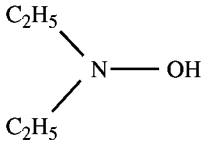
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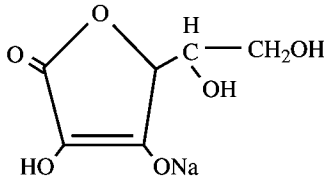
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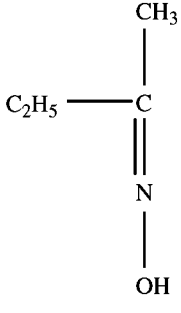
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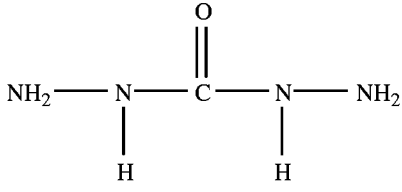
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Figure 11.1 (a) Hydroquinone; (b) 1-AP; (c) 1,2-dihydro-1,2,4,5 tetrazine, where R_1 and R_2 may be methyl, ethyl, or similar groups; (d) DEHA; (e) sodium erythorbate; (f) MEKO; (g) carbohydrazide.

and without benefit of a deaerator, which continue to utilize hydrazine. The feed rate is much higher, of course, generally around 12 to 15 ppm for 35% hydrazine, and the product is added to the delivery side of the FW pump.

The hydrazine-oxygen scavenging reaction is pH-dependent (like sulfite), and an increase in pH from 8 to 9 produces a threefold increase in reaction rate and a further three fold increase from pH 9 to 10.

All subsequent, novel organic chemistries and applications are simply competitive attempts to supplant hydrazine by demonstrating improved reaction rates, better health aspects, no corrosive ammonia decomposition products, and other benefits. Some of these novel organics may offer real benefits over hydrazine, but all at a higher application cost.

11.1.4.1 Feeding Hydrazine

There are numerous possible feed points for hydrazine injection, depending on specific boiler-train configurations. Feed points include:

- Base of the deaerator or discharge point from the deaerator
- Low-pressure injection between air ejectors and drain coolers
- Alternative LP injection prior to LP FW heaters
- High-pressure injection direct to the boiler drum
- Steam header
- General area after the desuperheating line
- Crossover steam line before the LP turbine
- Sucked into the surface condenser hot well under vacuum
- High-pressure heaters

Hydrazine is fed to provide a small BW reserve on the order of:

- 300 to 350 psig: reserve = 0.1 to 1.0 ppm N_2H_4
- 600 to 650 psig: reserve = 0.1 to 0.5 ppm N_2H_4
- 900 to 950 psig: reserve = 0.1 to 0.2 ppm N_2H_4
- Over 950 psig: reserve = 0.05 to 0.1 ppm N_2H_4

Feeding hydrazine hydrate of 35% strength (as N_2H_4) theoretically requires 2.85 ppm product per 1 ppm O_2. In practice, the actual 35% product feed rate typically is between 7 and 10 ppm per 1 ppm O_2.

Note: Hydrazine should be stored in aluminum, plastic, or stainless steel containers, but not mild steel because it attacks rust.

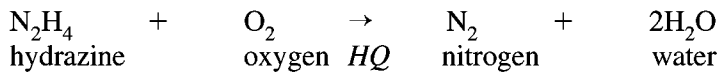
In a well-maintained boiler plant using hydrazine:

- Ammonia in the steam and condensate may be as low as 0.3 to 0.5 ppm (as NH_3), up to perhaps 1.5 to 3.5 ppm
- Iron pickup is from a low of 0.005 to a high of 0.025 ppm Fe
- Copper pickup is from a low of 0.002 to a high of 0.015 ppm Cu
- Steam pH is from a low of perhaps 8.4 to a little over 9.0
- Oxygen in the condensate is typically below 0.01 ppm O_2

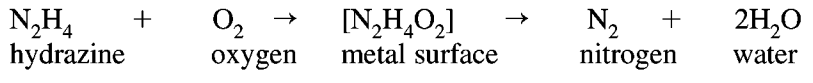
11.1.4.2 Hydrazine Reactions

Hydrazine produces several reactions with oxygen:

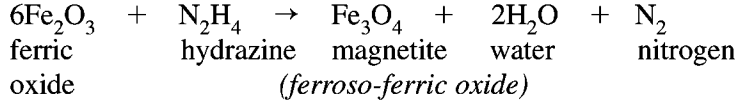
1. **Homogeneous oxygen scavenging reaction**, occurring in FW solution:



2. **Surface adsorption reaction**, which occurs on the surface of the metal and metal oxides:



3. **Heterogeneous reactions:** these various processes are cyclic and continuous, taking place in all sections of the boiler from the economizer to the condensate lines and including suspended **ferric oxide** and **cupric oxide** particles. Unless the hydrazine overfeed is extremely substantial (say, six to seven times theoretical), these latter reactions tend to predominate:



$$\underset{\text{magnetite}}{4Fe3O_4} + \underset{\text{oxygen}}{O_2} \rightarrow \underset{\text{ferric oxide}}{6Fe_2O_3}$$

$$\underset{\text{cupric oxide}}{4CuO} + \underset{\text{hydrazine}}{N_2H_4} \rightarrow \underset{\text{cuprous oxide}}{2Cu_2O} + \underset{\text{water}}{2H_2O} + \underset{\text{nitrogen}}{N_2}$$

The stoichiometric relationship for hydrazine with oxygen is 1:1, but it is always added at between two and four times theoretical to ensure that the reaction proceeds to completion. Even so, it may be some time after startup (often one to two weeks) before hydrazine appears in the BW as a reserve. This probably is due to the hydrazine reducing all existing *ferric oxide* in the system first. During this time, the color of the oxide debris and surface oxides change from reddish brown to black **(passivation)**.

NOTE: The stoichiometric relationship for hydrazine with Fe^{3+} is 0.048:1; it is 0.125:1 for Cu^{2+}.

Similarly, when hydrazine feed is discontinued, it continues to appear in the BW because the fully reduced iron oxides provide an alternate oxygen removal reaction.

Where hydrazine feed continues to be well in excess of scavenging needs, or at pressures exceeding 800 to 850 psig (520–525 °F), it begins to break down and liberate ammonia:

$$\underset{\text{hydrazine}}{2N_2H_4} \rightarrow \underset{\text{nitrogen}}{N_2} + \underset{\text{hydrogen}}{H_2} + \underset{\text{ammonia}}{2NH_3}$$

$$\underset{\text{hydrazine}}{3N_2H_4} \rightarrow \underset{\text{nitrogen}}{N_2} + \underset{\text{ammonia}}{4NH_3}$$

The volatile ammonia formed produces **ammonium hydroxide** in the steam-condensate system, which neutralizes carbon dioxide.

Additionally, at pressures over 7 psig (231 °F), hydrazine is also slightly volatile, and therefore hydrazine (together with its breakdown product ammonia) is considered a *functional neutralizing amine.*

Like oxygen, however, ammonia is corrosive to the post-boiler section, and therefore some care in the application of hydrazine is necessary.

Oxygen and ammonia together create a serious problem. Copper and brasses used in surface condensers, LP FW heaters, fan-coil space heating units, and process heat-exchangers are particularly vulnerable, as shown here:

$2Cu_2O$	+	O_2	→	$4CuO$
cuprous oxide		oxygen		cupric oxide

$4NH_4OH$	+	$2CuO$	→	$Cu(NH_3)4(OH)_2$	+	$3H_2O$
ammonium hydroxide		cupric oxide		copper ammonium complex		water

In practice, however, despite some ammonia production due to breakdown or an excess over theoretical feed, hydrazine is regularly used in copper-containing boiler systems operating at over 1,750 psig (121 bar) without necessarily encountering copper wastage. This situation is tolerated because corrosion of copper by ammonia is oxygen dependent. Consequently, if post-boiler section oxygen is effectively removed by traces of volatile hydrazine supplemented by the deliberate after-boiler/after-superheater addition of hydrazine (ideally catalyzed hydrazine), then copper corrosion generally will not take place to any significant degree.

In fact, following oxygen scavenging, the balance of hydrazine then proceeds to reduce any **cupric oxide** to reform a protective, passivated **cuprous oxide** layer. This premise is, of course, dependent on effective post-boiler scavenging.

$4CuO$	+	N_2H_4	→	$2Cu_2O$	+	$2H_2O$	+	N_2
cupric oxid		hydrazine		cuprous oxide		water		nitrogen

11.1.5 Diethylhydroxylamine (DEHA)

N,N-diethylhydroxylamine $[(C_2H_5)_2NOH]$ has a MW of 89.1 and a sp. gr. of 0.902. It is typically supplied as an 85% hygroscopic, corrosive yellow liquid, such as **Pennstop®** 85% from **Elf Atochem,** and is also present in many diluted or blended product forms, such as **Dearborn Neutrox®** 53 (30% DEHA and 3% hydroquinone) and **Calgon® RB-304** (17.5% DEHA and 7.5% hydroquinone). Japan is a major supplier of DEHA.

NOTE: Dearborn held an application patent for DEHA, which has since expired. Dearborn is now part of ***Betz-Dearborn****, recently acquired by* ***G.E. Specialties*** *(known as* ***G.E. Betz****) and formerly owned by* ***Hercules, Inc.***

Hydroxylamine [*oxyammonium* (NH_2OH)], **hydroxylamine sulfate** [$(NH_2OH)_2{\cdot}H_2SO_4$], other derivatives, and **aminothanolamines** were some of the earliest novel chemistry alternatives to hydrazine, but none have proved as useful as DEHA.

In its catalyzed form [catalyzed with *hydroquinone* (HQ), *benzoquinone,* or *copper*], DEHA has a very fast reaction rate, almost as fast as catalyzed sulfite. Hydroquinone is the most popular catalyst for DEHA, and it is likely that the rapid reaction rate is, in part at least, due to the catalyst simply acting as an oxygen scavenger in its own right.

NOTE: Sulfite, when catalyzed, is probably the fastest of all oxygen scavengers.

- DEHA is volatile and has a distribution ratio of approximately 1.3:1. Consequently, as a result of this volatility, it offers excellent oxygen-scavenging protection to the post-boiler section. In addition, it is a strong reducing agent, is an excellent passivator, and does not contribute to TDS.
- DEHA is most commonly used as a 15 to 30% solution; at this strength, products tend to have a pH level of approximately 9.2 to 9.6.
- The product feed rate is low, with a theoretical *combining ratio* of 1.24:1; in practice, however, it is used at 3 ppm per 1 ppm oxygen.
- Also, because of the volatility of DEHA, testing for a BW reserve is of little benefit. It is usual to simply confirm the presence of DEHA in the FW, aiming for a reserve of 0.1 to 0.25 ppm.

On the negative side, DEHA begins to decompose at relatively low pressures (650 psig, 45 bar) to produce **acetaldehyde.** At pressures over 1,000 psig (70 bar), it produces some **acetaldoxime** and eventually *acetates,* some *ammonia, nitrogen, water,* and *carbon dioxide.*

NOTE: The decomposition of DEHA should not be considered too seriously because it is very low initially. At 1,500 psig, DEHA breakdown only amounts to 3%, as measured by the total organic carbon (TOC) content. Compare this to HQ, which breaks down to the extent of 43% at the same pressure.

The reaction producing acetic acid, nitrogen, and water is shown here. Acetic acid eventually forms an acetate.

$$\underset{\text{DEHA}}{4(C_2H_5)_2NOH} + \underset{\text{oxygen}}{9O_2} \xrightarrow{Cu} \underset{\text{acetic acid}}{8CH_3COOH} + \underset{\text{nitrogen}}{2N_2} + \underset{\text{water}}{6H_2O}$$

DEHA oxidation products in LP boiler systems are primarily **acetate** and **actaldehyde**; whereas in HP boilers **diethylamine** and **aceteldehyde** are produced. An outline reaction is shown below:

$$(C_2H_5)_2NOH \xrightarrow{[O]} C_2H_5HCH_3CH \xrightarrow{[O]} CH_3CH = NOH \xrightarrow{[O_2]} CH_3CHO + HNO_2$$

The ammonia production is less than in hydrazine, but there may be a perceived of copper and brass corrosion. In fact, any corrosion risk is small, provided that DEHA-treated boiler plants are subjected to the same requirements as hydrazine-treated units, namely, ensuring that all in-leakage of oxygen in the condensate system is fully eliminated. If this objective is achieved, the oxidation of *cuprous oxide* to *cupric oxide* tends not occur to any significant degree, and the susceptibility for copper corrosion in the presence of ammonia is equally low.

Where copper corrosion occurs, the problem usually can be traced back to an excess feed of hydrazine, DEHA, or similar product, coupled with inadequate post-boiler oxygen scavenging.

DEHA breaks down at high pressure. Its **survival pressure** is probably not in excess of 1,250 psig, but because of its high volatility and rapid reaction rate, it generally provides *complete* boiler cycle oxygen-control coverage. Some limited ammonia is also generated, and this may be useful for carbon dioxide neutralization.

There are no "fall-out" products resulting from DEHA breakdown; consequently, it can generally be safely used at pressures in excess of 2,500 psig, similar to hydrazine. A complication, however, is that HQ (the primary catalyst for DEHA), breaks down above 1,250 psig, so the DEHA reaction rate tends to slow down.

NOTE: When calculating amine feed rates, in theory some allowance should be made for the production of carbon dioxide at high pressures. However, because of the recycling action provided by most amines and other variables, in practice this allowance calculation becomes a meaningless exercise.

Overall, DEHA is a low toxicity product, performs extremely well as a rapid oxygen scavenger and metal passivator, and is an excellent replacement for hydrazine. In addition, it is competitively priced and consequently a very popular product.

11.1.6 Erythorbic Acid and Sodium Erythorbate

Isoascorbic acid, l-ascorbic acid [$C_6H_8O_6$, or $OC_4H{:}O(OH)_2$-$CHOH(CH)_2OH$] has a MW of 176.1, It is available as white to yellow granular crystals, It is soluble in water to the extent of 43%.

Erythorbic acid is supplied as white granular crystals or a powder of **sodium erythorbate monohydrate** $C_6H_7O_6Na{\cdot}H_2O$, having a five-sided ring and a very reactive *ene-diol* structure ($-COH{=}COH-$); it is a sterioisomer of sodium ascorbate, with a MW of 216.1. It is approved under 21CFR §182.304, GRAS.

- A 10% solution of erythorbic acid has a pH of 2.1; a 10% solution of sodium erythorbate has a pH of 7.4.
- Erythorbic acid is available as a 98+% *Food Chemical Codex* product (as per **Pfizer sodium erythorbate FCC**, although as Pfizer is now a pharmaceuticals company, much of the world's erythorbate is now supplied from China and other Asian countries) and in many diluted or blended forms, such as **Nalco Sur-Gard™**. The ONDEO Nalco material is typical of products used within the industry, being based on erythorbic acid buffered with amine. A 1% solution of the product has a pH level of 6.3.

NOTE: Application patents for the use of erythorbates in BW were instituted by Nalco, Betz, and Calgon. The fact that three water treatment patents were issued for essentially the same product application shows the ease of finding alternative application protocols within the industry.

Erythorbic acid and sodium erythorbate are very safe products, widely used in the food industry as antioxidants and alternatives to vitamin C. In the water treatment industry, they are strong reducing agents that reduce *metal oxides* and *hydroxides* to their more soluble *ferrous* forms and promote the passivation of boiler waterside surfaces (*magnetite formation*).

The oxygen reaction with sodium erythorbate is catalyzed by traces of **nickel**, **copper**, or **iron** in solution, so stainless steel or plastic stor-

age tanks are recommended. *Ferric iron* in solution also can oxidize sodium erythorbate directly. **Citric acid**, **EDTA**, or other strong *chelants* are employed to stabilize erythorbates against this degradation. *Sodium erythorbate* is itself a chelant, forming complexes with most common divalent and trivalent metals. Very high BW salines (over 5,000 ppm) may inhibit the oxygen-scavenging reaction.

Formulated products tend to use a 10 to 20% neutralized erythorbate, buffered to pH of 5 to 6 with *ammonia, morpholine, cyclohexylamine, diethanolamine* (DEA), or *triethanolamine* (TEA) to reduce the acidity of erythorbic acid. Similarly, amines are used with sodium erythorbate to improve the reaction rate.

Various combination oxygen scavenger products exist that use erythorbate with, for example, *tannins* and *sulfite,* to obtain safe products having the benefits of low-cost scavenging and good passivation.

The reaction with oxygen is complex, initially forming **dehydroascorbic acid** (as shown in the following equation), which then produces **2,3 diketo-*l*-gluconic acid** [$COOH(C{:}O)_2(CHOH)_2CH_2OH$]. In turn, this oxidizes to **oxalic acid** [$(COOH)_2$] and ***l*-threonic acid** [$COOH(CHOH)_2CH_2OH$].

$$\underset{\text{erythorbic acid}}{OC_4H{:}O(OH)_2{-}CHOH(CH)_2OH} + \underset{\text{oxygen}}{O_2} \xrightarrow{Ni}$$

$$\underset{\text{dehydroascorbic acid}}{OC_4H(:O)_3{-}CHOH(CH)_2OH} + \underset{\text{hydrogen peroxide}}{H_2O_2}$$

Following the formation of *dehydroascorbic acid,* the reaction proceeds irreversibly; the degradation process produces *oxalates, formates,* and *carbon dioxide,* depending on temperature and pH. As usual, the oxygen-scavenging reaction rate is increased by raising the pH and the temperature.

Erythorbates are safe products and there are no harmful breakdown products, although when early formulations utilized **ammonia** as a pH buffer (and neutralizer for part of the carbon dioxide), copper corrosion problems resulted. However, erythorbates are not steam-volatile,and consequently there is no post-boiler oxygen scavenging potential available. Thus, in the event of complete breakdown of the product at high pressure, oxygen-induced, ammonia corrosion of copper may continue unchecked.

Erythorbates are claimed to be suitable for pressures of up to 1,800 or even 2,000 psig, with only moderate FW reserves required (200–500 ppb erythorbate). This is not borne out in practice because at these cor-

responding steam temperatures, some carbon charring may occur, and this results in waterside fouling. The breakdown starting point is 500 °F (260 °C), equivalent to 700 psig. But the catalyzed product is a good scavenger and easily can be used above this pressure because there is essentially nothing harmful produced up to approximately 1,500 psig, the maximum recommended pressure **(survival pressure)**.

Additionally, control of erythorbate reserves in the boiler is difficult and should thus be generous, as shown below:

- 0 to 300 psig: 15 to 20 ppm erythorbate in the BW
- 300 to 600 psig: 10 to 15 ppm erythorbate in the BW
- 600 to 900 psig: 5 to 10 ppm erythorbate in the BW
- 900 to 1,250 psig: 3 to 5 ppm erythorbate in the BW
- 1,250 to 1,500 psig: 2 to 3 ppm erythorbate in the BW

NOTE: The DEHA test can be adapted for erythorbates.

- Erythorbates react stoichiometrically, requiring 10 ppm per 1 ppm oxygen.
- Practical feed rates vary, but for a formulation containing, say, 10% erythorbate, the requirement is typically between 100 and 120 ppm whole product per 1 ppm O_2. Consequently, this type of adjunct product may be expensive because of the high combining ratio required.

NOTE: Formulations based on sodium erythorbate and stabilized with citric acid against premature reaction (thus, they remain safe products, despite the pH level being around 2.0). Formulations based on ammonium erythorbate lose their "safe" status but have an improved pH of 6.3 to 6.5.

Where sodium erythorbate is employed, expect the condensate pH to be at least one pH unit lower than with ammonium erythorbate. Sodium erythorbate can be buffered up to pH 4.0 by the addition of 1% DEHA (85% strength product), and this provides some marginal improvement in condensate pH. Where DEHA is added in excess of 1%, the product becomes unstable.

Some formulations include 0.02% copper sulfate.

11.1.7 Hydroquinone (HQ)

1,4-Benzenediol, quinol, or *p-dihydroxy benzene* [C_6H_4-1,4-$(OH)_2$] has a MW of 110.1. It is a white crystalline powder formed by the reduction of ***p*-benzoquinone** [*quinone*, $C_6H_4(:O)_2$].

Hydroquinone is another "safe" alternative to hydrazine and was originally covered under a Betz patent. Related compounds and their alkyl-substituted derivatives were similarly patented, including ***o-*** and ***p*-diamino** and **aminohydroxybenzenes**.

Hydroquinone is a good oxygen scavenger, even in cold water, so much so that it is commonly employed as a catalyst for **hydrazine**, **DEHA**, and **carbohydrazide**.

Hydroquinone is not designed simply for high-pressure boiler applications; it also is used in LP steam boiler formulations. Additionally, it enhances passivation by other oxygen scavengers, promoting the conversion of *ferric oxides* and *hydroxides* to *magnetite* and preventing degradation to *hematite.* This **passivation enhancement process** applies to copper as well as steel.

NOTE: A practical problem resulting from the rapid reaction kinetics of HQ is that when water containing HQ passes through an MBDI, it turns the resin black, obscuring visual observation of resin separation during regeneration.

Also, because of the speed of reaction, the chemical feed solution should be protected against reaction with atmospheric oxygen.

- Hydroquinone can be used at up to 1,500 psig. Above this pressure, breakdown to carbon dioxide takes place. No ammonia is formed. The breakdown starting point is 580 °F (304 °C, 1350 psig).
- At lower pressures HQ exhibits no volatility, but this changes at higher pressures, whereupon it begins to provide a useful oxygen scavenging capability in condensate systems, with its *distribution ratio* being proportional to pressure.
- Hydroquinone is not very soluble and, in order not to risk plugging dosing pumps or chemical feedlines, formulations tend to be dilute.
- Reactions are improved in alkaline pH conditions (and at higher temperatures), Consequently, HQ is usually blended with volatile amines, including **methoxypropylamine**, **diethylaminoethanol** (DEAE), or **(mono)ethanolamine**, to ensure that the correct alkaline pH condition is maintained.
- The HQ reaction with oxygen proceeds through several steps, and the precise reaction path is pressure-dependent. The first step is the formation of *benzoquinone* is shown in the following section. Further reactions result in the formation of *low MW alcohols, ketones,* andother compounds.

$C_6H_4(OH)_2$ + O_2 → $C_6H_4(:O)_2$
hydroquinone oxygen benzoquinone

- As a result of this multistep process, the combining ratio varies. Assume 7.0 ppm HQ per 1 ppm oxygen.
- Where steam pressures are high, expect to see between 1 and 2 ppm of HQ in the steam.
- Maintained BW reserves are low, on the order of 0.2 to 0.5 ppm HQ at the highest pressures.

NOTE: The test method is accurate down to 2 ppb, but some colorimetric interference may be noted, thus requiring a modification to the method.

Because HQ has limited volatility at lower pressures, when acting as a catalyst with other more volatile oxygen scavengers, it will not always follow the primary scavenger around the boiler cycle system. This creates operational difficulties because scavenging reaction rates are slowed and, in lower pH condensate systems, the post-boiler oxygen scavenging reaction may cease entirely.

Pyrogallol, another oxygen scavenger (and a reaction product of tannins), often is used as a catalyst for HQ.

11.1.8 Methylethylketoxime (MEKO)

2-Butanone oxime (C_2H_5,CH_3-C=NOH) has a MW of 87.1 and a sp. gr. of 0.92. It is available as a 97+% liquid or in various diluted forms, although solubility in water may be a problem. It is a low toxicity material, but possibly an irritant; it is patented as an oxygen scavenger as **Drew MEKOR®**.

MEKO is just one of a number of **oximes** (R_1R_2C=NOH) presenting oxygen-scavenging characteristics. Others include **acetaldoxime** and **butyraldehydeoxime.**

MEKO is a very volatile scavenger with a distribution ratio between that of DEAE and cyclohexylamine, which enables it to provide post-boiler oxygen scavenging protection in larger steam-condensate lines. It is fast-reacting, although in the boiler this reaction does not always proceed to completion, even in the presence of copper (perhaps only 60–70% complete).

Importantly, MEKO has little to no passivating characteristics and is thus unsuitable as an inhibitor for boiler lay-up.

- Because reaction breakdown products include a range of *carboxy compounds,* charring may result; therefore, it is not advisable to employ MEKO above 1,250 psig, although some product survival has been identified at 2,500 psig. The breakdown starting point is 570 °F (299 °C, 1,350 psig).
- The combining ratio for MEKO is 5.4 ppm of 100% product per 1 ppm oxygen.
- Maintain a BW reserve of 0.75 to 1.25 ppm MEKO, using an iron reduction test.

As a result of the limited solubility of MEKO, it is often formulated with other boiler treatment ingredients such as filming and neutralizing amines, sulfite, or erythorbates, which permit increased concentration, improved stability, and better overall effectiveness.

11.1.9 Carbohydrazide (CHZ)

Carbonic acid dihydrazide, carbazide, or *N,N-diaminourea* $C{:}O(NHNH_2)_2$] has a MW of 90.1. It is available as a 98+% liquid or in various diluted forms, typically a 6.5% formulated product.

Carbohydrazide was the first novel oxygen scavenger of any significance to provide a safe handling replacement for hydrazine; it was patented as an oxygen scavenger as **Nalco ELIMIN-OX®** in 1981.

Carbohydrazide is a derivative of hydrazine that hydrolyzes in the boiler to produce hydrazine, although CHZ is an oxygen scavenger in its own right. Other derivations of this oxygen-scavenging chemistry now exist, including **polyacrylic hydrazide.**

Copper and cobalt catalyze the direct CHZ hydrolysis reaction at temperatures below 275 °F (135 °C), as shown:

$C{:}O(NHNH_2)_2$	+	O_2	→	$2N_2$	+	H_2O	+	CO_2
CHZ		oxygen	*Co*	nitrogen		water		carbon dioxide

This reflects the basic FW reaction.

At lower temperatures of 300 °F/150 °C (equivalent to 65 psig, 4.5 bar, and typical of small industrial operations), CHZ hydrolyzes to form hydrazine and carbon dioxide (see equation 1).

At medium temperatures of 400 °F/205 °C (equivalent to 250 psig, 17 bar, and typical of slightly larger industrial boilers), CHZ decomposes without the production of TDS to form nitrogen, ammonia, and water (see equation 2).

1. $C{:}O(NHNH_2)_2$ + H_2O → $2N_2H_4$ + CO_2
   CHZ water hydrazine carbon dioxide

2. $C{:}O(NHNH_2)_2$ + H_2O → $2NH_3$ + N_2 + H_2 + CO_2
   CHZ water ammonia nitrogen hydrogen carbon dioxide

Although CHZ is a relatively slow oxygen scavenger, it is an excellent pre-boiler and boiler section passivator. As such, it has been found to be particularly useful in large sub- and supercritical, fossil utility boilers employed for peak-load and cycling duty, or in units subject to cold lay-up or hot standby.

Under these conditions, copper and iron pickup **(crud)** may reach devastatingly high levels, cleaning requirements are frequent, and start-up times are extended. Also, maintenance and repair costs are high.

The passivation process in large boilers is complex and not properly understood, but simplified pathway reactions may be proposed as follows:

$C{:}O(NHNH_2)_2$ + $12Fe_2O_3$ → $8Fe_3O_4$ + $2N_2$ + CO_2 + $3H_2O$
CHZ hematite magnetite nitrogen carbon dioxide water

$C{:}O(NHNH_2)_2$ + $8CuO$ → $4Cu_2O$ + $2N_2$ + CO_2 + $3H_2O$
CHZ cupric oxide cuprous oxide nitrogen carbon dioxide water

The use of CHZ as a passivator to reduce **crud** levels and minimize the associated problems has proved to be particularly beneficial in power-generating boilers. For other types of operations, however, involving the continuous operation of industrial boilers with much longer steam and condensate line systems, the benefits of CHZ are not so dramatic and the material is seldom the product of choice for nonutility applications.

Carbohydrazide itself is of very low volatility, but it decomposes at relatively low temperatures to produce volatile *carbon dioxide* and *ammonia*. In theory, the combined corrosive effects of these two materials should be negated in the condensate system, but in practice, this is not always so and both **steel** and **copper corrosion transport problems** may develop, primarily as the result of **corrosion-enhancement reactions** resulting from **oxygen in-leakage**. It is presumed, therefore, that (similar to hydrazine) some deliberate after-desuperheating line addition of CHZ is necessary if post-boiler section corrosion is to be avoided.

The combining ratio for CHZ is 1.4 ppm per 1 ppm oxygen, but this means little in practice, given that its primary benefit is in controlling iron and copper transport in utility boilers through improved passivation programs. Boiler start-up feed rates are relatively independent of DO content. Rather, the requirement is based on meeting passivation needs, and it may take longer than a month to satisfy this need and allow feed rates to decrease.

In reducing *start-up hold times* and *deaerator pegging,* the initial feed rates are often relatively high. Initial residual CHZ levels may be 100 to 200 ppb but decrease significantly (reducing down to only 20 to 50% of starting residuals) when transport levels are under control (typically aiming for Fe $\geq$ 10 ppb, Cu $\geq$ 2 ppb at both the economizer inlet and condensate pump discharge).

11.1.10 1-Aminopyrrolidine (1-AP)

1-Aminopyrrolidine ($C_4H_8N\text{-}NH_2$) has a MW of 86. It usually is supplied as the hygroscopic crystalline material *1-aminopyrrolidine hydrochloride,* which has a MW 122.6, or a 30% w/v aqueous solution.

1-AP is a low-volatile (distribution ratio of 0.7), safer alternative to hydrazine. It is relatively new on the market and was introduced by **Kurita Water Industries Ltd.** of Japan.

There is nothing particularly special about the product except its feed rate, which is fairly low in comparison to some of the other novel oxygen scavengers. It exhibits passivation characteristics (forming magnetite in a way similar to hydrazine), coupled with good corrosion and iron transport control.

The reactions of 1-AP with oxygen are shown here:

$$\underset{\text{1-AP}}{C_4H_8N\text{-}NH_2} + \underset{\text{oxygen}}{1/2\ O_2} \rightarrow \underset{\text{pyridazine}}{C_4H_8N_2} + \underset{\text{water}}{H_2O}$$

$$\underset{\text{1-AP}}{4C_4H_8N\text{-}NH_2} + \underset{\text{oxygen}}{7O_2} \rightarrow \underset{\text{4-aminobutanal}}{4C_4H_9NO} + \underset{\text{water}}{2H_2O} + \underset{\text{nitrogen}}{2N_2}$$

- Use a minimum of 1.6 ppm 1-AP per 1 ppm O_2 (5.33 ppm for a 30% solution, say, 6 ppm for practical purposes).
- The maximum recommended operating pressure is 1,450 psig (10 bar, 10Mpa) to avoid charring caused by breakdown products of *pyridazine* and *4-aminobutanal.*

11.1.11 Tetrazines

Several *dihydrotetrazine* materials have been promoted as oxygen scavengers, including **3,6-dimethyl,1-2-dihydro,1,2,4,5-tetrazine,** and the **diethyl-** and **diphenyl-**derivatives. *3,6-Dimethyl,1-2-dihydro,1,2,4,5-tetrazine* is a six-sided ring with a formula $H_3C\text{-}CN_2C\text{-}CH_3NHNH$; its MW equals 102. Its basic reaction with oxygen is shown here:

$$\underset{\text{DMDH tetrazine}}{H_3C\text{-}CN_2C\text{-}CH_3NHNH} + \underset{\text{oxygen}}{1/2\ O_2} \rightarrow \underset{\text{DM tetrazine}}{H_3C\text{-}CN_2C\text{-}CH_3NN} + \underset{\text{water}}{H_2O}$$

- At least 2 ppm of tetrazine is required per ppm O_2.

It is doubtful if there is any significant commercial demand for this product.

11.1.12 Dihydroxyacetone (DHA)

1,3 Dihydroxyacetone ($CH_2OHC{:}O$) has a MW of 90. Another novel organic oxygen scavenger introduced 20 years ago with little or no commercial success, DHA is catalyzed by HQ and Mn. The reaction requires at least 2 ppm DHA per 1 ppm oxygen.

11.1.13 Aminoguanidines

Aminoguanidines are yet another group of oxygen scavengers, introduced to the market 20 years ago, which appear to have been unsuccessful in the marketplace. They are nonvolatile derivatives of **hydrazine** (N_2H_4) and **guanidine** [*amino methanamidine,* $HN{:}C(NH_2)_2$] and are catalyzed by quinones and cobalt. The reaction requires at least 1 ppm aminoguanidine per 1 ppm oxygen.

Examples include *mono-, di-,* and *triaminoguanidines. Monoaminoguanidines* are represented as $HN{:}CNR(NH_2)_2$, where R = 1 to 4 carbon atoms.

11.1.14 Tannins

In contrast to novel oxygen scavengers, tannins have been available for a century or more. The **hydrolyzable tannin** component of **quebracho** and other tannins under alkaline BW conditions produce a number of oxygen scavengers, primarily as sodium salts. These include:

- **Tannic acid**
- **Ellagic acid**

- **Gallic acid,** *3,4,5-trihydroxybenzoic acid*
- **Quinic acid,** *1,3,4,5-tetrahydroxycyclohexane-carboxylic acid* [$(HO)_4C_6H_7COOH$]
- **Pyrogallol,** *pyrogallic acid, 1,2,3-trihydroxybenzene*
- **Hydroquinone** [C_6H_4-1,4-$(OH)_2$]
- **Catechol,** *pyrocatechol* [C_6H_4-1,2-$(OH)_2$]

Tannins are excellent pre-boiler and boiler section passivators and sludge conditioners but are nonvolatile, so that there is no specific post-boiler oxygen scavenging ability.

In theory, tannins are added to the FW based on the oxygen demand, with 10 ppm of 100% tannin-blend required per 1 ppm of oxygen (O_2). In practice, however, tannins are simply added to the FW to achieve a BW reserve of 100 to 160 ppm product.

As oxygen scavengers, tannins are suitable at boiler pressures in excess of 650 psig, although sludge conditioning properties begin to fall away at pressures over 300 to 450 psig. (See Section 10.3.1 for more details on tannin chemistry.)

A summary of the properties of some of the most important oxygen scavengers is shown in Table 11.2.

11.2 OXYGENATED TREATMENT (OT)

The previous section reviewed the use of various oxygen scavenger chemistries as a mechanism for minimizing boiler cycle corrosion and for the promotion of passivated surfaces. On the basis that passivation of steel and copper surfaces probably is more important than specific oxygen-scavenging abilities and that this function is critical in cycling utility boilers, many European utilities now focus their efforts on closely controlling oxygen reserves within very low-level ranges, rather than trying to totally eliminate DO from the boiler system.

The concept of deliberately retaining a small oxygen reserve within the boiler system, or adding oxygen to certain areas, gradually gained ground in the United States during the late 1990s, and several boiler conversions from AVT and other programs to OT have now taken place.

Oxygenated treatment technology is unlikely to ever influence operations personnel at an average industrial facility. It is strictly an esoteric protocol to retain knife-edge control in large power-generating boilers. However, an outline of the technology may be of interest.

Table 11.2 Properties of Oxygen Scavengers

Oxygen Scavenger *Note: Combining ratio is for 100% scavenger*	***Combining Ratio (Practical)***	***Max. Pressure psig***	***Volatility/ Distrib. Ratio***	***Passivation ability***
Sodium sulfite as solid or 32% soln. Cat. = Co or Eryth.	10:1 Rapid scavenger	950 max. Risk of SO_2/H_2S	Not volatile DR = Nil	Limited, only over 300 psig
Sodium bisulfite Typical is 40% soln. Cat. = Co or Eryth.	7:1 Rapid scavenger	950 max. Risk of SO_2/H_2S	Not volatile DR = Nil	Limited, only over 300 psig
Na metabisulfate 100% powder Cat. = Co or Eryth.	5:1 Rapid scavenger	950 max. Risk of SO_2/H_2S	Not volatile DR = Nil	Limited, only over 300 psig
Hydrazine as 15 or 35% soln. Cat. = HQ	3:1 Rapid scavenger	2500+ Produces NH_3	Poor volatility DR = 0.1	Excellent for all system
DEHA as 17.5 to 30% soln. Cat. = HQ or Cu	3:1 Rapid scavenger	2500+ Some NH_3	Good volatility DR = 1.3	Excellent for all system
Erythorbate as 10 to 20% soln. Cat. = Cu/Ni/Fe	10:1 Good scavenger	1500 Nothing harmful	Not volatile DR = Nil	OK, but only in the boiler
Hydroquinone as 15 to 25% soln. Cat. = pyrogallol	7:1 Scavenging enhancer	1500 Produces CO_2	Only at 1500 psig DR = 0.15	Acts as enhancer only
MEKO Poor solubility Cat. = Erythorbate	6:1 Weak scavenger	1250 Risk of charring	Highly volatile DR = 2.2	No true ability to passivate
Carbohydrazide as 6.5% solution Cat. = Cu or Co	1.5 Slow scavenger	2500+ Produces CO_2/NH_3	Some, but only over 130 psig	Excellent but only utilities
1-Aminopyrollidine as 30% solution Cat. = HQ	2:1 OK as scavenger	1250 Risk of charring	Some volatility DR = 0.7	OK, but not special
Hydrolysable tannins as 25 or 50% soln. Cat. = None or Eryth.	10:1 Good for cold FW	650 max. Product then fails	Not volatile DR = Nil	Excellent but only in boiler

NOTE: 1 std. atm = 14.696 pounds per sq. inch absolute (psia or lbf/in^2).
1 bar = 14.5 psia, or 1 kg/cm^2, or 100,000 Pascal, or 100 kPa, or 0.1 MPa.

11.2.1 The Background to Oxygenated Treatment

Over recent years, with the advent of new pretreatment and condensate polishing technologies and improved cleaning and operational control techniques, the cleanliness of utility boiler surfaces has continued to improve. Iron, copper, and nickel metal ion transport levels generally also have been reduced. These improvements, while desirable, have only served to highlight the corrosive role of oxygen and the potential for internal system damage due to **erosion-corrosion** (EC) mechanisms. Also, where improvements have been made within specific boiler cycles, new problems have sometimes emerged elsewhere.

Particularly critical areas for corrosive attack include economizer tube inlet headers, certain boiler tube areas, surface condenser tubes, and HP heaters. Problems occurring here may be related to EC or perhaps to the dissolution of copper or iron and its transport to some point elsewhere in the boiler system. If transported metal reaches certain critical areas (such as copper reaching turbine blades), very serious outages may occur.

In some boilers, despite a range of improvements, crud levels may still be very high (perhaps 100 g per sq ft) in certain critical flow areas (such as flow balancing tubes). The crud may be found in the form of **rippled magnetite,** and it causes unacceptably high pressure drops that necessitate unscheduled offline cleaning. The permanent reduction of transported metal oxides, by "sealing" critical areas with a thin but tough passivated film is clearly very important in such cases.

In facilities where boilers remain very clean, they may then be subject to excessive EC. Under these circumstances, the practical benefit obtained from providing a tough, durable, dense passivated film of magnetite as a means of protecting waterside surfaces against the ravages of erosion is appreciated.

The basis of OT therefore is to maintain a controlled level of oxygen in the FW (approximately 150 to 250 ppb O_2) to promote and enhance the development of these various Fe and Cu passivated surface films and thus reduce expensive operational corrosion problems of one sort or another.

Novel oxygen scavengers and polymer-based deposit control programs hardly figure in the operation of these large boilers because the treatment regimen is often simply **hydrazine** and **ammonia.**

To ensure optimum generating efficiency and minimize boiler outages and reductions in equipment life, a large number of operational functions must be both coordinated and tightly controlled. The use of

OT does not reduce this need; in fact, it probably requires even tighter control to ensure long-term success.

Some of the functions requiring coordination and control under an OT program are listed here:

- The use of hydrazine may be reduced partially or entirely omitted. Similarly, the application of oxygen may be partial to selective areas of the boiler cycle or used as a total replacement for hydrazine.
- Oxygenated treatment is seldom applied to all boilers in a power plant; usually only the most troublesome units receive OT.
- Where erosion is a problem, the FW pH level generally is increased from a typical level of 9.0 to 9.2 up to 9.4 to 9.6 because this improves the solublization of potential erodents and strengthens the magnetite film.
- Where copper corrosion and its subsequent transport is a problem, the FW pH level may be reduced to only 8.7 to 8.8 in order to reduce its aggressiveness toward copper.
- Elimination of all air in-leakage pathways is required.
- Chemical reducing conditions and flow geometrics are optimized to minimize EC. Reducing conditions especially must not be too severe (as may happen with excess hydrazine) to prevent autocatalytic EC mechanisms proliferating.
- Pathway temperatures must be strictly controlled (especially in single-phase systems) to create a balance between low-temperature oxide dissolution and high-temperature mass transfer limitations.
- Oxygen levels must always be higher than 1 ppb to minimize EC. Normally they are 5 to 10 times this level. Oxygen injection points include to the condensate after the polishers, to FW after the deaerator, and at the economizer inlet.
- Generally speaking, holding oxygen levels between 5 and 10 ppb in high purity water having a conductivity between 0.1 and 0.2 μS/cm tends to minimize iron and copper transport. Thus, oxygen, conductivity, and their ratios must be maintained within appropriate ranges at all times. Nevertheless, where excessive corrosion of, say, an economizer takes place, OT injection may need to reach a level of up to 30 ppb.
- The condensate polishing system must be in excellent working order and typically operating in the ammonia cycle.

- Isokinetic samplers, automatic online conductivity, and oxygen injection devices are required at various locations.
- The ratio of oxygen in the economizer inlet to boiler waterwall downcomer must be controlled because this varies with load. The ratio typically is 4:1.
- Heater vents must be properly controlled to avoid air pocket accumulation.

Benefits of OT are obtained in several ways, for example:

- The reduction of iron and copper corrosion
- Reduced crud levels
- A drop in economizer and condenser tube leaks
- Savings in hydrazine and other chemicals
- Improved MB polisher throughput
- Extended periods between planned outages and cleaning programs from, say, every 16 months to every 24 months

11.3 AMMONIA AND AMINE ADJUNCTS

Ammonia and especially amine adjuncts complement the use of oxygen scavengers, The synergistic interaction of *catalyzed hydrazine, DEHA,* or *carbohydrazide* with **neutralized** or **filming amines** provides a reliable way of obtaining cost-effective corrosion protection for steam-condensate systems. Consequently, operators of most boiler plants, large or small, tend to use some form of amine treatment. Generally, however, ammonia is used only in very large, high-pressure units, where it is primarily employed as an adjunct to boost FW pH levels.

The FW oxygen scavengers mentioned earlier are volatile and can therefore provide additional protection against post-boiler section corrosion induced or enhanced by oxygen in-leakage. These particular scavengers also break down under pressure to produce some level of volatile **ammonia,** which can neutralize any *carbon dioxide* found in the steam-condensate system.

NOTE: The CO_2 itself may result from several possible sources, such as low levels of bicarbonates in the FW, air in-leakage, or even from thermal disintegration of the oxygen scavenger used as part of the treatment program.

Whether ammonia arises from its use as a FW pH level adjuster or from adventitious provision as a result of DO scavenger breakdown, it should be recognized that any excess ammonia will clearly end up in the steam-condensate system. Although the benefit of carbon dioxide neutralization may be legitimately claimed, unfortunately, excess ammonia also may permit the corrosion of copper and its alloys, especially if some oxygen persists.

The question, therefore, of whether to tolerate ammonia in a boiler, either directly or indirectly, is not necessarily easy to answer, despite its benefits of being a low-cost material and highly *basic* in nature. When it is used, normally it is as a component of AVT programs in high-purity boiler systems.

In lower pressure commercial and industrial boilers, handling and safety are issues of more concern than relative chemical effectiveness, and the fact is that because of such problems, ammonia simply is not used in these smaller plants. *Caustic* generally provides the necessary **FW alkalinity** and *amines* are then employed to overcome the problems of **carbonic acid corrosion** in the steam-condensate system.

Nevertheless, which particular amine or combination of amines to use (and there are several) is again not a simple question, and selection depends on several parameters.

Apart from the design, complexity, age, and operating characteristics of the boiler plant itself, a checklist of various chemical and physical considerations includes the following:

- **Basicity,** the ability to raise the pH to a specified level
- **Neutralization capacity,** generally relating to carbonic acid
- **Distribution ratio** (DR) or *partition coefficient*
- **Volatility** or *relative volatility*
- **Thermal stability,** or *product breakdown temperatures*
- **Resultant by-products,** including *ammonia*
- **Azeotrope formation,** *constant boiling mixtures in deaerators*
- **Safety, health, and environmental issues** such as *flashpoint*
- **Product costs,** which may vary considerably
- **Effect on condensate polishing capacity** due to *amine loading*

However, DR, *volatility,* and some other factors are also important points to consider in the selection of **volatile oxygen scavengers** (VOSs). And to further complicate matters, at least one common VOS

is also a corrosion-inhibiting amine (**diethylhydroxylamine**, DEHA). Consequently, the selection and use of ammonia and/or amine adjuncts cannot be considered in isolation; rather, they should be reviewed in conjunction with oxygen scavenger requirements (especially with VOS) to produce a synergistic program, tailored to the specific design, operating requirements, and economics of a particular facility.

11.3.1 Post-Boiler Section Corrosion Summary

Corrosion of steel by carbonic acid is probably the most common problem in the post-boiler section, producing pipe grooving and general metal wastage, especially in threaded joints. This form of corrosion is not self-regulating and the reaction products can produce more carbon dioxide, thus perpetuating the corrosion problem. Typically, the condensate pH level is depressed to around 5.0 to 5.5.

CO_2	+	H_2O	→	H_2CO_3
carbon dioxide		condensate		carbonic acid

The initial reactions with the condensate pipework are:

$2H_2CO_3$	+	Fe	→	$Fe(HCO_3)_2$	+	H_2
carbonic acid		iron/ steel		ferrous bicarbonate		hydrogen

H_2CO_3	+	Fe	→	$FeCO_3$	+	H_2
carbonic acid		iron/ steel		ferrous carbonate		hydrogen

The resulting **ferrous bicarbonate** and **carbonate** salts produced are not particularly stable and various secondary reactions subsequently take place, resulting in the formation of *ferrous* and *ferric oxides, hydroxides,* and *carbonates:*

$Fe(HCO_3)_2$	→	FeO	+	H_2O	+	$2CO_2$
ferrous bicarbonate		ferrous oxide		water		carbon dioxide

Where pressure drops and oxygen infiltration occurs, **enhanced condensate line corrosion** results, which generates more carbon dioxide and becomes self-perpetuating:

$$\underset{\substack{\text{ferrous}\\\text{bicarbonate}}}{4Fe(HCO_3)_2} + \underset{\text{oxygen}}{O_2} \xrightarrow{\Delta P} \underset{\substack{\text{ferric}\\\text{oxide}}}{2Fe_2O_3} + \underset{\substack{\text{carbon}\\\text{dioxide}}}{8CO_2} + \underset{\text{water}}{4H_2O}$$

Depending on the condensate temperature and level of oxygen infiltration, other reactions may occur. For example, hot condensate in the absence of oxygen produces ferrous hydroxide.

$$\underset{\text{iron}}{Fe} + \underset{\text{water}}{2H_2O} \rightarrow \underset{\substack{\text{ferrous}\\\text{hydroxide}}}{Fe(OH)_2} + \underset{\text{hydrogen}}{H_2}$$

In the continued absence of oxygen the corrosion is often self-limited as **magnetite** is formed:

$$\underset{\substack{\text{ferrous}\\\text{hydroxide}}}{3Fe(OH)_2} \leftrightarrow \underset{\substack{\text{magnetite}\\\text{(black)}}}{Fe_3O_4} + \underset{\text{water}}{2H_2O} + \underset{\text{hydrogen}}{H_2}$$

However, where oxygen continues to infiltrate, the corrosion reaction continues unabated and **ferric hydroxide** is formed:

$$\underset{\text{iron}}{4Fe} + \underset{\text{water}}{6H_2O} + \underset{\text{oxygen}}{3O_2} \rightarrow \underset{\substack{\text{ferric}\\\text{hydroxide}}}{4Fe(OH)_3}$$

Or, alternatively, where **ferrous hydroxide** is present in the steam-condensate system, ferric hydroxide may again result:

$$\underset{\substack{\text{ferrous}\\\text{hydroxide}}}{4Fe(OH)_2} + \underset{\text{oxygen}}{O_2} + \underset{\text{water}}{2H_2O} \rightarrow \underset{\substack{\text{ferric}\\\text{hydroxide}}}{4Fe(OH)_3}$$

Over time and at the relatively high temperatures involved in the steam-CR system, some red **ferric oxide** is also formed from ferric hydroxide:

$$\underset{\substack{\text{ferric}\\\text{hydroxide}}}{2Fe(OH)_3} \xrightarrow[\textit{high temp.}]{\textit{time and}} \underset{\substack{\text{ferric}\\\text{oxide}}}{Fe_2O_3} + \underset{\text{water}}{3H_2O}$$

These and other similar reactions may take place, including the corrosion of copper and nickel. The most noticeable effect is often the increased level of maintenance and pipe replacement work required resulting from the effects of pitting corrosion.

As an example of this, typical carbonic acid **penetration** or **pitting corrosion rates** (at, say, 300 lb/hr condensate flowing in a 1 inch pipe), are as follows:

- Average of 2 ppm (mg/l) CO_2 produces 12 mils/year
- Average of 3 ppm (mg/l) CO_2 produces 18 mils/year
- Average of 6 ppm (mg/l) CO_2 produces 25 mils/year
- Average of 12 ppm (mg/l) CO_2 produces 35 mils/year
- Average of 20 ppm (mg/l) CO_2 produces 60 mils/year

NOTE: 1 mil = 1 thousandth of one inch. It can be seen that only 6 ppm carbon dioxide in condensate flowing through a pipe of 1/4 inch (250 mil) wall thickness will eat away 50% of the wall thickness in only 5 years, at which point the structural integrity of the pipe is essentially lost.

Oxygen corrosion in condensate pipelines is recognizable as large pits and are a typical result. Where the condensate pH level is low (say, due to the presence of carbonic acid), the pits may be particularly large, but as the pH level rises (say, due to the use of neutralizing amines), the layer of *iron oxide corrosion product* becomes more protective and the resulting pits tend to be smaller.

The presence of **red ferric oxide** usually indicates an *inactive pit* but **black oxide** infers *active pitting.* Condensate receivers are common points for oxygen infiltration (especially in smaller boiler plants).

Erosion processes also may take place, especially where high pressure steam is discharged into low pressure CR lines. The resulting flashing and pressure reduction effects encourage steam impingement around the point of discharge.

11.3.2 Carbon Dioxide and Carbonic Acid

The natural supply source of carbon dioxide in MU water is primarily **calcium bicarbonate alkalinity** [$Ca(HCO_3)_2$], which reacts under conditions of heat to form insoluble *calcium carbonate* and *carbon dioxide.* Because the precipitated carbonate cannot decompose further, no additional carbon dioxide is released. As a result, the total amount of

carbon dioxide released is only a little over half that produced when the alkalinity starting point is **sodium bicarbonate**.

Where sodium bicarbonate is present (as when MU water pretreatment includes a water softener), given enough time and temperature it decomposes to form *hydrate alkalinity, carbon dioxide,* and *water:*

1. $2NaHCO_3 \xrightarrow{heat} Na_2CO_3 + CO_2 + H_2O$
   sodium bicarbonate → *heat* → sodium carbonate + carbon dioxide + water

Under BW temperature conditions, this first-stage decomposition reaction proceeds to 100% completion, producing *carbonate alkalinity* and *carbon dioxide.* Thus, 1 ppm of bicarbonate initially produces 0.44 ppm of carbon dioxide.

2. $Na_2CO_3 + H_2O \xrightarrow{heat} 2NaOH + CO_2$
   sodium carbonate + water → *heat* → sodium hydroxide + carbon dioxide

This second-stage decomposition reaction (carbonate hydrolysis) proceeds to approximately 80% completion at 150 psig, producing *hydroxide alkalinity* and *carbon dioxide* and providing a further 0.35 ppm carbon dioxide (80% of 0.44 ppm). Consequently, the total production of carbon dioxide from 1 ppm of bicarbonate alkalinity is 0.79 ppm at 150 psig.

The formation of carbon dioxide from FW alkalinity varies, depending on boiler pressure, as shown in Table 11.3.

Carbon dioxide released into the steam ultimately dissolves in condensate to produce **carbonic acid**. This acid is normally controlled by neutralization and beyond to provide a pH level of over 8.0, via the use of appropriate amines or amine blends. Examples of neutralization reactions for **morpholine** and **cyclohexylamine** (CHA) are shown here:

$OC_4H_8NH + H_2CO_3 \rightarrow OC_4H_9N^+H{\cdot}HCO_3^-$
morpholine + carbonic acid → morpholine carbonate

$C_6H_{13}N + H_2CO_3 \quad C_6H_{13}N^+H{\cdot}HCO_3^-$
CHA + carbonic acid → CHA carbonate

NOTE: A common condensate pH level to aim for is 8.5 to 9.5, but only 8.5 to 9.2 where a high Cu content is present in the system.

Table 11.3 Carbon Dioxide Evolution from FW Alkalinity

Boiler pressure	***Bicarbonate alkalinity starting point:*** *1 ppm carbonate (as $CaCO_3$) produces the following ppm of CO_2*	***Carbonate alkalinity starting point:*** *1 ppm carbonate (as $CaCO_3$) produces the following ppm of CO_2*
50 psig	0.62	0.18
100 psig	0.70	0.26
150 psig	0.79	0.35
200 psig	0.84	0.40
250 psig	0.86	0.42
500 psig	0.88	0.44

Condensation occurs constantly in steam pipes, and steam traps are installed to separate the steam from the condensate. In long steam-pipe runs most of the carbon dioxide remains in the steam phase, although if only a single neutralizing amine with a low *DR* is used, much of the amine will be present in the condensate. The result is that the amine feed quickly becomes depleted, and further down the steam/condensate pipe the pH level becomes progressively lower.

The extent to which carbon dioxide dissolves is proportional to its *partial pressure* in the steam phase *(Henry's Law)*. Also, CO_2 (like most gases) is less soluble in hot condensate than in cool condensate.

In the first part of any steam-condensate system the CO_2 provides only a small fraction of the total steam-vapor mass, but as the steam condenses, it contributes a greater percentage of the remaining vapor. Toward the end of the run, the carbon dioxide, having a greater partial pressure, dissolves to a greater percentage (in the cooler condensate) and results in a lower pH level.

It should be noted that in intermittently operated steam processes, where condensate is allowed to cool in carbon dioxide-rich atmospheres, the pH level can drop significantly, resulting in devastatingly high localized corrosion, even though the *average* CO_2 content of the steam may be relatively low.

In view of the variable levels of carbonic acid produced throughout the average steam-condensate system network, in order to provide adequate neutralization coverage, it is generally necessary to provide a blend of amines.

Whether a blend of two or three neutralizing amines is required is debatable. It all depends on the needs of the specific steam-condensate

system configuration and the ability to provide a comprehensive but cost-effective solution.

From a practical point of view, it is seldom possible to provide complete coverage from a *twin-blend neutralizing amine program* in a very large or difficult system.

Even *triple amine blends* do not always provide full protection, especially when the system is old and has suffered corrosion at some prior time, or when operating conditions are variable, and especially when air in-leakage occurs.

Under these conditions, because the neutralizing amine has no effect on oxygen ingress, it is common to supplement the neutralizing amine blend with a filming amine. The *filmer* may be applied separately (usually to a steam header) or blended with the neutralizers and added to the FW, or sometimes directly to the boiler. **Care should be exercised when filmers are employed in previously corroded systems because it is very likely that old corrosion debris will be transported away to cause severe blockages in steam traps and valves.**

NOTE: Under these circumstances, it is common to provide a time-phased treatment program, whereby the ratio of filmer to neutralizer is gradually increased over time. This reduces the tendency for old deposits to cause blockage problems.

Where both oxygen and carbon dioxide are a problem, an alternative to the **neutralizer-filmer blend** is the use of a **neutralizer-VOS blend.**

11.3.3 Types of Neutralizing Amines

Amines are ammonia derivatives in which one or more hydrogen atoms have been replaced by an organic radical. Amines are sometimes called nitrogen bases. Basic chemistries include **fatty amines** (as *primary, secondary, tertiary,* and *polyamines*), **amine salts, quaternary ammonium compounds**, **amine oxides**, and **amides**.

There are many hundreds of "raw material" amines commercially available, and a wide variety are used for water treatment applications. They typically have low flash points and are therefore normally dissolved in water down to 20 to 40% strength, to minimize fire risks and permit blending. Additionally, each material has its own specific functional profile covering molecular weight, solubility, volatility, *DR,* basicity, thermal stability, and other parameters. The standard water treatment amines have all been known and used for 30 to 40 years or more.

All neutralizing amines employed in water treatment formulations are based on single amine type or blends, drawn from this commercial stockpile. Unfortunately, they are not all drawn from a common class of amines, simply with progressively higher molecular weight or additional radical groups added; instead they are drawn from a wide range of classes. For example,

- **Benzylamine** is a *primary aromatic amine*
- **Cyclohexylamine** is a *primary cyclic paraffin amine*
- **Hexylamine** is a *primary alkyl amine*
- **Morpholine** is a *six-membered heterocyclic amine*

Some of the more common water treatment amines employed today are listed here. Most are corrosive and lachrymatory. Those with a low flash point are usually employed as a dilution in water.

- **Ammonia.** NH_3, MW = 17. Usually available as **ammonium hydroxide,** NH_4OH, containing 28 to 30% NH_3, Sp. gr. = 0.88. Boiling point = −33 °F. This was the first volatile base employed to minimize carbonic acid corrosion in condensates. It is inexpensive, has a low equivalent weight, and is relatively easy to handle (despite its being a strong irritant that immediately affects the nasal mucous membranes and therefore demands the use of appropriate safety equipment and due care and attention). Commonly available through chemical distributors.
- **2-Amino,2-methyl,1-propanol** (AMP), also known as **Isobutanolamine** (IBA), $(CH_3)_2CNH_2CH_2OH$, MW = 89. Available as a 95% solution (**AMP-95®**) from **Angus Chemical Company.** Sp. gr. = 0.942. Flash point = 87 °C/188 °F (PMCC). Boiling point = 329 °F. Suitable for short to medium steam-condensate pipe runs provided the operating pressure is at least 75 psig. A safe replacement for morpholine. Reasonable thermal stability.
- **Cyclohexylamine** (CHA), $C_6H_{11}NH_2$, MW = 99.2 .Flash point = 90 °F (open cup). Sp. gr. = 0.865. Boiling point = 274 °F for the 100% amine (equivalent to 30 psig), but it forms an azeotrope with 44% amine in water, boiling at 205 °F. CHA functions well in LP systems and has the ability to stay with the steam-condensate in long pipe runs. As a single material, it may form an amine carbonate and generally is blended with morpholine for best effect. Available as a strongly alkaline, primary amine, 99+% commodity

product from manufacturers such as **Monsanto Chemical Company** and **Abbott Laboratories, Inc.** Commonly available through chemical distributors. Good thermal stability.

- **Dicyclohexylamine** (DCHA), $C_6H_{11}NHC_6H_{11}$, MW = 181.3. Sp. gr = 0.914. Flash point = 219 °F (ASTM D56/closed cup). Available as strongly basic, secondary amine, 99+% commodity product, from manufacturers such as **Monsanto Chemical Company** and **Abbott Laboratories, Inc.**
- **Diethanolamine** (DEA), *2,2-iminodiethanol; di(β-ethyloxy)aniline.* $HN\text{-}(CH_2CH_2OH)_2$, MW = 105.1. Sp. gr. = 1.097. Flash point = 280 °F. Also used as an absorbent for acidic gases in petrochemical operations. Hygroscopic. Available as a 98.5+% alkyl amine commodity product from various international manufacturers, including **Texaco Corporation**. Commonly available through chemical distributors.
- **Diethylaminoethanol** (DEAE); also known as **diethylethanolamine** (DEEA), *2-hydroxytriethylamine; N,N-diethylethanolamine* and *ethanol,2-(diethylamino);* $[CH_3CH_2]_2NCH_2CH_2OH$. MW = 117.2. Sp, gr. = 0.885. Flash point = 125 °F (TAG closed cup), 130 °F (ASTM-D1310/TAG open cup). A very versatile amine with a DR between CHA and morpholine. Suitable for short to medium steam-condensate pipe runs. Boiling point = 321 °F for the 100% amine but it forms an azeotrope with 26% amine in water, boiling at 210 °F. Available as a 99.5+% strength, *alkylalkanolamine* under the name **Pennad 150®** from **Elf Atochem, Inc.**, or **Morlex® DEEA** from **Union Carbide Corporation**. Reasonable thermal stability.
- **Diethylhydroxylamine** (DEHA) *N,N-diethylhydroxylamine,* $(C_2H_5)_2NOH$, MW = 89.1. Sp. gr. = 0.902. Typically supplied as a 85% hygroscopic, corrosive yellow liquid, such as **Pennstop®** 85% from **Elf Atochem**; Japan is a major supplier of DEHA.
- **2-Dimethylaminoethanol** (DMAE), also known as *N,N-dimethylethanolamine* (DMEA); $HOCH_2CH_2N(CH_3)_2$ MW = 89.1. Sp.gr. = 0.887. Flash point = 105 °F/40 °C. Available as a 98.5+% amine commodity product from various international manufacturers and commonly available through chemical distributors.
- **Dimethylisopropanolamine** (DMIPA), or **dimethylamino-2-propanol** (DMAP), $(CH_3)_2NCH_2CHOHCH_3$, MW = 103.2. Sp. gr. = 0.913. Flash point = 99 °F (TAG closed cup). Available as a 77%, *alkylalkanolamine* under the name **DMA-2-P 77®** from **Elf Atochem, Inc.**

- **3-Methoxy,*n*-propylamine** (MOPA, or 3-MPA), $CH_3O(CH_2)_3NH_2$, MW = 89.1. Sp. gr. = 0.874. Flash point = 73 °F/22 °C. Flammable and corrosive liquid. Commonly available through chemical distributors. Good thermal stability.
- **Monoethanolamine** (MEA), *ethanolamine* (ETA); *2-aminoethanol; 2-hydroxyethylamine;* $NH_2CH_2CH_2OH$. MW = 61.1. Sp. gr. = 1.012. Flash point 93 °C. Also used as an absorbent for acidic gases in petrochemical operations. A breakdown product of morpholine and so is often found in secondary steam cycles systems. Thought to be superior to morpholine. Available as a 99+% *alkylamine*, commodity product, from several international manufacturers, including **BP Chemicals PLC**, **Union Carbide**, and **Texaco Corporation**. Commonly available through chemical distributors.
- **Morpholine**, *tetrahydro-p-isoxazine; diethyleneimidoxine; diethyleneoximide;* OC_4H_8NH. MW = 87.1. Sp. gr. = 1.002. Flash point = 37.7 °C/99.9 °F (open cup). Boiling point = 262 °F. A very low *DR* and particularly suitable for steam-condensate systems with a very short path, most notably utility power systems, where it provides good protection to turbine blades against carbonic acid attack. Morpholine will not provide protection on long runs and therefore is often blended. This amine is the only one generally permitted or recommended for use in direct steam sterilization processes. Available as a 99+% heterocyclic amine commodity product from several international manufacturers, including **BASF A.G.** and **Texaco Corporation**. Commonly available through chemical distributors. Good thermal stability.

This list is by no means exhaustive. Many other amines have been employed from time to time, and novel materials are occasionally tested under high temperature conditions to control problems specific to critical units, especially in PWR secondary cycles and other power applications.

Morpholine is still the standard by which other amines are compared for *pH control,* and **AMP** has commonly been employed to control carbon steel boiler tube *erosion-corrosion problems* in European gas-cooled reactor stations.

Other amines include:

- **Dimethylaminoethylpropanol** (DMAEP)
- **3-Hydroquinuclidine**

- **1,2-Diaminoethane** (DAE)
- **3-Methoxypropylamine** (MPA)
- **5-Aminopentanol** (AP)

11.3.4 Functional Properties of Neutralizing Amines

Neutralizing or **volatile amines** such as **morpholine** and **cyclohexylamine** neutralize carbonic acid, which generally raises the condensate and FW pH levels in high-pressure units.

Ammonia is usually classified as a neutralizing amine because it provides post-boiler section corrosion inhibition through the same carbonic acid neutralization mechanism as "regular" amines. Similarly, **hydrazine** and other **VOSs** that produce ammonia, may be classified as *functional neutralizing amines.*

The various functional properties of neutralizing amines, such as *basicity, neutralizing capacity, DR,* and *volatility* often have little or no direct relationship with each other, but *all* these properties are significantly different at boiler temperatures. This vital consideration is often insufficiently highlighted in manufacturers' data sheets. Consequently, some of the commonly available information comparing amines records data at ambient temperatures, making it next to useless.

Thus, when selecting amines for specific boiler cycle applications, any and all information provided should *not* be taken at face value, but should be carefully reviewed for relevance, in order to make the right choice and to ensure that proposed cost-benefits are realizable.

11.3.4.1 Neutralization Capacity

Where amines are employed to counter acidic system water (as when condensate contains carbonic acid) it is necessary to consider the *neutralization capacity* (NC or CO_2 *absorption value*) of the amine. A higher NC means that, for any given concentration, the amine has a greater capacity to neutralize acids.

The NC of an amine is an important functional property to consider with **high-alkalinity feed waters.** The NC is inversely proportional to the MW of the amine in question, so amines with the lowest MW (such as *ammonia* and *MEA*) have the highest NC. Also, the NC for any class of amine tends to be proportional to the number of amine groups on the molecule.

In steam-condensate systems, we are primarily concerned with the effect of carbon dioxide on pH levels. For example (and assuming all carbon dioxide is fully hydrated to carbonic acid):

- 1 ppm CO_2 produces a pH of 5.53
- 3 ppm CO_2 produces a pH of 5.28
- 5 ppm CO_2 produces a pH of 5.17

The **relative neutralizing capacity** (RNC) of amines can be calculated from the **reaction mole ratios**; thus, from the reaction of *ammonia* with *carbonic acid,* shown here, the RNC is 17/44 = 0.386 ppm neutralizing amine required per ppm CO_2:

$$\underset{17}{NH_3} + \underset{44}{CO_2} + H_2O = NH_4^+ \cdot HCO_3^-$$

- **Ammonia:** 17/44 = 0.386, or approximately 0.795 for ammonium hydroxide, or RNC of 2.7 ppm amine/ppm CO_2 for a 30% ammonia solution
- **AMP:** 88/44 = 2, or RNC of 6.7 ppm amine/ppm CO_2 for a 30% AMP solution
- **CHA:** 99/44 = 2.25, or RNC of 7.5 ppm amine/ppm CO_2 for a 30% CHA solution
- **DEAE:** 117/44 = 2.66, or RNC of 8.9 ppm amine/ppm CO_2 for a 30% DEAE solution
- **Morpholine:** 87/44 = 1.98, or RNC of 6.6 ppm amine/ppm CO_2 for a 30% morpholine solution

The **neutralization pH** (pH_{neut}) is calculated as:

$$pH_{neut} = 1/2\ [pK_a(H_2CO_3) + pK_a(\text{amine})]$$

where, $pK_a = -\log_{10}K_a = 14 - pK_b$

and, pK_a = **acidity constant,** pK_b = **basicity constant**

NOTE: Also see the next section concerning basicity.

The neutralization pH levels for some amines are:

- **Ammonia:** $pH_{neut} = \frac{1}{2}\ (6.37 + 10.26) = 8.3$
- **AMP:** $pH_{neut} = \frac{1}{2}\ (6.37 + 9.72) = 8.05$
- **CHA:** $pH_{neut} = \frac{1}{2}\ (6.37 + 10.66) = 8.5$

- **DEAE:** $pH_{neut} = \frac{1}{2}(6.37 + 9.72) = 8.05$
- **Morpholine:** $pH_{neut} = \frac{1}{2}(6.37 + 8.33) = 7.35$

Once *neutralization capacity* is considered, the next factor is the solubility of *amine carbonates* formed by neutralization. This characteristic varies by product and temperature.

For example, **isobutanolamine** (IBA, *2-amino,3-methyl,1-propanol,* AMP) forms a carbonate **(IBA carbonate)** that is soluble to the extent of 38% w/w at 25 °C, whereas **cyclohexylamine carbonate** is only soluble to the extent of 10.5% at 25 °C. This difference in solubility and lack of any significant carbonate stability may result in the fouling of steam traps at the end of long runs of condensate line.

Neutralizing capacity functionality is important in lower pressure plants because it is common for some carbon dioxide derived from alkalinity breakdown to be carried over into the steam. It is less important in high-pressure units where demineralized water (or water of similar high purity) is employed because the FW is assumed to be essentially free of alkalinity.

Neutralizing capacity is not the only measure of a required amine feed rate. Once all acidic characteristics have been neutralized, **amine basicity** becomes the important issue because this raises the pH above the neutralization point, to a more stable and sustainable level. Consequently, in practice we are concerned with the level of amine necessary to raise the condensate pH to a "noncorrosive" level. This practical amine requirement is difficult to obtain from theoretical calculations because it must take account of the *amine volatility, DR,* and the boiler system *amine recycling factor* (as well as temperature). As noted earlier, the basicity of an amine has little or no relationship to its volatility or *DR,* so that reliable field results are probably a more important guide in assessing the suitability of an amine product than suppliers' tables.

Table 11.4 gives the typical levels of amine required to reach specific condensate pH levels with varying amounts of CO_2 in the steam.

11.3.4.2 Basicity

Basicity is the ability of an amine to boost the pH level of an aqueous system in the boiler cycle to a level at which, under normal operating temperatures, the various materials of construction are reasonably stable.

Table 11.4 Amine Requirement to Reach a Stable Condensate pH

ppm CO_2 in stream	18	18	32	32	58	58
Desired condensate pH	7.5	8.0	7.5	8.0	7.5	8.0
AMP: ppm 40% strength reqd.	68	73	155	168	298	312
CHA: ppm 40% strength reqd.	95	103	168	173	310	328
DEAE: ppm 40% strength reqd.	88	103	180	190	325	338
Morph: ppm 40% strength reqd.	93	125	193	313	350	380

*NOTE: Under normal boiler operating conditions, the pH required to ensure relative waterside stability (**operational stability pH**) for copper and copper alloys is typically 8.8 to 9.2, and for steel alloys it is 9.2 to 11.0. However, for any specific system the precise operational stability pH range is a function of boiler pressure, temperature, and system metallurgy.*

Basicity nearly always arises from the presence of *unshared electron pairs.* Consequently, amines produce an alkaline reaction in aqueous solution by functioning as an electron donor (or **Lewis base**), withdrawing hydrogen ions from water and leaving an excess of hydroxyl ions in the solution.

The base properties of the amine are represented by its **basicity constant** *(basicity dissociation constant, K_b),* which identifies the amount of the amine (in moles) that is ionized (i.e., available to raise pH) in liquid water-condensate at any given temperature and pressure. The **dissociation reaction** for a primary amine is shown in equation 1, and the value of the **dissociation constant** is shown in equation 2.

1. $RNH_2 + H_2O \leftrightarrow RNH_{3+} + OH^-$
2. $K_b = [RNH_3^+]\,[OH^-] / [RNH_2]$

Where R = an organic radical
and [ ] represents a molar concentration

An increase in K_b means that, for any given concentration, the amine has a greater capacity to raise the pH.

Sometimes the **acidity constant** *(acidity dissociation constant, K_a)* is employed for the *conjugate acid* of the amine used. Under these circumstances:

3. $K_a = [RNH_2]\,[H^+] / [RNH_3^+]$
4. $K_b = K_w/K_a$

Where K_w is the dissociation constant for water
and, $pK_a = -\log_{10} K_a$
also, $pK_a = 14 - pK_b$

Information reflecting the various basicity properties of amines may be presented as K_b or as the pertinent **dissociation constants** pK_d/pK_b, as shown in Table 11.5.

Basicity also may be regarded as a measure of **amine hydrolysis**, and it governs the increase in pH level, per additional unit measure of amine. The law of diminishing returns applies of course, and beyond a certain point there is little further increase in system pH. Also, the *basicity constant* for individual amines varies considerably with temperature, so it is important to consider K_b at the relevant operating temperature, rather than simply at ambient temperature.

Referring to each amine shown in Table 11.5, as the temperature *increases* so the dissociation constant K_b *decreases* (although ratios between amines may change). Conversely, as temperature decreases, so K_b increases. Generally, because we are concerned with relatively high temperatures, the K_b value is likely to be lower than shown in some published tables, and so *more* product will be required than possibly anticipated.

From Table 11.5 it can be seen that to raise the pH to a specified level, or to neutralize a given quantity of carbonic acid, it would take 142 moles of morpholine (12,350 grams) to provide the same effect as only 1 mole of CHA (99 grams), as shown here:

$$440 \times 10^{-6}\,(\text{CHA})/3.1 \times 10^{-6}\,(\text{morpholine}) = 142\ \text{mole}$$

Table 11.5 Amine Basicity Dissociation Constants

Amine	*MW*	K_b	pK_d/pK_b
Morpholine	87	3.1×10^{-6}	8.4/5.6
Ammonia	17	18×10^{-6}	9.3/4.7
DMIPA	103	40×10^{-6}	9.5/4.5
DEAE	117	45×10^{-6}	9.7/4.3
AMP	89	55×10^{-6}	9.7/4.3
MOPA	89	102×10^{-6}	10.1/3.9
CHA	99	440×10^{-6}	10.6/3.4
Carbonic acid	62		6.4/7.6

NOTE: Values given are for atmospheric pressure condensation at 100°C. Higher K_b equates to a lower amine dosage. Carbonic acid pK^a/pK_b values also provided for comparison purposes only.

Consequently, amines with high K_b values require lower concentrations than do low K_b materials to raise pH levels. Nevertheless, volatility, *DR,* thermal stability, and other factors also need to be taken into account. Inevitably, amine selection is a compromise between these various functional properties.

From a practical perspective, **amine basicity** is clearly an important functional property because (as has been noted) when temperatures rise and K_b decreases, amine concentration must increase simply to maintain pH level. Often a sharp increase in concentration is needed to actually raise the pH.

For larger boiler plants suddenly placed on high-fire and full-load conditions, the amine feed may need to be increased even where no increase in MU water is necessary. And for those steam generators using high-purity FW, particularly fine operational control may be required because maintenance of the correct pH within a very narrow range is usually a critical requirement, irrespective of temperature changes.

In many of the largest boiler plants around the world **AVT programs** are often employed that commonly provide for *hydrazine* (as an oxygen scavenger) and a volatile amine such as *morpholine* (to boost the pH level). Where funds are limited, however, some facilities instead use **ammonia** as a pH booster because it is a low-cost item with a low *equivalent weight* and a high *DR.* Unfortunately, this approach may lead to downstream problems as ammonia becomes less chemically bound with increases in FW pH and a weaker base as temperatures rise. Consequently, a point is reached when ammonia ceases to further influence the pH level upward.

Ammonia is, in fact, a poor choice for pH adjustment at higher temperatures. In practice, the lower **alkylamines** are effectively stronger bases than ammonia, not least because of the inductive effect of *methylene* groups.

To determine **relative amine basicity cost-effectiveness** for a specific amine concentration, compare amine K_b (at the desired operating temperature and pH) to amine cost for each of various neutralizers under consideration.

11.3.4.3 Volatility, Relative Volatility, and Distribution Ratio (DR) or Partition Coefficient

A fundamental functional property of a neutralizing amine (**vapor-phase amine**) is its *volatility.* Derived from this function is relative volatility and the *DR.*

- **Volatility:** This denotes how much of the total amine supplied will be present in the steam and thus available to neutralize the carbon dioxide (also in the steam). In water, a portion of the total amine hydrolyzes to form an *ammonium ion* and a *hydroxyl ion* (the **dissociation reaction**); the balance of the amine (the **free-amine** portion) is volatile. Clearly, it is important to know the size of this volatile fraction, which depends on the particular amine selected and the pH of the system. In turn, the pH depends on the concentration of total amine originally present so that, the higher the pH, the greater the volatile fraction.

Without sufficient volatility, there is an inadequate concentration in the steam to neutralize CO_2 and an excessive level in the BW, which is lost during BD. Amines with very high volatilities fail to provide protection in that region of the steam-condensate system where condensate is first formed.

- **Relative volatility:** This term expresses the tendency of an amine to vaporize, relative to water under the same conditions. It is, again, pH-dependent and a function of total amine concentration.

- **Distribution Ratio (DR):** The DR relates the concentration of an amine present in the steam phase to that concentration in the condensate phase (*vapor-liquid distribution ratio*). Consequently, it identifies in which condensate production region of a steam-condensate system any particular amine will concentrate and thus provide protection against corrosion. It also helps to indicates the portion of amine loss due to vaporization in a condenser or venting of a deaerator. The expression for *DR* is shown here:

$$DR = \text{Amine}_{\text{steam}} / \text{Amine}_{\text{condensate}}$$

Where, $\text{Amine}_{\text{steam}}$ = Portion of amine in the steam phase
And, $\text{Amine}_{\text{condensate}}$ = Portion of amine in the condensate phase

From a practical perspective, *DR* (along with neutralization capacity and basicity) is one of the most important functional properties of amines and is always referred to when selecting amines for application in a steam-condensate system. Amine *DR* values vary considerably, however, and for each amine the *DR* value changes with variation of temperature and pressure.

Consequently, it is important to ensure that amines under consideration are matched to the relevant system pressure; unfortunately, many

commonly available charts provide *DR* values without mentioning this, or simply record values at ambient pressure, which is unlikely to be of benefit. Table 11.6 identifies some *DR* values for carbon dioxide, ammonia, and other neutralizing amines.

Table 11.6 Some DR Values for CO_2, NH_3, and Neutralizing Amines at Various Pressures

psig	***0***	***100***	***200***	***300***	***400***	***500***
CO_2	3.0					
NH_3	10					
AMP	0.1	0.47	0.95	0.84	0.85	0.85
CHA	4.0	9.3	23.3	19.5	8.0	6.7
DEA	0.004		0.11			
DEAE	1.7	3.4	4.5	4.4	3.9	3.8
DEHA	1.3					
DMAE	1.0					
DMAEP	1.4					
DMIPA	1.7					
MEA	0.07		0.15			
MOPA	1.0					
Morph	0.4	0.98	1.6	1.4	1.2	1.2
psig	***600***	***700***	***900***	***1000***	***1250***	***1500***
CO_2			99			
NH_3	4.2		3.9	3.57		
AMP	0.85	0.82	0.91	0.90	0.93	0.92
CHA	6.6	6.1	5.3	4.7	4.4	4.1
DEA				0.07		
DEAE	3.9	3.8	4.5	2.9	2.8	2.6
DEHA						
DMAE	1.9			3.4		
DMAEP						
DMIPA	3.5			3.3		
MEA				0.29		
MOPA	1.9			2.5		
Morph	1.31	1.26	1.24	1.2	1.2	1.2

NOTE: The above data represent results from test work. Some small variation in results is to be expected. Comprehensive data are only available for the most commonly used amines.

As an example, it can be seen that at 0 psig, morpholine *DR* = 0.4. This means that, in effect 28.6% of the total morpholine remains as free amine and volatilizes into the steam, while 71.4% is present in ionic form in the condensate (i.e., 28.6/71.6 = 0.4).

Carbon dioxide has a very high *DR* at all pressures; consequently, it is present in all regions of the condensate system, but especially at the furthest points where condensing temperatures are lower.

NOTE: As an example of the high DR of carbon dioxide, 400 psig steam, carrying 5 ppm CO_2, and passing through a heat exchanger, produces condensate that can be led to a flash tank. Perhaps only 15% will flash as 100 psig steam, but it will carry 90% of the CO_2 loading, giving rise to 30 ppm in the steam. The flash process produces an 85% balance of low pressure condensate, but this only carries 10% of the CO_2 loading, giving rise to a concentration of only 3 ppm in the condensate.

Consequently, it is important to devise an amine blend that will be present in the condensate, wherever in the system it forms. Thus, it is common practice to blend two, three, or even four amines to achieve a balance of *DR* values and to improve corrosion protection throughout the steam-condensate system. For most general types of commercial or industrial application, a minimum blend of two amines is necessary, while three may be particularly beneficial.

Some technical papers question the prudence of blending more than two amines together, essentially on the grounds of cost. In fact, the blending process adds little to the overall cost of manufacture, and selling prices for blends generally have little to do with manufacturing costs, as by far the biggest component of the total price is the technical support and service element.

It is also true that the use of multiblend formulations helps to raise operator confidence levels, and, provided the technical support function justifies this confidence by a proactive and responsive approach, there is further "added value" in the blend.

Examples of neutralizing amine formulations reflecting the use of blends with different DR values are shown in the following formulatons.

Standard Twin-Neutralizing Amine Blend

Materials	
Cyclohexylamine (CHA) 99%	15.0%
Morpholine 99%	17.0%
Water	68.0%
	100.0%

This type of formulation is extremely common and various product strengths exist.

Typical Triple-Neutralizing Amine Blend Materials	
Cyclohexylamine (CHA) 99%	13.0%
Diethylethanolamine (DEAE) 99%	16.0%
Morpholine 99%	11.0%
Water	60.0%
	100.0%

A derivative of the triple-blend formulation to include DEHA for control of O_2 (resulting from air in-leakage to the condensate line) is shown next. The concentration of DEHA must not be too high, and the blending process requires careful control because of the limited solubility of hydroquinone.

Blending four amines together may be "overkill," but even this can be justified where one of these amines is DEHA and is added for the express purpose of controlling problems of air in-leakage.

Four Neutralizing Amine Blend for CO_2 and O_2 Control Materials	
Cyclohexylamine (CHA) 99%	10.0%
Diethylethanolamine (DEAE) 99%	13.0%
Morpholine 99%	8.0%
Diethylhydroxylamine (DEHA) 25%	8.0%
Hydroquinone	0.4%
Water	60.6%
	100.0%

11.3.5 Thermal Stability of Amines

All amines, except for ammonia, decompose under high temperature and pressure boiler conditions. Where hydrazine feed continues to be well in excess of scavenging needs or at pressures exceeding 800 to 850 psig (520–525 °F/271–274 °C), it begins to break down and liberate ammonia. All other functioning vapor-phase amines rapidly decompose at temperatures above 550 °F/288 °C (approximately 1,000 psig).

Apart from ammonia, other breakdown products include *primary amines* and *hydroxylamines,* which may be corrosive to cuprous metals, and various *organic acids* that may be corrosive to ferrous metals and turbine blades. These organic acids also neutralize any remaining

amine, leading to a reduction in condensate pH. This pH level reduction has a follow-on effect where **coodinated** or **congruent phosphate programs** are employed.

Thermal stability tables are available for the various amines, but they are of little practical value because decomposition products vary, depending on specific operating conditions. Morpholine is an exception, as the breakdown products are first DEA and then MEA, which is a particularly effective amine in some nuclear power plant facilities (PWRs). Thermal stability and the types of decomposition by-products only become important in boiler plants with superheaters operating in excess of 1,000 °F.

In practice, DEHA, morpholine, and DEHA/morpholine/CHA blends are commonly used at pressures ranging from 50 to 2,400 psig. CHA is sometimes used as a stand-alone product at temperatures of up to 1,200 °F/650 °C.

11.3.6 Health, Safety, Storage, and Handling of Amines

In most countries specific rules govern the handling and application of amines and other BW additives (see Note in section 11.1.1).

11.3.6.1 Amines in Steam Contacting Food

In the United States, those amines covered under 21CFR §173.310 may be used safely in the preparation of steam that contacts food, provided that the amount of additive required is not in excess of functional needs and the steam usage is not more than required to achieve the intended effect. Control limits for amines are:

- **CHA:** 10 ppm maximum in steam, and excluding the use of such steam in milk and milk products
- **DEAE:** 15 ppm maximum in steam, and excluding the use of such steam in milk and milk products
- **Hydrazine:** Not permitted in steam
- **Morpholine:** 10 ppm maximum in steam, and excluding the use of such steam in milk and milk products
- **Octadecylamine:** (filming amine) 3 ppm maximum in steam, and excluding the use of such steam in milk and milk products.

NOTE: The USDA does make an exception on the use of ammonium hydroxide for this purpose, based on its GRAS listing (21CFR §184.1139).

11.3.6.2 Amines in Steam Humidifiers

The use of direct steam injection into air is a common method of increasing humidity levels for both commercial and industrial applications. The process kills most types of bacteria and similar organisms that may contribute to fouling, health, or other **indoor air quality (IAQ) problems**. Where amines are present in the steam, however, even small concentrations can be detected by their odor and may be objectionable, even though they may be well under guidelines for concentrations in air.

Considerable work has been carried out on this subject and some findings are:

- Depending on the specific operation conditions, tests for amines in condensed steam typically identify levels between 2 and 6 ppm.
- Depending on the desired level of humidification and the type of amine used, amine concentrations in air subjected to steam humidification averaged between 0.6 and 8 ppb.
- The allowable concentration of amines in air, based on an 8-hour day, **permissible exposure limits** (PELs) are:
  - Morpholine: 20 ppm
  - CHA: 10 ppm
  - DEAE: 10 ppm
- The threshold odor concentration of amines in air is typically 10 to 40 ppb. These levels are considerable less than any regulatory limit but offer potential for triggering complaints in laundries, kitchens, and sterilizing equipment rooms.

Despite the fact that certain amines are permitted in steam used for food preparation, and that amine concentrations in humidified air are never likely to exceed PELs, there remains some general concern over the use of amines in such situations. Filming amines generally are employed at significantly lower feed rates than neutralizers and therefore probably are more suitable in practice. However, this is a classic case where perception is reality and consequently, where there is concern, it probably is a better strategy to employ alternative technologies than to fight the issue. Several options exist, including:

- The use of pretreatment equipment such as **dealkalization** or **demineralization** to remove *bicarbonates* and *carbonates* in the MU.

- The use of **degassers** and **FW deaerators** to remove *carbon dioxide gas* at source.
- The use of **filming amines**, which have very low *DRs* that limit their spread through all regions of the steam lines.
- Maintaining condensate temperatures at or near saturation points to minimize carbonic acid formation. This includes heating intermediate condensate receivers to maximum practical temperatures.
- The use of more corrosion-resistant materials, such as certain stainless steels, and an increased pitch in condensate lines to minimize temperature drop and limit the pickup of both carbon dioxide and oxygen.
- The use of **electric powered steam generators, steam-to-steam heat exchangers,** or **reboilers** to provide steam to steamtables, humidifiers, autoclaves, and for direct injection into the process. Where this type of approach is employed, it generally is necessary to provide a high quality water source to avoid rapid internal deposition of crystalline scales and foulants.

11.3.6.3 Storage and Handling

Vapor pressure, which is the tendency of a liquid to release vapors to the surrounding area, goes down as MW increases but goes up as temperatures rise. By definition, the more volatile a liquid, the higher its vapor pressure and the lower its boiling point. Examples are:

- **Water:** 17.0 mm Hg at 20 °C/68 °F, (MW = 18)
- **Hydrazine:** 10.0 mm Hg at 20 °C/68 °F, (MW = 32)
- **Morpholine:** 7.0 mm Hg at 20 °C/68 °F, (MW = 87)
- **CHA:** 6.3 mm Hg at 20 °C/68 °F, (MW = 99)
- **DEAE:** 1.4 mm Hg at 20 °C/68 °F, (MW = 117)

It can be seen that water has the highest vapor pressure; therefore, provided these amines are stored in cool places with adequate ventilation, there is little risk of dangerous inhalation. Drums should not be stored in confined spaces.

However, most common amines tend to have a **flash point** below 200 °F/93 °C and are therefore classified as either *combustible* or *flammable.* CHA and morpholine have particularly low flash points (88 °F closed cup/90 °F open cup and 95 °F closed cup/99 °F open cup, respectively). Fire points are higher and the risk of a flash is therefore

limited; nevertheless, products should be stored in cool areas with good ventilation.

Problems of flash and fire hazards may be minimized by diluting amines with water. No amine should ever be delivered to a boiler house at more than 70% strength. A good working limit is 40% strength.

All common amines present at least a moderate degree of skin and eye irritation. Most are corrosive. Also, CHA is toxic and is described as an *extremely hazardous substance.*

Concentrated amines are handled in steel drums. Copper alloy, zinc, or aluminum equipment cannot be used because of the strongly alkaline nature of the amines.

11.3.6.4 Amine Feeding and Sampling

Neutralizing amines are generally fed to the FW line but may be fed directly to the boiler or to the steam header. Day tanks may be polyethylene or carbon steel.

Steam condensate samples should be cooled in a stainless steel sample cooler. Samples should be run for 5 to 10 minutes before being collected in a 100-ml amber glass jar with a **Teflon®** lid. The jar should be filled completely with no air space, but without over flowing. The cap should be tight, taped if necessary, and the sample kept cool prior to laboratory analysis.

11.3.7 Neutralizing Amine Summary Notes

- The primary reason for employing *vapor-phase* or *neutralizing amines* in steam-condensate systems is to reduce the level of corrosion of both ferrous and nonferrous metals. A further beneficial consequence of this function is the reduction of metal transported back to the FW system.

  Where corrosion problems exist, rates may vary considerably throughout the system, but total metal loss may typically exceed 0.25 ppm M (where M = Fe/Cu/Ni) in the condensate without the use of amine. This compares badly to recommended maximum limits of 0.05 ppm M for up to 580 psig/40 bar boilers, 0.03 ppm M for up to 870 psig/60 bar, and 0.02 ppm M beyond that.

  It is clearly easier to achieve low corrosion rates in newer boiler systems, but, where badly corroded systems are provided with an appropriate amine blend, it is still possible to bring corrosion rates down to acceptable levels over a period of time.

- Under particularly difficult conditions, neutralizing amines are expensive and not always totally successful. The use of *satellite dosing points* and programs that combine **neutralizers** with **filmers** (either fed separately or as a combination product) may produce the desired result. Proof of effectiveness requires pH and Fe/Cu/Ni *mass balance profile* trials to be undertaken.
- Demand for amine **(neutralization capacity)** is determined by CO_2 loading and amine equivalent weight. *Polyfunctional amines* appear to have a large equivalent weight advantage, but in practice they often have very low volatility and poor thermal stability.
- The final pH, after neutralization, is determined by the remaining amine hydrolysis **(basicity constant).**
- Morpholine or AMP, having low *DRs,* tend to protect the front end of steam-condensate systems, while CHA (with a high *DR*) protects the furthest regions. DEHA or DMIPA protect the middle regions.
- Rather than calculating CO_2 loading from first principles, a simple measure is to assume a total breakdown evolution of 0.79 ppm CO_2 from every 1 ppm bicarbonate alkalinity in the FW, or only 0.35 ppm/1 ppm, if the starting point is carbonate, at 150 psig; for other boiler pressures, see Table 11.3.
- Again, at its simplest, allow 5 to 7 ppm of 40% strength amine (any single amine or blended material) for every 1 ppm of CO_2 loading. For most applications, theory seldom matches practice, and the first feed rate calculation should be considered as simply a reference point to establish a base condensate pH level.
- Despite a perceived loss of amine due to carbonic acid neutralization, in practice much of the amine added is recycled and returned to the FW system. Morpholine tends to suffer a greater recycling loss following passage through the deaerator than either CHA or DEHA. For all amines, loss increases with increase in deaerator operating pressure (from approximately 5% loss of recycled capacity at 5 psig, to nearly 50% at 30 psig). Where amine is applied to FW, the losses are higher than in those facilities where amine is applied overhead (due to BD losses). As operating pressure drops and BD increases, the trend is for amine losses to be higher.
- When calculating amine consumption rates in industrial and process boilers, estimate the maximum recycling level to be perhaps 75 to 80% of the condensate percentage. Thus, with 80% CR, the amine recycle level may be perhaps 60 to 65% of the initial feed. This does not hold

true for facilities where steam is lost in humidification or in process plants and very large, complex, multipressure steam-generating units.

- Against the amine feed "gain" due to recycling, it is necessary to offset amine losses of 5% or more from BD, 5% from a deaerator, 5 to 10% where steam system leaks in older systems may occur, and 5 to 10% loss in large, complex, multipressure systems.
- In large boiler plants employing ion-exchange condensate polishers, a side effect of amine use is the additional load they impose on the cation polisher, leading to early breakthrough and slightly higher sodium leakage rates. Where resins are employed using ammonia as a regenerant, this is not a problem, although sodium leakage will still be higher because of the greater selectivity of ammonia. A typical practical response to this problem is to ensure a higher **cation to anion resin ratio** (which may be as much as 2:1).
- In large and extensive industrial process plants, it is not unusual to find **unvented condensate receivers** or **reboilers** at the end of a long steam-condensate line. These vessels tend to act as collection and storage points for carbon dioxide, which may redissolve in condensate. These satellite stations should be vented and receive an amine booster feed.

11.3.8 Filming Amines

Filming amines (**filmers**) provide an alternative technology to that of neutralizing amines for the prevention of corrosion in steam and condensate systems. Filmers are *long-chain cationic surfactants* and function by providing a uniform, waterproof protective coating over all metal surfaces that acts as a physical barrier against the corrosive gases dissolved in condensate.

Additionally, the surfactant properties of filmers reduce the potential for stagnant, heat-transfer-resisting films, which typically develop in a **filmwise condensation process,** by promoting the formation of condensate drops (**dropwise condensation process**) that reach critical mass and fall away to leave a bare metal surface (see Figure 11.2). This function, together with the well-known scouring effect on unwanted deposits keeps internal surfaces clean and thus improves heat-transfer efficiencies (often by 5–10%).

Some commonly used filming amines are better at promoting *dropwise condensation,* whereas others, notably **octadecylamine (stearylamine),** are better at reducing friction and improving the *drop runoff rate.*

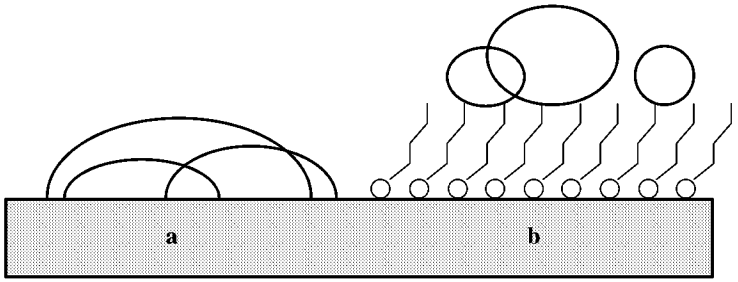


Figure 11.2 Surface activity on the waterside of a condensate line, showing filmwise condensation of water on an unprotected area (a) and dropwise condensation on an area protected by a closely packed arrangement of filming amine molecules (b).

In recent years there has been a resurgence of interest in the use of filming amines because the feed and control arrangements and general technology are relatively simple and, for any specific water quality, operating costs tend to be lower than for neutralizing amines. There also has been special interest in **soya-based filmers,** on the grounds of their good environmental acceptability and "natural" characteristics. But the fact is that all the commonly used filming amines, including those based on *soya* [e.g., **ethoxylated soya amine** (ESA)], *tallow,* and similar plant and animal extracts have been available for perhaps 40 to 50 years, with minimal technology changes made during this period. The soya- and tallow-based filmers also tend to be more soluble than the primary amines such as ODA, and this significantly reduces the risk of the amine sloughing off and causing **gunk balls** *(goof balls).* It also tends to reduce their film forming properties, however, and hence their corrosion protection potential.

Filming amines may be fed direct to the main steam header (where they generally provide the lowest cost solution to condensate corrosion problems) or to isolated satellite systems as a support to neutralizing amine-based programs. They also can be blended with neutralizing amines to provide a single product, **dual-amine technology program** and fed to the feedwater line or the steam header.

11.3.8.1 Functional Properties and Mode of Action of Filming Amines

Filmers are based on *primary, secondary,* or *tertiary* **monoamines** or **diamines** and contain alkyl chains with from 8 to 22 carbons. The most prominent material is the 18-carbon-chain *aliphatic monoalkylamine,* **octadecylamine** (ODA).

The long chain length renders the alkyl group strongly **hydrophobic** (water-repelling) while the nitrogen atom contained in the amine group is **hydrophilic** (water-loving). The hydrophilic properties are enhanced by *protonation* or *ethoxylation.*

Alkyl- and fatty acid–derived filming amines are examples of **amphiphilic compounds** (molecules containing groups with opposite functions), and their amphiphilic molecular structure gives rise to various *surface active properties.* These include **substantivity** (surface adsorption resulting from the attraction of the cationic nitrogen group to the anionic metal surface), **molecular orientation** at the metal-water interface, and a **dewetting functionality** resulting from interfacial tension.

NOTE: The orientation of surfactant molecules at an interface (water-solvent, water-gas, water-metal) confers performance characteristics on the molecule that permit it to be employed as an emulsifier, demulsifer, wetting agent, antifoam, lubricant, or other agent.

These characteristics are typically classified as a ***hydrophile-lipophile balance (HLB value).*** *For example,* ***hydrophilicity*** *may be denoted within a range of 2 to 20, with true solutions being obtained at HLB values >14 and poor dispersibility occurring at HLB values <6. Oil-in-water emulsification requires a high HLB value surfactant, while water-in-oil emulsification needs a low HLB value surfactant.*

Filming amines are steam-volatile and in the steam-condensate system will condense and migrate to the metal-water interface to form a nonwettable film with polar groups adsorbed to the metal surface.

Protection is provided generally within the pH range of 4 to 8.5 or 9.0, although condensate more usually ranges from a low of pH 5.5 (untreated) to a high of 8.5 (when treated by neutralizing amines). Filmers are stable to 1,200 psig (538 °C).

For the most part, the corrosion protection potential of filmers improves with increased packing of amines onto the metal surface, so **straight-chain-only amines** are preferred (no side chains or branched-chain amines) for formulation purposes.

Also, in general, amines of longer chain length are *less* water soluble and offer *more* protection as film-forming corrosion inhibitors because they are not so susceptible to being gradually washed away by hot condensate. Furthermore, as there is no practical difference in the metal-wall adhesion abilities of either short- or long-chain molecules, formulators tend to use the longer chain length filmers.

Filming amine programs are often selected because the feed rate of "actives" generally is significantly lower than that required for neu-

tralizers, but where rates are too low, the level of protection is seriously impaired because of inadequate coverage of the total metal surface. Enough filmer product must be fed to the steam to enable the amine molecules to condense at the metal-water interface and orient into a parallel, closely packed formation. It is well to remember that from the onset of feeding amine to a system, it may take up to six months for complete internal coverage to be provided. During this time it is normally possible to demonstrate a gradual but continuously reducing rate of corrosion (through the use of corrosion coupons, iron transport studies, and lower maintenance and repair costs), but it is only when the film becomes continuous that minimum corrosion rates can be expected.

When the filming amine condenses, the hydrophilic polar radical of the molecule *(the head)* adsorbs onto the metal surface and the hydrophobic, long chain *(the tail)* is directed at a 90° angle of inclination away from the metal surface. Provided the feed rate is adequate, the critical concentration is eventually reached and a continuous monomolecular surface film is formed. At this stage, the physical size of the interstices between the polar groups is smaller than the molecules of water, carbon dioxide, or oxygen, and these molecules are thus physically prevented from reaching the metal surface.

11.3.8.2 Types of Filming Amines

A number of filming amines are available for boiler water treatment. These include:

- **Primary (monoalkyl) aliphatic amines:** [R–NH_2], containing long-chain alkyl groups having from 8 or 10 to perhaps 20 or 22 carbons in the chain. Examples include ***dodecylamine*** (DDA), where carbon chain = 12, equivalent weight = 186, melting point = 24 °C; ***hexadecylamine*** (HDA), where carbon chain = 16, equiv. wt. = 243, m.p. = 48 °C; and ***octadecylamine*** (ODA), a waxy solid, where carbon chain = 18, equiv. wt. = 270, formula = $C_{18}H_{37}NH_2$, m.p. = 55 °C.

  NOTE: In simple filming amine formulations ODA is the most widely employed ingredient. Formulations are typically available as 100% concentrated flakes, 2 to 5% strength aqueous solutions, or 5 to 10% strength emulsions. Solid ODA should be stored without exposure to air because it gradually reacts with carbon dioxide to form ***ODA carbonate****, which is white and crumbly in composition.*

- **Monoalkyl tertiary amines:** [R–N$(CH_3)_2$]. Examples include ***soyaalkyl-dimethylamine,*** where equiv. wt. = 297, m.p. = −10 °C; and tallowalkyl-dimethylamine, where equiv. wt. = 291, m.p. = 5 °C.
- **Diamines:** [R–NH$(C_3H_6)NH_2$]. An example is **N-tallow-1,3-diaminepropane,** where equiv. wt. = 161 and the material has a consistency of a paste at 25 °C.
- **Ethoxylated diamines:** [R–N(–C_2H_4OH)(C_3H_6)N(–$C_2H_4OH)_2$. An example is ***ethyoxylated (3) N-tallow-1,3-diaminepropane,*** where equiv. wt. = 239 and the material has a liquid consistency at 25 °C.
- **Amine acetates:** [R-NH_2-CH_3COOH]. Examples include ***hydrogenated tallowalkylamine acetate*** and ***octadecylamine actetate.*** Both materials are in the form of soap-like flakes at 25 °C and may be supplied in 10 to 20% concentration emulsions.

*NOTE: A wide variety of **fatty amines** are available from global corporations such as **Akzo** and **Lonza S.A.***

*Because of their surfactant and filming properties fatty amines such as **coco-alkylamine acetate** (and more especially **diamines**, such as **tallow propylenediamine**) are also occasionally employed in other types of water treatment programs. For example, they may be used as corrosion inhibitors for steel cooling systems, especially those smaller units where minimal operational control is provided. The amines must be continuously dosed to ensure good film formation (and thus corrosion protection), typically at 5 to 10 ppm "active" amine. They also tend to have good biostatic control properties, which provide a benefit of algal and bacterial control at no extra cost.*

The smallest cooling systems may simply be treated with filming amines in the form of slowly dissolving waxy blocks that are suspended in baskets, whereas larger or more difficult systems employ feed and control systems to dispense liquid products containing diamine acetates in an alcohol-water solvent system.

These same diamine materials find further application in, for example, formulations for mussel and barnacle control in large once-through, condenser cooling systems, as corrosion inhibitors and biostats for hydrostatic testing of oil and gas pipelines, and as corrosion inhibitors in food industry retort cookers.

11.3.8.3 Application of Filmers

- Most commonly, filming amines are aspirated into the steam line from a steel dilution tank to increase the potential for complete coverage of the post-boiler section, although steam distillation with

neutralizing amines is also widely employed. For steam header injection, an injection quill should be used to ensure proper dispersion of the amine into the steam flow. The quill should be of stainless steel to prevent localized corrosion and should be designed to prevent steam collapse, which may lead to incomplete film formation and film disruption, similar to a **cavitation effect**.

- A typical feed rate is 1 to 3 ppm of "active" amine. Most filmer products contain between 3 and 10% amine (3–5% being the norm), so that product feed rates are around 10 to 30 ppm, dosed continuously to achieve 0.1 to 0.5 ppm amine (as ODA) in the returned condensate. However, products generally are diluted to 2 to 20% strength before application. Solutions are best prepared by using warm to hot condensate (150–160 °F/66–71 °C maximum) and agitated with a mechanical mixer until a uniform solution is reached. The solution should always be kept over 60 °F/16 °C.
- Amines can be blended into multifunctional product formulations containing *alkali, polymer,* and *phosphate;* and where *sulfite-* or *hydrazine-based* oxygen scavengers are part of the formula, but not where tannins are employed. Amines must be fed separately from tannins.
- Condensate is best treated with filming amines within the pH range of 6.5 to 8; outside this range the film will not form properly. This may result in **gunk balls** *(goof balls)* in the boiler or plugged pumps and valves. Where carryover of BW into the steam occurs, the condensate may develop a high pH, which encourages gunk balls, or may have a high TDS, which encourages the monomolecular amine film to strip away from the metal surface.
- Where a solid or paste ODA product is used, it should be diluted to 1% strength with hot condensate (160–180 °F/71–82 °C) and maintained at a sufficiently high temperature in the dilution tank to prevent the formation of ODA wax in the injection quill, pump, or feedline.
- Diluted ODA may be fed directly to saturated and superheated steam without adverse effects; however, ODA acetate solution should not be fed directly to superheated steam because dehydration of the salt occurs, resulting in the production of various **amine acetamides**. These are not corrosion inhibitors and may cause gunking and deposits to occur. Similarly, ODA acetate should not be fed directly to saturated steam ahead of pressure reducing (PR) valves or other types of appurtenances that may cause localized superheat conditions.

- With regard to the nature of the metal-wall surface requiring protection, the physical size of any surface imperfection is relatively large compared to the size of the filmer molecule, and the **close-packing arrangement** simply rides over the imperfections with no discernible change in filmer straight-chain alignment or loss in film continuity. Therefore, there is no tangible reduction in protection despite the character of the surface imperfection.
- **Mono-** and **diamines** have good *surfactant* properties and are therefore particularly useful for continuous online cleaning of condensate systems that are subject to fouling and for the deliberate stripping of old corrosion films. Care is needed, however, when treating older, corroded condensate systems because the tendency to strip *iron oxide* deposits, then transport and redeposit them elsewhere in the system, may cause line blockages, plugging problems (resulting in reductions in flow rate), and inoperative steam traps. As a consequence, it is common to feed filmers at a very low dose rate and gradually increase it over time to the normal level. Alternatively, a blend of neutralizer and filmer may be used and the ratio changed over time from a *high neutralizer-low filmer mix to a low neutralizer-high filmer mix.* Other filming-amine application notes include:
  - Once a filmer program starts, feeding of amine must be continuous because with the gradual removal of old iron oxide debris, the clean metal surface is subject to rapid corrosion should the continuous film cease to be maintained.
  - Where the rapid removal of corrosion debris occurs or where amine feed rates are initially kept low and the condensate still contains iron oxide, the dirty condensate should be polished or simply dumped until the condition improves.
  - Where ODA is employed in steam that may come into contact with food products, it is limited to 3 ppm maximum in the steam, and its use is prohibited in milk and milk products (see section 11.3.6.1).
  - It is unlikely that ODA concentration in steam-humidified air can ever rise to hazardous levels, but amines are detectable by smell at very low levels and their presence may be found objectionable. It is therefore prudent to minimize all possible exposures, even to the extent of modifying system engineering so that amines are not required (see section 11.3.6.2).
  - Sampling for the presence of amines in condensate should be taken by drawing the condensate into silicone-coated test tubes.

Testing is undertaken by several methods, including *chloroform extraction* and use of a *sulfonphthalein dye* (absorbance of yellow-colored complex using *bromophenol blue* and *bromocresol green*); or the use of **eosin** *(sodium tetrabromofluorescein)* solution in *acetone* and *tetrachloroethane* solvent. After shaking with a *citric acid buffer* and eosin addition, upon standing the lower layer turns pink if filmer is present. Subsequent titration with **Manoxol OT** *(sodium dioctyl sulfosuccinate)* quantifies the filmer, with loss of the pink color indicating the end point.

- Where manufacturing process operations operate cyclically, control of iron and copper corrosion in the post-boiler section may be extremely difficult because of atmospheric oxygen being pulled into the system during off periods and compounding the traditional problem of carbon dioxide corrosion. Problems are exacerbated if steam traps are waterlogged, BW carryover occurs, or if equipment such as steam driers are fouled by metal oxide transport. Under these circumstances, formulations containing a volatile oxygen scavenger together with a blend of neutralizing amine and a filmer can provide excellent results (see the next section). Amine formulation practices vary around the world; in India, for example, the use of *combination neutralizer-filmer* products for general application is very common. These materials are generally added to the FW system rather than the steam header.

11.3.8.4 Filming Amine and Filming-Neutralizing Amine Blend Formulations

As with neutralizing amine formulations, there is a wide range of filmer raw materials employed. These are available in a myriad of straight filmer or filmer-neutralizer blends, of varying active strengths. A few examples are shown here:

Simple Filmer Formulation (a)	
Materials	
Octadecylamine 10% emulsion	100.0%
Simple Filmer Formulation (b)	
Materials	
Hydrogenated tallow-alkylamine acetate (flake)	5.0%
Water	95.0%
	100.0%

Basic Filmer-Neutralizer formulation

Materials

Hydrogenated tallow-alkylamine acetate (flake)	3.0%
Morpholine	6.0%
Polyoxyethylene (POE) lauryl sulfate	1.0%
Water	90.0%
	100.0%

Complex Filmer-Neutralizer-Volatile Scavenger Formulation

Materials

Ethoxylated (3) N-tallow-1,3-diaminepropane	5.0%
Morpholine (99%)	5.0%
DEAE (99%)	5.0%
CHA (99%)	5.0%
DEHA (25%)	2.5%
POE-20 Sorbitan monostearate	0.5%
Water	77.0%
	100.0%

11.3.9 Non-Amine-Based Condensate Treatments

In certain direct steam-contact process applications (such as in food and beverage processing or pharmaceutical preparations) the use of amine-based products in steam and condensate systems is subject to legal restrictions. Also, the use of ammonia or amines may be dependent on the materials of construction employed or technical limitations (such as the risk of **copper alloy corrosion**).

As a result, various non-amine-based products have been introduced to the market that continue to provide appropriate levels of corrosion protection, yet do not exhibit the limitations normally associated with amines. The most promising of these are the **sorbitan-based, nonionic surfactant treatments,** such as those marketed by **ONDEO Nalco** under the **Tri-Act®** brand (U.S. patent 5,849,220, December 1998).

Sorbitan [$C_6H_8O(OH)_4$] products have a particularly low toxicity level, being derived from the *hexahydric alcohol* **sorbitol** [$CH_2OH{\cdot}(CHOH)_4{\cdot}CH_2OH$], which is, in turn, produced by the reduction of glucose sugar.

Essentially, Tri-Act corrosion inhibitors are based on various combinations and ratios of different *sorbitan fatty acid esters* (e.g., **sorbitan tristearate**) and *polyoxyethylene sorbitan fatty acid esters* (e.g., **POE**

4 sorbitan monolaurate). Some products include an additional but different *POE sorbitan fatty acid ester* as an emulsifying agent. An ideal ratio for a *triple-active* product is 1:1:0.3. The formulations are injected into water or vapor phases (or nonaqueous phases) at feed rates of (preferably) up to 100 ppm of total surfactant and are suitable for temperatures of up to 550°F and pH ranges of 4 to 9. They function as *film-forming emulsifiers* and are adsorbed on the metal surface.

The ingredients are *nonionic surfactants.* It is their application as amine replacements in steam-condensate systems that is novel, not the raw materials. These products are commonly found in skin and hair products and in cosmetics because of their mildness and their excellence as *water-in-oil emulsifiers* and *co-emulsifiers in oil-in-water emulsions.* Raw material brands include **Tween™ (ICI, PLC)**, **Crill™**, and **Crillet™ (Croda PLC)**.

11.4 ALKALINITY BOOST CHEMISTRIES

When using standard water treatment regimens (such as **precipitating phosphate programs, all-polymer programs**) in FT boilers, it is necessary to ensure adequate (but controlled) free alkalinity, in both the FW system and the BW, to minimize corrosion and support the primary program chemistry. In addition to FT boilers, treatment programs for lower heat-flux WT boilers, coil boilers, electrode boilers, and the like generally also require the provision of an adequate free alkalinity reserve.

Control over alkalinity is important for several reasons, including ensuring the proper formation and maintenance of a magnetite film on all boiler surfaces, managing calcium phosphate sludge in precipitating programs, and in forming magnesium hydroxide in the bulk BW.

Where the alkaline constituents of the FW are low, or where simply raising BW cycles of concentration fails to provide adequate BW alkalinity without incurring risks of foaming, carryover, or similar problems, the use of an **alkalinity booster (alkalinity builder)** is recommended.

Alkalinity boost chemistries typically are based on adjunct products containing primarily **potassium hydroxide** (for maximum solubility) or **sodium hydroxide** (for lowest cost), although **sodium carbonate** is still used in certain limited applications. These adjuncts may also contain (in almost any combination) smaller percentages of *tannins, sodium ligonsulfonate, phosphate* or *polymers.*

11.4.1 Notes on Boiler Water Alkalinity

Alkalinity content may be tested and reported in various ways, but for BW, the most important tests are **methyl orange/total alkalinity** (reported as M or T alkalinity, expressed as mg/l, mg/kg, or ppm $CaCO_3$), and **caustic /hydroxide alkalinity** (reported as OH alkalinity, expressed as mg/l, mg/kg, or ppm $CaCO_3$).

- Total alkalinity is generally the most relevant alkalinity test, especially in FT boilers where the FW has a low silica content. Testing for T alkalinity provides the best correlation with pH, corrosion inhibition, and tendencies for carryover.
- When silica levels increase, *hydroxide alkalinity* measurements become increasingly important to ensure maximum **silica solubilization** and the reduction of risk of silica deposition. This is especially so for **coil boilers** because, more than any other boiler type, the use of hydroxide is critical in keeping the waterside surface of the coiled tube clean and deposit free.
- In higher pressure WT boilers, where **AVT programs (zero solids programs)** or **coordinated** or **congruent phosphate** (and similar) **programs** are employed, high quality FW is demanded and free hydroxide (caustic) alkalinity in the BW is not permitted.

NOTE: With these types of programs, free sodium hydroxide is not formed, even in the event of complete evaporation; thus the damage caused by localized concentration effects (dissolution of iron forming the soluble, nonprotective, sodium ferroate [sodium hypoferrite] salt, together with hydrogen liberation, tube wastage, and ultimate failure) does not occur.

Free caustic alkalinity usually is not recommended for **jet-type electrode**, as foaming conditions may develop rapidly because of the high recirculation rate. Where high alkalinity is present and FW contamination from colloidal or organic matter takes place, the foaming that develops quickly causes the boiler to be shut down.

In the boiler, the BW phenolphthalein alkalinity (P alkalinity) usually is more than half of the total or methyl orange alkalinity (T or M alkalinity):

- P alkalinity $>$ M alkalinity/2, and consequently:
- BW caustic alkalinity (OH alkalinity) $= 2P - M$
- BW carbonate alkalinity (CO_3^{2-} alkalinity) $= 2(M - P)$

Typically, for FT boilers operating at below 435 psig (30 bar):

- Maintain BW M alkalinity at 350 to 700 ppm $CaCO_3$
- M alkalinity generally should not exceed 20% of the TDS.

NOTE: Although some standards recommend a 1,000 ppm ceiling for M alkalinity, there are many boiler plants operating at over 1,200 to 1,300 ppm because the MU water naturally contains a high alkalinity. In all cases, specific BW alkalinity control ranges should be set by appropriately qualified chemists or water treatment engineers.

Maximum M alkalinity and conductivity or TDS limits must be consistent with acceptable steam purity, as determined by steam purity tests. In many cases, alkalinity limitations, rather than conductivity, determine BD requirements.

- Maintain OH alkalinity at a minimum reserve level of 350 ppm $CaCO_3$
- Maintain BW silica (SiO_2) in boiler at less than 0.4 of OH alkalinity

NOTE: All these recommended limits relate to moderately rated FT boilers. Where highly rated FT boilers are concerned, limits should be set significantly lower. Where a higher quality FW is employed, limits may be only perhaps 10% of the above.

11.4.2 Calculating Alkalinity Feed-Rate Requirements

The alkalinity feed-rate requirement is based on FW consumption and calculated as follows:

$$[0.67 \times FWCaH + (FWMgH - FWMA + \underline{RBWPA})] \times \frac{100}{\%\ \text{NaOH in product}}$$

$$\text{COC}$$

$$= \text{lb of product required, per } 1 \times 10^6 \text{ lb of boiler FW}$$

Where:
FWCaH = FW calcium hardness, as mg/l (ppm) $CaCO_3$
FWMgH = FW magnesium hardness, as mg/l $CaCO_3$
FWMA = FW methyl orange/total alkalinity, as mg/l $CaCO_3$
RBWPA = Required BW phenolphthalein alkalinity, mg/l $CaCO_3$
COC = Cycles of FW concentration present/desired in the BW

NOTE: If the value within brackets is negative, adequate free alkalinity exists in the FW and the addition of supplementary alkalinity is not required.

11.4.3 Products for Boosting Alkalinity

Products used for boosting or building alkalinity in BW generally are relatively simple formulations and may or may not contain tannins, antifoamers, phosphates, polymers, and the like. Where these adjuncts are included, the selection of raw materials generally is made on the basis of ensuring compliance with G6 USDA approval, for application in USDA-inspected plants.

Simple, Alkalinity Boost Conjunctional Formulation	
Materials	
Potassium hydroxide, commercial solution	50.0%
Water	50.0%
	100.0%

Alkalinity Boost and Adjunct Formulation	
Materials	
Sodium hydroxide, commercial solution	40.0%
Sodium polyacrylate (45%)	4.0%
Tannin blend (50%)	4.0%
Polyalkylene glycol monobutylether (PAGMBE)	0.05%
Water	51.95%
	100.00%

11.5 ANTIFOAM AND DEFOAMER CHEMISTRIES

Various types of foams can develop in boilers—some are stable, some are very elastic, and some collapse and reappear continuously. Still other types of foam are temperature- or chemical-sensitive.

Boiler water foaming and *frothing* is undesirable because it contributes to overheating, carryover, and loss of operational control. As a result, antifoam and defoamer products are commonly employed in BW treatment programs. The same active ingredients are also widely used in all types of industrial processes (industrial grades), as well as in cosmetic, food, potable water, and kosher applications (all agents typically are odorless, colorless, and tasteless).

- **Antifoams** inhibit or suppress the formation of foam.
- **Defoamers (foam breakers)** destroy foams that have already occurred.

Most BW programs utilize very small amounts of these products, usually built into one or another of the formulations employed. In general, a **specialist surface acting agent (surfactant)** antifoam or defoamer chemical is selected to provide both actions. However, care is required when formulating, because under boiler conditions, some types of antifoam agent will not prevent foam from developing but will act simply as **foam stabilizers**, whereby at a certain point they will prevent the foam from establishing itself any further.

NOTE: In-use concentrations of antifoam and defoamer materials are very small, often as low as 5 to 20 ppm product, or 0.25 to 2 ppm "actives". However, the persistence of the agent will vary and if not replenished will eventually fail. When antifoam is fed periodically, it usually is dosed as a stand-alone product at a higher rate, but when fed continuously, it is present at a lower concentration and forms part of a multicomponent additive.

11.5.1 Mechanisms of Foaming and Its Control

Foam formation in a boiler is primarily a surface active phenomena, whereby a discontinuous gaseous phase of steam, carbon dioxide, and other gas bubbles is dispersed in a continuous liquid phase of BW. Because the largest component of the foam is usually gas, the bubbles generally are separated only by a thin, liquid film composed of several layers of molecules that can slide over each other to provide considerable elasticity. Foaming occurs when these bubbles arrive at a steam-water interface at a rate faster than that at which they can collapse or decay into steam vapor.

Foaming in boilers is most commonly caused by:

- High BW alkalinity (which generally also infers a high BW TDS)
- The presence of colloidal materials
- Metal oxides and silt transported back to the boiler
- Saponified oils or fats

Foaming may be caused by *organic sols* and *process chemicals* having a surface active effect, *silica micelles*, and especially **saponifiable**

oil. These same contaminants may cause additional problems of **emulsification**; consequently, antifoams and defoamers also may need to exert a **demulfsiication effect**.

In addition, even where foaming is not a specific problem in a boiler, carryover may occur, especially in lower pressure boilers with very high TDS (i.e., over 10,000 to 15,000 ppm TDS) because of the collapse of surface bubbles. This leads to BW aerosol generation and *entrainment* of the spray in steam. Under these circumstances, antifoam agents such as **polyamides** are useful in preventing these entrainment problems. Furthermore, the antifoaming action of polyamides is often enhanced by *protective colloid* materials such as **tannins**, and consequently, formulations containing polyamide emulsions in an alkaline tannin base are available.

*NOTE: Early **polyalkylene polyamide** antifoam formulations (1940s) developed by **Dearborn Chemical Company** (now **G.E. Betz**, formerly **Hercules Betz-Dearborn**) employed protective colloid technology. These products generally were in powder or briquette form.*

High-quality FWs (and most other pure liquids) do not foam or froth easily because their molecules are farther apart at the surface layer than in the bulk water. This leads to a density difference, tension at the water surface (surface tension), and failure of the thin film to sustain itself. Consequently, foaming in boilers is commonly caused by impure FW containing high concentrations of *alkali* and *salts*, or *transported iron and copper oxides, silt,* and other deposits found in "dirty" boilers. In addition, *proteinaceous material* and other **organic-solute process contaminants** having *surface-acting properties* (surfactants), arising from food and beverage, dairy, ink, pulp and paper, laundry, textiles and similar industries, cause rapid foaming. These **proteinaceous foams** are particularly long-lasting because the bubble films do not rupture easily and consequently carryover rates are enhanced.

Foam persistence increases with rise in BW TDS because the bubbles are stabilized by the combined repelling forces of electrical charges at the steam-water interface that result from the high concentration of dissolved salts. The repulsion effect of similar charges prevents *bubble thinning, bubble rupture* and *coalescence* mechanisms from taking place.

When bubbles accumulate at the steam-water interface, dissolved solids pass into the **post-boiler steam section,** and this carryover contaminates the steam and causes fouling of the system. Where the foam-

ing rate is both particularly high and stable, an apparent BW volume increase takes place. This phenomena is known as **light water**.

The general mode of action for the control of foam is to displace organic solutes or other materials that are absorbed into the bubble film at the gas-BW interface. The new film tends to lack elasticity and is therefore prone to rupturing and instability.

11.5.2 Antifoam and Defoamer Selection

When evaluating materials for BW antifoam and defoamer duty, some important considerations are:

- Products must be chemically inert with regard to the foaming solution and the other BW treatment additives.
- Products must be able to withstand elevated temperatures and pressures, and highly alkaline and strongly reducing conditions.

NOTE: In cooling water treatment, although temperatures tend to be lower, antifoams and defoamers must be able to withstand strongly oxidizing conditions.

- Products must be relatively insoluble in hot water but easily dispersible within the foam.

*NOTE: Antifoam materials such as **polyoxyalkalene glycols (PAGs)** are soluble in cold and warm water (i.e., <40 °C) but insoluble in hot water.*

- Products should possess a good surfactant action with a surface tension lower than that of the BW.

NOTE: The surface tension of water is 72 dynes/cm at 25 °C, 67.9 dynes/cm at 50 °C, and 58.9 dynes/cm at 100 °C. Typically, suitable surfactants reduce the surface tension to below 30 dynes/cm.

- Antifoams and defoamer surfactants must possess a good surface spreading action (spreading coefficient).

NOTE: S_a is the spreading coefficient in dynes/cm.

Many of the materials used for boiler water antifoams are also employed as synthetic lubricant replacements for mineral oils, brake fluids, emulsion polymerizers, emolients, solvents for inks, cleaners, and antifoams for saltwater evaporators. These materials have been

available for 40 years or more and include dozens, if not hundreds of permutations of surfactants based on:

- **Block copolymers**
- **Polyalkylene glycol (PAG) derivatives**
- **Polyamides**
- **Silicones**

11.5.2.1 Block Copolymers

Block copolymers are molecules containing long stretches of two or more monomer units linked together by chemical valences in a single chain. These are the same nonionic materials that are used as *cooling water biodispersants* (e.g., **Pluronic® L62LF,** from **BASF AG**). For the most part, they are water-soluble copolymers of various **linear polyols**, and more specifically certain **polyoxypropylene (POP)** and **polyoxyethylene (POE) condensates**. Individual grades are defined by specifying molecular weight ranges, such as L62LF (a liquid, POP/POE copolymer having low foaming characteristics). Brands such as **Pluronic L62LF** and **Synperonic® L62LF (ICI PLC)** are essentially the same materials. Antifoams include L61, L62D, L62LF and L101.

Derivatives of the *nonionic block copolymers* that are used as antifoams include chemistries containing *silicones*. These **silicone-block copolymers** are molecules that possess improved antifoam and defoamer durability and excellent stability under high alkalinity, high temperature boiler conditions.

Typically, the product contains 30 to 50% by weight of *organopolysiloxane* and 50 to 70% of polyoxyalkylene. As the silicone level increases, the durability improves and water solubility decreases and vice-versa. Antifoams using this chemistry employ 1,000 to 5,000 MW silicones and are hydrophobic.

NOTE: ***Drew Industrial Division*** *of Ashland Chemicals, Inc. patented such products for BW antifoam duty 25 years ago.*

11.5.2.2 Polyalkylene Glycol (PAG) Derivatives

The various POPs and POEs are all PAGs, and various derivatives are available. They are also called **polyoxyalkylenes polyglycols** or **polyether glycols**.

The most common BW antifoam employed today is **UCON® 50-HB-5100,** from **Union Carbide Corporation**, which is the linear *POP(33), POE(45) ether of butyl alcohol,* or **polyalkylene glycol monobutylether (PAGMBE)**.

UCON® 50-HB-5100 is approved by the FDA under 21CFR §173.310 and has the formula:

$$C_4H_9(OCH_3CHCH_2)_x(OCH_2CH_2)_yOH,$$

where avg. $x = 33$, and avg. $y = 45$

NOTE: The 50-HB designation refers to an alcohol-started polymer containing equal parts by weight of POP and POE. The 5100 designation equals the viscosity in Saybolt Universal Seconds at 38 °F (100 °F). This product is water-soluble only below 40 °C.

Other common *polyglycol-based* antifoams include certain derivatives of **polyethylene glycol (PEG)**, which are condensation polymers of ethylene glycol. An example is **polyethylene glycol-8 dioleate.** Apart from its antifoam properties, PEG-8 dioleate is also used in cooling water inhibitor formulations as a *surface cleaner,* in the formation of a corrosion-inhibiting surface film. Additionally, it is employed as an *oil-soluble emulsifier* for other defoamer chemistries.

NOTE: To further confuse matters, PEG-8 dioleate is also known as PEG 400 dioleate. Similarly, PEG-4 is also known as PEG 200, and PEG-6 is also known as PEG 300, etc. These various PEGs are available as cocoamides, dicoates, dilaurates, distearates, ditallates, and other fatty acid derivatives.

11.5.2.3 Polyamides

Polyamide antifoams generally are **alkylene polyamides** and are made by acylating a *polyamine* with a *fatty acid.* Most products are a mix of higher MW polyamides and polyamide derivatives. Polyamides have been available for over 50 years and are still employed, especially in developing nations, for lower pressure boilers with very high BW TDS. They also are used as antifoams in the pulp and paper industry. Originally, the higher melting point polyamides were used for high-pressure boilers and the lower melting point products for low pressure boilers and evaporators.

Materials employed include **distearoylethylenediamide (distearoylethylenediamine, ethylene bistearamide)**, which provide a hydrophilic and hydrophobic balance by virtue of the separation of two polar radicals. *Distearoylethylenediamide* has the formula

$$C_{17}H_{35}CONH\text{-}CH_2CH_2NHCOC_{17}H_{35}$$

Other polyamides employed include **ethylene bisricinoleamide** and **ethylenediaminetallowdiamide**. *Alkanolamides* such as **coconut monoethanolamide** also are used. Polyamides also have been used in combination with *polyglycols*, *phosphate esters*, *silicones*, and the like, together with a suitable carrier. A typical formulation is:

Antifoam Formulation

Materials	
Ethylene bistearamide	3.0%
Diethylene glycol monooleate	2.0%
Polydimethylsiloxane (50 centistokes @ 25 °C)	0.5%
Primary alcohol (mixture of C_{14}, C_{16}, C_{18})	94.5%
	100.0%

11.5.2.4 Silicones

Dispersible silicone emulsions are generally preferred for aqueous systems, whereas silicone fluids and compounds are preferred for nonaqueous systems. Silicones are widely employed in cooling water treatment programs, less so in boiler plants because of higher operating costs than available alternatives, but also because of sometimes questionable emulsion stability at higher temperatures.

Where employed for BW applications, silicone emulsion strengths, emulsion stability, spreading coefficients, and effectiveness rates may vary considerably and the preferred product should be identified by comparative evaluation.

The "standard" materials used are nonionic **dimethylpolysiloxanes**, and these are available in ranges of controlled MWs with viscosities varying from 10,000 to 50,000 centistokes (cs). These silicones follow the general formula:

$$CH_3\text{–}(SiCH_3CH3O\text{–})_nSiCH_3CH_3CH_3$$

Typical BW antifoam emulsion products include **SAG® 10** and **SAG® 30** (10 and 30% milky white emulsions, each with a viscosity of 2,000 cS at 25 °C) from **Union Carbide Corporation**. These same products also are used for food processing (under FDA 21CFR §173.340), for petroleum processing (as amine scrubbers, gas-oil separators, etc.), and as functional chemicals (antifreezes, hydraulic fluids, cutting oils, etc.).

Where required, silicones are usually added to the feedline at concentrations of 0.1 to 0.5% w/w. They are of long-lasting durability and generally applied to prevent foams developing, rather than to destabilize existing foams.

Silicone polymers such as **ethoxylated aryl/organosiloxane polymer** and **siloxane glycol/PAG copolymer** also are used occasionally.

11.6 MULTIBLEND FORMULATIONS

Many smaller vertical and horizontal fire tube boilers, as well as some coil and electrode boilers, are treated with *multiblend* or *multicomponent, one-drum products.*

One-drum product programs are typically based on **sulfite** or **tannin**, coupled with phosphate, organic dispersants, and a conjunctional alkali treatment. Antifoam and neutralizing amine ingredients also may be included. Alternative chemistries include sulfite or tannin coupled with a blend of organic polymers. **All-organic BW programs** are also widely available; these may use *tannin, DEHA* or *erythorbate* as the oxygen scavenger.

Typically, each vendor devises a program and makes available a limited range of individual products based on the chosen chemistry. The oxygen scavenger component usually is always a fixed percentage. Within this range, the **phosphate** and **caustic** components (or organic equivalents for *hardness control* and *alkalinity boost*) vary, depending on the specific FW quality (i.e., the degree of hardness, alkalinity, condensate return, etc.). These comprehensive blends are usually sold on the basis of providing:

- Simplicity of chemical feed system and chemical addition
- Minimum chemical stock holding
- Limited control testing and operator involvement

These features may indeed provide cost-effectiveness and other tangible benefits; however, unless the boiler plant operates constantly and FW quality remains consistent, these benefits are unlikely to be fully realized. Where operating conditions vary, the use of multiblend programs exposes the potential for constant readjustment, poor waterside treatment (scales, deposits, oxygen pitting, etc.), and water-level control problems.

Multiblend programs are seldom suitable under circumstances where a process boiler plant shuts down each night because this permits air ingress into vented feed tank systems and the condensate return. Without a separate oxygen scavenger boost in the evening, there is unlikely to be an adequate reserve of scavenger. Under these same conditions, where a sulfite boost product is employed, the increased contribution to BW TDS may lead to a high demand for blowdown (to avoid carryover) and a cycle of cause-and-effect operating control problems develops.

Similarly, where a facility uses both well water and city water as sources of MU, this generally produces FW with periodically widely differing contaminant concentrations. The resultant changes in demand for DCA concentration and adjustments to alkalinity also prove difficult to match when one-drum programs are used.

For the smallest low-pressure heating boilers, simple one-drum programs that are designed for greater than 99% condensate return are used. Where condensate is only 70 to 80%, boiler waterside surfaces get dirty quickly, under-deposit and oxygen pitting corrosion may develop, and tubes may fail.

Under all these scenarios, one-drum multiblend programs should not be used. However, it usually is quite possible to improve control by devising a suitable program based on a two-drum program approach, provided that a suitable feed system is available. Chemical feed pumps are best controlled by a MU water meter. Timer control or wiring through the FW pump are possible alternatives. Nevertheless, there is no doubt that one-drum programs are popular, and the following formulations are provided to illustrate the common chemistries available.

Traditional Multiblend, One-Drum Programs, Based on Sulfite

Materials	*Formulation*		
	1	2	3
Sodium hydroxide 50%	—	—	13.0%
Sodium sulfite 100%	6.0%	6.0%	6.0%
Morpholine 20%	9.0%	9.0%	4.5%
TSP 100%	1.5%	9.0%	3.0%
PCA	2.0%	3.0%	2.0%
PAGMBE	0.1%	0.1%	0.1%
Water	81.4%	72.9%	71.4%
	100.0%	100.0%	100.0%

Note:
1 = For use with high alkalinity, soft MU water
2 = For use with high alkalinity, medium hardnesss MU water
3 = For use with low alkalinity, soft MU water

Tannin-Based Chemistry: Multiblend, One-Drum Programs

Materials	*Formulation*		
	4	5	6
Sodium hydroxide 50%	2.5%	2.5%	13.0%
Tannin blend 50%	11.5%	11.5%	11.5%
SHMP 33%	3.5%	13.0%	3.5%
PAA	4.0%	6.0%	5.0%
Water	78.5%	67.0%	67.0%
	100.0%	100.0%	100.0%

Note:
4 = For use with high alkalinity, soft MU water
5 = For use with high alkalinity, medium hardnesss MU water
6 = For use with low alkalinity, soft MU water

- Use of amine requires a two-drum approach.
- These formulations may be modified to further reduce the impact of adding dissolved solids to the program by substituting the SHMP for an organic polymer calcium carbonate control agent, such as PMA.

All-Organic Chemistry, Multiblend, One-Drum Programs

Materials	*Formulation*		
	7	8	9
DEHA 20%	11.0%	11.0%	11.0%
Morpholine 20%	9.0%	9.0%	25.0%
PMA	2.0%	4.0%	2.0%
PCA	2.0%	3.0%	2.0%
PAGMBE	0.1%	0.1%	0.1%
Hexylene glycol	1.0%	1.0%	2.0%
Water	74.9%	71.9%	57.9%
	100.0%	100.0%	100.0%

Note:
7 = For use with high alkalinity, soft MU water
8 = For use with high alkalinity, medium hardnesss MU water
9 = For use with low alkalinity, soft MU water

- Ensure FW is 180 °F minimum, to lower the DEHA demand.

12

CONTROL OF BOILER WATER CHEMISTRY

Under most circumstances, boiler plant operators are not limited to employing one specific water treatment chemistry—usually there is some choice and the optimum program takes into account a variety of factors, such as the quality of MU water pretreatment and percentage of condensate return. Even when the choice of suitable chemistries is slim, some modification of a "standard" program usually is necessary to make allowance for older equipment designs, unusual operating conditions, or environmental concerns before program control guidelines can be issued.

Earlier chapters discuss many of these standard internal treatments and provide waterside chemistry and program guidelines in the form of charts, tables, and accompanying notes.

NOTE: The principal guides to internal treatment chemistry found in earlier chapters are:

1. *Table 9.3 Specification for Water for Higher Pressure Boilers* *p341*
2. *Table 10.1 Guide to Tannin Residuals* *p408*
3. *Table 10.2 Carbonate Cycle: BW Carbonate Reserves* *p415*
4. *Table 10.3 Carbonate Cycle: BW Control Limits* *p417*
5. *Table 10.4 Phosphate Cycle: FT Boiler Control Limits* *p428*
6. *Table 10.5 Phosphate Cycle: WT Boiler Control Limits* *p429*
7. *Table 10.7 Chelant/All-Polymer/All-Organic Program Limits* *p459*
8. *Figure 10.5 Coordinated/Congruent Phosphate Control* *p471*
9. *Section 10.9 AVT Program Control Limits* *p475*
10. *Section 10.11.1 Chemical Program for PWR Primary Coolant* *p477*

However, truly effective monitoring and control of waterside chemistry requires that these programs be considered from additional perspectives. Control parameters often must be changed, depending on boiler design, operating pressure, or heat flux, and several other useful, independent guidelines and recommendations are available that take

these factors into account. This chapter looks at some of these other sources of reference and, where appropriate, certain tables have been extracted and are reproduced with permission of the copyright holder. References discussed include:

1. ***Consensus on Operating Practices for the Control of Feedwater and Boiler Water Chemistry in Modern Industrial Boilers,*** 2nd edition. American Society of Mechanical Engineers, 1994 (ASME Consensus).
2. ***BS 2486: Recommendations for Treatment of Water for Land Boilers,*** 2nd edition. British Standards Institution, 1978 (BS 2486:1978).
3. ***BS 2486: Recommendations for Treatment of Water for Steam Boilers and Water Heaters,*** 3rd edition. British Standards Institution, 1997 (BS 2486: 1997).
4. ***Boiler Water Requirements and Associated Steam Purity for Commercial Boilers.*** American Boiler Manufacturers Association, 1998 (ABMA Commercial BW Requirements).
5. ***The Treatment of Water for Shell Boilers,*** 4th edition, 1988, and 6th edition, 1997. Association of Shell Boilermakers and Allied Equipment Manufacturers (UK) (ASB BW Guide).
6. ***The Chemical Treatment of Boiler Water.*** James W. McCoy, Chemical Publishing Company, 1984 (McCoy BW).

NOTE:

1. Tables extracted from BS: 2486 are reproduced with kind permission of the British Standards Institute, London, England.

2. Tables extracted from ASME Consensus are reproduced with kind permission of The American Society of Mechanical Engineers, New York, NY, USA.

3. Tables extracted from McCoy BW are reproduced with kind permission of the Chemical Publishing Company, New York, NY, USA.

12.1 WATER TREATMENT RECOMMENDATION PERSPECTIVES

Although the tables reproduced here from the ***ASME Consensus, BS 2486*** and **McCoy BW** are important, the respective texts and footnotes that accompany each of these guidelines are at least as important as the

tables themselves. Readers are advised to seek out these books as additional sources of reference. Readers are also referred to the ***ABMA Commercial BW Requirements*** and ***ASB BW Guide***.

In general, the tables simply provide recommendations for the operational control of FW and BW chemistry and are not designed to be a set of inflexible rules. Consequently, if experience confirms that alternative program control limits will lead to safer, easier, and more reliable operation of the boiler plant, then experience should be the deciding factor.

12.1.1 *ASME Consensus*

The *ASME Consensus* was first published in 1979 and has been a standard reference ever since for boiler water treatment practice in the United States and its sphere of influence. The ASME Consensus 1994 update reflected the need to cover technical advances in boiler design and water conditioning, and also new and different types of steam generator, steam purity issues, and similar matters.

This book was not intended as a strict guide for pretreatment, boiler water treatment, or post-treatment programs, but rather to suggest best practices for designing and operating steam boiler plants and systems. Consequently, it does not consider the merits of particular water treatment chemicals or programs; rather, it provides six tables, each covering a different class of boiler. Within each table, control limit ranges are given based on boiler pressure (see Tables 12.2 to 12.7).

The *ASME Consensus* was prepared by a subgroup of the Research and Technology Committee on Steam and Water in Thermal Power Stations, and this background is evident in the perspective of the guidelines. These tables primarily cover industrial and marine boilers, with five of the six tables assuming that a deaerator is in service (which is unlikely to be the case in most small industrial and commercial facilities). Certain types of boiler are not covered; these are:

- Mobile locomotive boilers
- Boilers of copper or other unusual materials
- Immersion and low-voltage electric boilers
- Boilers of special design or unusual construction
- Hot water and oil field steam flood boilers

In some areas, a consensus could not be reached and some details are excluded; nevertheless, for larger boiler plants the *ASME Consensus* is an invaluable guide.

12.1.2 *BS 2486*

The **British Standards Institute** (BSI) is the independent national body responsible for preparing *British Standards* and presents the British view on many issues, including boiler water treatment practice. It is held in much the same level of esteem in Europe and the Commonwealth as ASME is in the United States.

BS 2486 was first published in 1954, revised in 1978, and revised again in 1997. The 1978 revision contained two primary tables setting out water chemistry guidelines; these were both quite broad in nature and covered FT (shell) boilers and WT boilers. This revision has now been withdrawn by BSI and replaced by the 1997 revision. The latest revision brings the technical content up to date, reflecting considerable additional experience gained in boiler design and operation by the subcommittee and 14 other bodies that provided contributions.

The 1997 revision also widened the scope of boiler design types to seven, enlarged the range of acceptable chemical treatments, and simultaneously tightened the water chemistry controls for FT and WT boilers (see Tables 12.9 to 12.15).

The BSI perspective is quite different from that of ASME. It includes considerable information on water treatment chemicals and tackles its standard with a strong chemistry emphasis, whereas the *ASME Consensus* maintains an engineering stance.

- *The BS 2486:1978* water chemistry table for FT plants categorized boilers by FW *hardness* (unlike the 1997 revision, which charted by *heat flux,* and the *ASME Consensus,* which uses *pressure* to define boiler groups). This 1978 edition has been withdrawn by BSI. However, for the purposes of providing guidelines for those many thousands of smaller FT boiler plant owners around the world (especially those in newly industrializing countries) operating *lower heat-flux units* and without benefit of first-class pretreatment, it remains a valid standard.

  In addition, it is a useful guide for those operators of LP steam, FT boilers in areas that have naturally soft water and where BX softeners are seldom specified.

  For these reasons, the 1978 table on **Recommended Water Characteristics for Shell Boilers** is reproduced in this book (see Table 12.8), together with the 1997 version (see Table 12.10).

NOTE: As an example, 90% of water supplied to New York City has a total hardness below 15 to 20 ppm $CaCO_3$. Pretreatment softeners are not the norm and consequently there are many thousands of nondomestic LP steam boilers (in addition to greater numbers of domestic LP steam boilers) in daily operation, where the FW hardness is 2 to 5 ppm or more as $CaCO_3$. The BSI 2486:1978 table for shell boilers remains a valid standard for these commercial and institutional boilers.

12.1.3 *ABMA Commercial BW Requirements* and *ASB BW Guide*

These two trade organizations represent the views of their members, who between them manufacture some of the most common types of boiler found in general industrial and commercial applications. Their respective guidelines are very useful supplements to the detailed operating instructions provided by manufacturers.

The *ABMA Commercial BW Requirements* is very strong on practical engineering and operations (similar to the *ASME Consensus*) but contains almost no chemistry, whereas the ASB *BW Guide* is a chemistry-oriented, water treatment primer.

- The *ABMA Commercial BW Requirements* provides maximum BW concentration recommendations for steam boilers:
- For boilers of up to 250 psig, BW TDS should be controlled within the range 3,500 to 5,000 ppm and T alkalinity within 900 to 1,200 ppm as $CaCO_3$.
- Boilers of between 251 and 350 psig should be controlled so as to maintain BW TDS within the range 3,000 to 4,000 ppm and T alkalinity within 700 to 900 ppm as $CaCO_3$.
- Boilers of between 351 and 500 psig should be controlled so as to maintain BW TDS within the range 2,500 to 3,000 ppm and T alkalinity within 600 to 800 ppm as $CaCO_3$.
- **Recommendations for maximum BW total iron in steam boilers** are 10, 8, and 5 ppm Fe, respectively.

NOTE: These are all very generous recommendations and probably represent the maximum values that can be maintained in modern boilers without risk of carryover.

- The *ABMA Commercial BW Requirements* gives **water condition guidelines for resistance-type boilers**.

- The FW total hardness should be maintained below 3 ppm as $CaCO_3$.
- BW should be limited to a maximum TDS of less than 3,500 ppm and alkalinity below 700 ppm.
- BW pH should be above 8.0, oxygen below 0.005 cc/l O_2.
- BW iron should be maintained below 3.0 ppm.

NOTE:

1. *ABMA assumes TDS (ppm) is 50% of electrical conductivity (micromhos). It is assumed that tests are made on unneutralized samples.*
2. *1 micromho/cm (μmho/cm) = 1 microSeimen/cm (μS/cm), usually stated at 25 °C.*
3. *It is assumed that alkalinity refers to total alkalinity as ppm $CaCO_3$ and that iron is total iron as ppm Fe.*
4. *These guidelines all appear quite reasonable, especially as they are simply ABMA starting points.*

- The *ABMA Commercial BW Requirements* gives **water condition guidelines for electrode-type boilers**, both low voltage (LV) and high voltage (HV):
  - The FW total hardness should be maintained below 3 ppm as $CaCO_3$ for LV and below 0.5 ppm for HV.
  - BW should be limited to a maximum TDS of less than 750 ppm and alkalinity below 400 ppm for LV. TDS for HV is dependent on the amount of BD and frequency; alkalinity is also below 400 ppm.
  - The BW pH should be between 8.5 and 10.5 for both LV and HV, and oxygen below 0.005 cc/l O_2 for both LV and HV.
  - Iron should be below 0.5 ppm for both LV and HV. Other values for HV boilers may be based on manufacturers' recommendations.

NOTE:

1. Although LV TDS guidelines propose <750 ppm micromhos, the LV conductivity proposed is <3000 ppm, which infers TDS = 25% of conductivity, rather than the norm of 50% for un-neutralized BW (N.B. the ratio is 65% for city water).

2. These guidelines are, again, simply ABMA starting points.

The *ASB BW Guide* takes its tables, notes, and comments for **recommended water characteristics for shell boilers** directly from BS: 2486.

Table 12.1 Guide to Authoritative Recommendations for Operational Control of BW Chemistry, by Boiler Type

	ASME 1994 Consensus	*BS 2486: 1997*	*ABMA Commercial Boilers*	*ASB Shell Boilers*	*McCoy Boiler Water*
WT + turbine	✔	✔[1]			✔[4]
WT land boiler	✔	✔[1]			✔[4]
WT <500 psig	✔	✔	✔[3]		✔[4]
WT non-fired		✔[2]			
WT marine boiler	✔				
Once-through		✔			
FT (shell) boiler	✔[5]	✔[5]	✔[3]	✔	✔[4]
Coil boiler	✔	✔			
Electrode boiler	✔	✔	✔		
Hot water boiler		✔			
Resistance boiler			✔		
Locomotive boiler					
Special designs					

NOTES:

1. *BS 2486 does not distinguish between WT boilers with or without turbines.*
2. *Includes combined cycle plant (CCP) and combined heat and power plant (CHP or cogeneration plant).*
3. *ABMA Commercial does not distinguish between various types of lower pressure boilers, they are simply "steam" boilers.*
4. *McCoy does not distinguish between land boilers within the range 100 to 3200+ psig boilers, they are simply "industrial" boilers.*
5. *ASME provides ranges of control limits for FT boilers based on boiler pressure, BS 2486: 1978 ranges are based on FW hardness, and BS: 2486: 1997 ranges are based on heat flux. All these guides may have equal relevance, depending upon specific boiler operational circumstances.*

The 4th edition (1988) and 5th edition (1994) employed BS 2486:1978 (see Table 12.8) and the 6th edition employs BS 2486: 1997 (see Table 12.10).

12.1.4 McCoy BW

The Chemical Treatment of Boiler Water by James W. McCoy remains the most comprehensive boiler water treatment guide of its time. The text reflects the background of Mr. McCoy, who was the supervisor of refinery services for Standard Oil Company of California. Consequently, the book and the FW/BW quality guideline tables reflect

higher pressure, industrial WT land boilers, although marine boilers are also discussed. There is little specific mention of FT or other types of boilers, and although the information provided concerning water chemistry and water treatment programs is extremely thorough, it is not always particularly valid for smaller boilers.

Nevertheless, the overall body of work remains valid for much of today's larger boiler plants and consequently the McCoy recommendations for *very high pressure and supercritical boilers, industrial boiler FW quality,* and *boiler salines* are also reproduced in this chapter (see Tables 12.16 to 12.18).

12.2 TABLES AND SUPPORTING NOTES

In addition to the author's guidelines covering BW and treatment program control (listed on the first page of this chapter) and the ABMA recommendations discussed in 12.1.3, an additional 17 tables from other sources are reproduced in this section.

12.2.1 Summary Guide

Table 12.1 above provides a summary guide to these additional 17 tables and is classified by boiler type.

12.2.2 Notes and Comments to Table 12.2

1. ASME recommends that for **industrial WT, high-duty, primary-fuel-fired, turbine drive boilers,** where local heat fluxes are greater than 1.5×10^5 Btu/hr/ft^2 (> 473.2 kW/m^2), use values for at least the next highest pressure range.
2. Minimum hydroxide alkalinity concentrations in boilers below 900 psig (6.21 MPa) must be individually specified by a qualified water treatment consultant with regard to silica solubility and other components of internal treatment.

   NOTE: Consensus on specific free hydroxide alkalinity values could not be reached and are not provided. See Table 12.11 for BS 2486 recommendations concerning caustic alkalinity.

3. ASME recommends that the maximum total alkalinity should be consistent with acceptable steam purity. If necessary, operators should override conductance as a BD control parameter. If MU is demineralized quality water and the boiler operates at less than 1,000

Table 12.2 (ASME Consensus table 1): Suggested water chemistry limits. Industrial watertube, high duty, primary fuel fired, drum type

Makeup water percentage: Up to 100% of feedwater. Conditions: Includes superheater, turbine drives or process restriction on steam purity

Saturated steam purity target: See tabulated values below

Drum Operating psig **Pressure** (1) (11) (MPa)	0–300 (0–2.07)	301–450 (2.08–3.10)	451–600 (3.11–4.14)	601–750 (4.15–5.17)	751–900 (5.18–6.21)	901–1000 (6.22–6.89)	1001–1500 (6.90–10.34)	1501–2000 (10.35–13.79)
Feedwater (7) Dissolved oxygen ppm (mg/l) O_2—measured before chemical oxygen scavenger addition (8)	<0.007	<0.007	<0.007	<0.007	<0.007	<0.007	<0.007	<0.007
Total iron ppm (mg/l) Fe	≤0.1	≤0.05	≤0.03	≤0.025	≤0.02	≤0.02	≤0.01	≤0.01
Total copper ppm (mg/l) Cu	≤0.05	≤0.025	≤0.02	≤0.02	≤0.015	≤0.01	≤0.01	≤0.0
Total hardness ppm as $CaCO_3$	≤0.3	≤0.3	≤0.2	≤0.2	≤0.1	≤0.05	ND	ND
pH @ 25°C	8.3–10.0	8.3–10.0	8.3–10.0	8.3–10.0	8.3–10.0	8.8–9.6	8.8–9.6	8.8–9.6
Chemicals for preboiler system protection	NS	NS	NS	NS	NS	VAM	VAM	VAM
Nonvolatile TOC ppm C (6)	<1	<1	<0.5	<0.5	<0.5	<0.2	<0.2	<0.2
Oily matter ppm (mg/l)	<1	<1	<0.5	<0.5	<0.5	<0.2	<0.2	<0.2
Boiler Water Silica ppm (mg/l) SiO_2	≤150	≤90	≤40	≤30	≤20	≤8	≤2	≤1
Total alkalinity ppm as $CaCO_3$	<350 (3)	<300 (3)	<250 (3)	<200 (3)	<150 (3)	<100 (3)	NS (4)	NS (4)
Free OH alk. ppm $CaCo_3$ (2)	NS	NS	NS	NS	NS	NS	ND (4)	ND (4)
Specific conductance (12) μmhos/cm (μS/cm) @ 25°C without neutralization	5400–1100 (5)	4600–900 (5)	3800–800 (5)	1500–300 (5)	1200–200 (5)	1000–200 (5)	<150	<80
TDS in Steam (9) TDS (maximum) ppm (mg/l)	1.0–0.2	1.0–0.2	1.0–0.2	0.5–0.1	0.5–0.1	0.5–0.1	0.1	0.1

NOTES: NS = not specified, ND = not detectable. VAM = Use only volatile alkaline materials upstream of attemperation water source (10).

psig (6.89 MPa) drum pressure, the BW conductance should be that in the table for the 1,001 to 1,500 psig (6.9–10.34 MPa) range. In this case, the necessary continuous BD will usually keep these parameters below the tabulated maximum values. Alkalinity values in excess of 10% of specific conductance values may cause foaming.

NOTE: Alkalinity values in excess of 20 to 25% of specific conductance values gives a more practical guide for the onset of foaming.

4. *Not detectable* (ND) in these cases refers to **free sodium** or **potassium hydroxide alkalinity**. Some small variable amount of total alkalinity will be present and measurable with the assumed congruent or coordinated phosphate-pH control or volatile treatment employed at these high pressure ranges.
5. Maximum values of specific conductance are often not achievable without exceeding maximum T alkalinity values, especially in boilers below 900 psig (6.21 MPa) with greater than 20.0% MU water whose alkalinity is >20% of TDS naturally or after pretreatment by lime-soda or sodium cycle ion exchange softening. Actual permissible conductance values to achieve any desired steam purity must be established for each case by careful steam purity measurements. The relationship between conductance and steam purity is affected by too many variables to allow its reduction to a simple list of tabulated values.
6. Nonvolatile TOC is that organic carbon not intentionally added as part of the WT regimen.

NOTE: There are various types of organic contaminants that can be present in boiler FW, including trace amounts of pesticides and naturally occurring humic, fulvic, and tannic acids, and solvent-extractable oily matter, such as nonvolatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, and the like.

Contamination by volatile organics becomes of increasing concern in higher pressure boilers because they can cause severe turbine damage.

7. Boilers below 900 psig (6.21 MPa) with large furnaces, large steam release space, and internal chelant, polymer, and/or antifoam treatment may tolerate higher levels of FW impurities than those in the table and still achieve adequate deposition control and steam purity. Removal of these impurities by external pretreatment is always a

more positive solution. Alternatives must be evaluated for practicality and economic benefit in each individual case.

8. Values for dissolved oxygen assume the presence of a deaerator.
9. Achievable steam purity depends on many variables, including BW TA and specific conductance as well as design of steam boiler drum internals and operating conditions. Since boilers in this category require a relatively high degree of steam purity for protection of superheaters and turbines, more stringent steam purity requirements, such as process steam restrictions on individual chemical species, or restrictions more stringent than 0.1 ppm (mg/l) TDS turbine steam purity must be addressed specifically.

   NOTE: For any specific WT boiler, where high steam purity is required, the BW chemistry parameters should be set as low as necessary to achieve the desired quality. Careful observation of the relationship between steam purity and boiler conductivity, alkalinity, and other parameters quickly establishes the particular control conditions required.

10. As a general rule, the requirements for attemperation spray water are the same as those for steam purity. In some cases boiler FW is suitable; however, additional purification frequently is required. In all cases, the spray water should be obtained from a source that is free of deposit-forming and corrosive chemicals such as sodium hydroxide, sodium sulfite, sodium phosphate, iron, and copper. The suggested limits for **(attemperator) spray water quality** are:

    - $<$ 30 ppb (μg/l) TDS maximum
    - $<$ 10 ppb (μg/l) Na maximum
    - $<$ 20 ppb (μg/l) SiO_2 maximum
    - Essentially oxygen-free

11. Low-pressure boilers frequently use FW that is suitable for use in higher pressure boilers. In these cases, the boiler water chemistry limits should be based on the pressure range that is most consistent with the FW quality.

    NOTE: Industrial boilers employing high-purity MU water should be operated with a minimum of 1.0% BD (100 cycles of FW concentration maximum), to avoid extremely high concentrations of trace contaminants and impurities (especially iron, copper, hardness, silica, and suspended solids) and the formation of deposits in the boiler.

12. Conversion from ppm (mg/l) TDS values in the ABMA standards uses a factor of 0.65, i.e.:

Specific conductance (μmho/cm or μS/cm) @ 25 °C (unneutralized sample) × 0.65 = total dissolved solids (TDS) ppm or mg/l

NOTE: The specific conductance factor varies considerably, depending on several factors, including the concentration of ionic species present in the water. In general, the factor decreases with increase in the concentration of ionic species. Thus, for city water a factor of 0.65 is a good approximation; for BW in higher pressure WT boilers, a factor of 0.575 is preferred by the author, and for BW in lower pressure FT boilers, a factor of 0.5 is preferred by the author.

ASME recommends 0.65 as a starting point, but recommends that the actual value be determined empirically because it varies with change in the composition of BW.

BSI commonly uses a factor of 0.5.

12.2.3 Notes and Comments to Table 12.3

1. Values in the table for **industrial WT, high-duty, primary-fuel-fired, nonturbine drive boilers** assume the existence of a deaerator.
2. ASME recommends that chemical deaeration be provided in all cases, especially if mechanical deaeration is nonexistent or inefficient.
3. Boilers with relatively large furnaces, large steam space, and internal chelant, polymer, and/or antifoam treatment can often tolerate higher levels of FW impurities than those in the table and still achieve adequate deposition control and steam purity. Removal of these impurities by external pretreatment is always a more positive solution. Alternatives must be evaluated as to practicality and economics in each individual case. The use of some dispersant and antifoam internal treatment is typical in this type of boiler operation; therefore, it can tolerate higher FW hardness than the boilers in Table 12.2 (ASME Table 1).
4. Minimum and maximum hydroxide (OH, caustic) alkalinities must be individually specified by a qualified water treatment consultant with regard to silica solubility and other components of internal treatment.

NOTE: Refer to Table 12.11 (BS 2486: 1997 Table 3) for starting point recommendations for OH alkalinity and silica limit ratios.

Table 12.3 (ASME Consensus table 2): Suggested chemistry limits. Industrial water-tube, high duty, primary fuel fired, drum type.

Makeup water percentage: Up to 100% of feedwater.

Conditions: No superheater, turbine drives, or process restriction on steam purity

Steam purity (7): 1.0 ppm (mg/l) TDS maximum

Drum Operating Pressure psig (MPa)	0–300 (0–2.07)	301–600 (2.08–4.14)
Feedwater (3) Dissolved oxygen ppm (mg/l) O_2—measured before chemical oxygen scavenger addition (1) (2)	<0.007	<0.007
Total iron ppm (mg/l) Fe	<0.1	<0.05
Total copper ppm (mg/l) Cu	<0.05	<0.025
Total hardness ppm (mg/l) as $CaCO_3$	<0.05	<0.03
pH @ 25°C	8.3 to 10.5	8.3 to 10.5
Nonvolatile TOC ppm (mg/l) C (6)	<0.1	<0.1
Oily matter ppm (mg/l)	<0.1	<0.1
Boiler Water Silica ppm (mg/l) SiO_2	<150	<90
Total alkalinity ppm as $CaCO_3$	<1000 (5)	<850 (5)
Free OH alkalinity ppm as $CaCO_3$ (4)	not specified	not specified
Specific conductance μmhos/cm (μS/cm) @ 25°C without neutralization	<7000 (5)	<5500 (5)

5. Alkalinity and conductance values are consistent with steam purity limits in the same table. Practical limits above or below tabulated values should be individually established by careful steam purity measurements.
6. Nonvolatile TOC is that organic carbon not intentionally added as part of the WT regime.
7. The steam purity limit represents an achievable level if other tabulated water quality values are maintained. ASME points out that the limit is not intended to be, nor should it be construed to represent, a boiler performance guarantee.

12.2.4 Notes and Comments to Table 12.4

1. Values in the table for **industrial FT, high-duty, primary-fuel-fired boilers** assume the existence of a deaerator.

Table 12.4 (ASME Consensus table 3): Suggested chemical limits. Industrial fire-tube, high duty, primary fuel fired.

Makeup water percentage: UP to 100% of feedwater.

Conditions: No superheater, turbine drives, or process restriction on steam purity

Steam purity (7): 1.0 pm (mg/1) TDS maximum

Drum Operating Pressure psig (MPa)	0–300 (0–2.07)
Feedwater (3) Dissolved oxygen ppm (mg/1) O_2— measured before chemical oxygen scavenger addition (1) (2)	<0.007
Total iron ppm (mg/1) Fe	<0.1
Total copper ppm (mg/1) Cu	<0.05
Total hardness ppm as $CaCO_3$	<1.0
pH @ 25°C	8.3 to 10.5
Nonvolatile TOC ppm (mg/1) C (6)	<10
Oily matter ppm (mg/1)	<0.1
Boiler Water Silica ppm (mg/1) SiO_2	<150
Total alkalinity ppm as $CaCO_3$	<700 (5)
Free OH alkalinity ppm as $CaCO_3$ (4)	not specified
Specific conductance μmhos/cm (μS/cm) @ 25°C without neutralization	<7000 (5)

2. ASME recommends that chemical deaeration be provided in all cases, especially if mechanical deaeration is nonexistent or inefficient.
3. FT boilers with relatively large furnaces, large steam space, and internal chelant, polymer, and/or antifoam treatment can often tolerate higher levels of FW impurities than those in the table [$\leqslant$ 0.5 ppm (mg/l) Fe, $\leqslant$ 0.2 ppm (mg/l) Cu, $\leqslant$ 0.2 ppm (mg/l) TH] and still achieve adequate deposition control and steam purity. Removal of these impurities by external pretreatment is always a more positive solution. Alternatives must be evaluated for practicality and economics in each individual case.
4. Minimum and maximum hydroxide (OH, caustic) alkalinities must be individually specified by a qualified water treatment consultant with regard to silica solubility and other components of internal treatment.

NOTE: Refer to Tables 12.8 (BS 2486 1978 Table 2) and 12.10 (BS 2486 1997 Table 2) for starting point recommendations for OH alkalinity and silica limit ratios.

5. Alkalinity and conductance values are consistent with steam purity limits in the same table. Practical limits above or below tabulated values should be individually established by careful steam purity measurements.
6. Nonvolatile TOC is that organic carbon not intentionally added as part of the WT regime.
7. The steam purity limit represents an achievable level if other tabulated water quality values are maintained. ASME points out that the limit is not intended to be, nor should it be construed to represent, a boiler performance guarantee.

12.2.5 Notes and Comments to Table 12.5

1. Tabulated values for **industrial coil-type WT, high-duty, steam generators** are based on the assumption of no superheaters or turbine drives. If the steam is used for superheat or turbine drives, use values for 901 psig (6.22 MPa) and up. If unit operation approaches superheat conditions within the coil, use values in the 601 to 900 psig (4.15–6.21 MPa) range to avoid silica deposition on near-dry surfaces. ASME points out that the target is not intended to be, nor should it be construed to represent, a boiler performance guarantee.
2. Boiler antifoams are frequently used to improve steam purity.
3. Water to the coil can be FW (**FW definition** = MU plus condensate) alone or a combination of FW and concentrated water from the steam separator drains.
4. Chemical deaeration with catalyzed oxygen scavenger is necessary in all cases because FW temperature limits imposed by manufacturers of coil-type steam generators preclude efficient mechanical deaeration. Feed of chemical oxygen scavenger must be sufficient to maintain a detectable residual in the water to the coil. For those units that include **steam separator-water storage drums** and recirculate substantial amounts of BW, oxygen scavenger residuals should be maintained in the higher ranges typical of those employed for drum-type boilers.

Table 12.5 (ASME Consensus table 4): Suggested water chemistry limits. Industrial coil type, watertube, high duty, primary fuel fired rapid steam generators

Makeup water percentage: Up to 100% of water to the coil.

Steam to water ratio (volume to volume): Up to 4000:1.

Total evaporation: Up to 95% of the water to the coil.

Saturated steam purity target: See tabulated values below.

Drum Operating Pressure psig (MPa)	0–300 (0–2.07)	301–450 (2.08–3.10)	451–600 (3.11–4.14)	601–900 (4.15–6.21)	>900 (>6.21)
Steam Purity Targets (1) Specific conductance μmhos/cm (μS/cm) @ 25°C	≤50 (2)	≤24 (2)	≤20 (2)	≤0.5	≤0.2
Dissolved solids ppm (mg/l)	≤25	≤12	≤10	≤0.25	≤0.01
Silica ppm (mg/l) SiO_2	NS	NS	NS	≤0.03	≤0.02
Water to coil (3) Dissolved oxygen ppm (mg/l) O_2—measured *after* chemical oxygen scavenger addition (4)	<0.007	<0.007	<0.007	<0.007	<0.007
Total iron ppm (mg/l) Fe	<1.0	<0.3	<0.1	≤0.05	≤0.02
Total copper ppm (mg/l) Cu	<0.1	<0.05	<0.03	≤0.02	≤0.02
Total hardness ppm (mg/l) as $CaCO_3$	0–trace	0–trace	0–trace	ND (6)	ND (6)
pH @ 25°C	9.0–11.0	9.0–11.0	9.0–11.0	9.0–11.0	9.0–11.0
Total alkalinity ppm (mg/l) as $CaCO_3$	<800	<600	<500	<200	<100 (7)
Hydroxide alkalinity ppm (mg/l) as $CaCO_3$ (5)	<300	<200	<120	<60	≤50 (7)
Silica ppm (mg/l) SiO_2	≤150	≤100	≤60	≤30	≤10 (7)
Specific conductance μmhos/cm (μS/cm) @ 25°C without neutralization	<8000	<6000	<5000	<4000	<500 (7)

NOTE: NS= not specified, ND = not detectable.

5. Treatment chemicals should preferably be fed to the FW tank to minimize sludge deposits in the coils. Hydroxide alkalinity in ppm (mg/l) $CaCO_3$ must be maintained at a sufficient concentration to keep silica soluble and avoid complex silicate deposits. These precautions are necessary because scale-control internal treatment chemicals usually are not employed to assist in the prevention of such deposits in coil-type steam generators.

NOTE: Refer to Table 12.14 (BS 2486: 1997 Table 6) for starting point recommendations for OH alkalinity and silica limit ratios for coil boilers.

6. Demineralization of MU water is recommended practice in these pressure ranges.
7. Suggested values of T alkalinity hydroxide alkalinity, and silica vary with the operating pressure, decreasing in inverse proportion to pressure increases above 900 psig (6.21 MPa).

12.2.6 Notes and Comments to Table 12.6

1. FW values for **marine propulsion, WT, oil-fired, drum-type boilers** assume 100 cycles of concentration (COC) to BW and are not restricted to any specific MU water pretreatment.
2. Suggested maximum conductance values are intended to serve as an alarm for saltwater condenser leaks and can be correlelated with chloride ion content in FW and/or BW.
3. ASME proposes that the maximum hydroxide alkalinity that is consistent with the steam purity target and sufficient to maintain silica solubility should be employed. If necessary, this value should override conductance as the BD control parameter.
4. Nondetectable (ND) OH alkalinity in this case refers to free sodium or potassium hydroxide alkalinity. Some small amount of total alkalinity will be present and measurable with the assumed congruent or coordinated phosphate-pH control or volatile treatment usually applied at these high-pressure ranges.
5. Dissolved oxygen values in the table assume the existence of a deaerator.
6. The steam purity limit represents an achievable level if other tabulated water quality values are maintained. ASME points out that the limit is not intended to be, nor should it be construed to represent, boiler performance guarantees.

Table 12.6 (ASME Consensus table 5): Suggested water chemistry limits. Marine propulsion, watertube, oil fired drum type

Makeup water percentage: Up to 5% of feedwater

Pretreatment: At sea, evaporator condensate; in port, evaporator condensate or water from shore facilities meeting feedwater quality guidelines.

Saturated steam purity (6): 30 ppb (µg/1) TDS max., 10 ppb (µg/1) Na max., 20 ppb (µg/1) SiO_2 max.

Drum Operating Pressure psig (MPa)	450–850 (3.1–5.86)	851–1250 (5.87–8.62)
Feedwater (1) Dissolved oxygen ppm (mg/1) O_2— measured before chemical oxygen scavenger addition (5)	<0.007	<0.007
Total iron ppm (mg/1) Fe	<0.02	<0.01
Total copper ppm (mg/1) Cu	<0.01	<0.005
Total hardness ppm (mg/1) as $CaCO_3$	<0.1	<0.05
pH @ 25°C	8.3–9.0	8.3–9.0
Chemical for preboiler system protection	VAM	VAM
Oily matter ppm (mg/1)	<0.05	<0.05
Boiler Water		

Table 12.7 (ASME Consensus table 6): Suggested water chemistry limits. Electrode, high voltage, forced circulation jet type

Makeup water percentage: Up to 100% of feedwater

Conditions: No superheater, turbine drives, or process restriction on steam purity

Operating Pressure psig (MPa)	0–450 (0–3.1)
Feedwater (2) Dissolved oxygen ppm (mg/1) O_2— Measured before chemical oxygen scavenger addition (1)	<0.007
Total hardness ppm (mg/1) as $CaCO_3$	<0.25
pH @ 25°C	8.3–10.5
Nonvolatile TOC ppm (mg/1) C (6)	NS (8)
Boiler Water pH @ 25°C	8.3 - 10.5
Silica ppm (mg/1) SiO_2	<150
Total alkalinity ppm (mg/1) as $CaCO_3$	<350 (3)
OH alkalinity ppm (mg/1) as $CaCO_3$ (8)	NS (8)
Total iron ppm (mg/1) Fe plus total copper ppm (mg/1) Cu	2.0 (2) (7)
Suspended solids	NS (7)
Organic matter	NS (8)
Specific conductance μmhos/cm (μS/cm) @ 25°C without neutralization	NS (5)

silica solubility, organic matter concentration, and other components of internal treatment.

NOTE: Refer to Table 12.15 (BS 2486: 1997 Table 7) for starting point recommendations on OH alkalinity and silica limit ratios for electrode boilers.

5. Boiler performance is determined by the conductivity of the BW. The optimum conductivity range is dependent on the specific boiler design.
6. Nonvolatile TOC is that organic carbon not intentionally added as part of the WT regime.
7. Suspended solids (SS) present in the BW contribute to erosion-corrosion of the electrodes and counter-electrodes. Additionally, the presence of SS in the BW increases the potential for foaming and **ground fault arcing**.

8. Naturally occurring organics, particularly when combined with hydroxide alkalinity, may cause foaming in the BW. *Ground fault arcing* between the electrode and upper boiler shell may result.

12.2.8 Notes and Comments to Table 12.8

1. The BSI table of **water characteristics for shell boilers up to 25 bar** provides recommendations for FW hardness. Boilers with high output relative to water content and/or employing high heat-flux density usually require FW of low hardness, not only to avoid scale formation on heat transfer surfaces but also to minimize the formation of SS or sludge in the boilers. Consequently, water with the characteristics given in the 2 mg/l FW hardness column should be used in these situations.
2. **Dissolved oxygen** (DO) **in the FW** should be reduced to the lowest practical level before adding an oxygen scavenger. **Hydrazine** is recommended as an alternative to **sodium sulfite** only when it is dosed to the FW at a substantial distance from the boiler and where the FW is sufficiently hot to enable the removal of oxygen to be 90% complete before entry to the boiler.

   CAUTION NOTE: Hydrazine is toxic, and suitable precautions for its handling should be observed. Its use is usually prohibited in hospitals, the food manufacturing industry, and where steam may come into contact with food or beverages. The use of sodium sulfite may also be unacceptable in some of these applications. The existence of any regulations governing the use of either should be ascertained and observed.

3. The concentration of **solids, alkalinity and silica in the FW** should not be so high as to require BD of BW in quantities exceeding the boiler design value or exceeding the FW pump capacity.
4. Organic matter other than oil may be innocuous in a boiler depending on the temperature of operation and the amount and type of organic matter. Maximum values that would be universally applicable cannot be stated, and the operator should therefore be alert to the operating difficulties that may be associated with the presence of organic matter; these are as follows:
   - Interference with heat transfer, usually attributable to the presence of organic matter that is immiscible with water (e.g., hydrocarbons)
   - Foaming, attributable to organic surface-active agents

Table 12.8 (BS 2486: 1978 table 2): Recommended water characteristics for shell boilers

For pressures up to 25 bar*

Total hardness in feed water, mg/l in terms of $CaCO_3$ max.	2	20	40	(a)
Feed water pH value	7.5 to 9.5	7.5 to 9.5	7.5 to 9.5	
Oxygen	†	†	†	(b)
Total solids, alkalinity, silica	†	†	†	(c)
Organic matter	†	†	†	(d)
Boiler water Total hardness, mg/l in terms of $CaCO_3$, max.	ND‡	ND	ND	—
Sodium phosphate, mg/l as Na_3PO_4 §	50 to 100	50 to 100	50 to 100	(e)
Caustic alkalinity, mg/l in terms of $CaCO_3$ min.	350	300	200	—
Total alkalinity, mg/l in terms of $CaCO_3$ max.	1200	700	700	—
Silica, mg/l as SiO_2 max.	Less than 0.4 of the caustic alkalinity			
Sodium sulfite, mg/l as Na_2SO_3 *or* Hydrazine, mg/l as N_2H_4	30 to 70 0.1 to 1.0	30 to 70 0.1 to 1.0	30 to 70 0.1 to 1.0	(b) (b)
Suspended solids, mg/l max.	50	200	300	(f)
Dissolved solids, mg/l max.	3500	3000	2000	—

NOTES:

– Not applicable

** 1 bar = 10^5 N/m^2 = 100 kPa = 0.1 MPa = 14.5 psig*

† Numerical values depend upon circumstances but the comments are relevant

‡ ND not detectable

§ Phosphate is usually added as sodium phosphates but determined as phosphates (PO_4^{3-}); $Na_3PO_4 = 1.73 \times PO_4^{3-}$

- Diminished alkalinity, attributable to thermal decomposition of organic matter to acidic compounds
- Impairment of steam purity, attributable to thermal decomposition of organic matter to volatile compounds; this is especially important where steam is used directly in processing food, pharmaceuticals, or beverages

- Modification of SS to form adherent deposits of intractable sludges

5. **Carbonate and phosphate control** is vital. If a minimum carbonate alkalinity of 250 mg/l expressed in terms of $CaCO_3$ is consistently maintained when carbonate control or sodium ion exchange softening is used, a residual of soluble phosphate need not be maintained. A residual of soluble hardness up to 5 mg/l expressed in terms of $CaCO_3$ is then usually found in the BW, but scale formation may be minimized by phosphate or carbonate conditioning treatment.

NOTE: It has been shown that in the absence of phosphate, ***carbonate conditioning*** *can produce precipitated solids in a non-adherent and mobile form by adjusting the proportion of calcium, magnesium and silica to correspond with the relationship:*

$$M > 0.2\,(C + 3S)$$

where:
M = the magnesium hardness expressed as $CaCO_3$ in the FW
C = the calcium hardness expressed as $CaCO_3$ in the FW
S = the silica expressed as SiO_2 in the FW

Polymers may act as weak chelating agents and thus retain hardness salts in solution in BW. In this event the hardness as determined by EDTA titration is measurable, particular attention should be given to maintaining the recommended level of carbonate or phosphate. In appropriate circumstances, chelating agents may be used in place of phosphate.

6. **Suspended solids** figures represent theoretical values and are not necessarily measurable in practice. They may be used as one basis for calculating boiler BD requirements, based on the actual FW hardness.

12.2.9 Notes and Comments to Table 12.9

1. BSI recommends in the **table of water treatment for hot water systems** that chromate inhibitors should not be used because of their undesirable impact on the environment. It should also be noted that some treatment chemicals are microbiologically degraded in storage.

NOTE: Sodium nitrite–based corrosion inhibitors are commonly employed as corrosion inhibitors for LPHW systems; however, they can be subject to

Table 12.9 (BS 2486: 1997 table 1): Water treatment for hot water systems

System type	Low and medium temperature hot water systems up to 120°C			High temperature hot water systems above 120°C		
Materials of construction (note 2)	Iron only	Iron with copper and copper alloys aluminum	Iron with copper, copper alloys and	Iron only	Iron with copper and copper alloys aluminum	Iron with copper, copper alloys and
Water quality (note 4)	Raw water	Raw water	Raw water (notes 5 and 6)	Raw water (note 7)	Raw water (note 7)	Raw water (notes 5, 6 and 7)
pH limits	8.0 to 10.5	7.5 to 9.2	7.0 to 8.0	8.0 to 10.5	7.5 to 9.2	7.0 to 8.0
Alkalinity control	Sodium hydroxide	Sodium hydroxide	Untreated or buffered	Sodium hydroxide or amines	Sodium hydroxide or amines	Amines
Copper corrosion inhibitor	None	Benzotriazole/ toyltriazole	Benzotriazole/ toyltriazole	None	Benzotriazole/ toyltriazole	Benzotriazole/ toyltriazole
Oxygen scavenger and/or Corrosion inhibitor (note 3)	Sodium sulfite, tannin, hydrazine or DEHA Suitable inhibitor blend (note 1)	Sodium sulfite, tannin, hydrazine or DEHA Suitable inhibitor blend (note 1)	Sodium sulfite, tannin, hydrazine or DEHA Suitable inhibitor blend (note 1)	Volatile oxygen scavengers (e.g. hydrazine, DEHA, carbohydrazide, MEKO)	Volatile oxygen scavengers (e.g. hydrazine, DEHA, carbohydrazide, MEKO)	Volatile oxygen scavengers (e.g. hydrazine, DEHA, carbohydrazide, MEKO)
Sludge conditioner	Suitable organic polymer or blend	Suitable organic polymer or blend	Suitable organic polymer or blend	Suitable organic polymer or blend	Suitable organic polymer or blend	Suitable organic polymer or blend

microbiological degradation in the HW system, especially if fed to a system that has dead legs, poor circulation, and temperature stratification problems, or where poor cleaning and treatment has been the norm. Cleaning and passivation programs are always recommended when using nitrite/borate programs. A single-shot dose of a suitable microbiocide may also be useful.

It is not usual for unopened drums of nitrite-based chemical to degrade, and the product should remain in good condition for several years. However, it is possible for ***tannin-based corrosion inhibitors*** *to degrade, even in unopened drums. Under warm conditions (such as storage in a boilerhouse) and in the absence of a small amount of suitable microbiocide in the formulation, plastic drums containing tannin products may swell considerably because of microbiological degradation and gas formation. Care is needed to avoid accidents.*

2. Galvanized steel is not considered suitable for HW systems.
3. Alkaline oxygen scavengers may be used as alternative treatments to some corrosion inhibitors where toxicity restrictions prohibit proprietary blends.

NOTE: Where toxicity restrictions prohibit proprietary blends, phosphate-based inhibitors normally may also be used.

4. Raw water MU may be used, although in areas where the hardness exceeds 200 mg/l as $CaCO_3$ and MU exceeds 1% of system capacity per week, a supplementary dispersant should be used.

NOTE: Where MU rates are high, a supplementary oxygen scavenger may also be required to avoid the problem of pitting corrosion in the boiler and associated pipe work.

5. Some naturally soft mains waters may be unsuitable because they contain dissolved copper ions that could lead to aluminum failure. Poor buffer control can also cause attack.
6. Hard waters that have been fully softened should be avoided when aluminum is present.
7. Anions such as chloride and sulfate should not exceed 10 mg/kg (mg/l) in HTHW. Where the available water contains more than 10 mg/kg of each anion, demineralized water should be used.

12.2.10 Notes and Comments to Table 12.10

1. BSI **recommended water characteristics for shell boilers (FT boilers) up to 30 bar (435 psig)** note that when copper alloys are present in the feed system, the pH should not exceed 9.2 if corrosion of these materials is to be avoided.

Table 12.10 (BS 2486: 1997 table 2): Recommended water characteristics for shell boilers up to 30 bar

Feed water			
Parameter	**Units**	**Values**	
Appearance		Clear, produces no stable foam	
pH value @ 25°C		8.5 to 9.5 (note 1)	
Total hardness	mg/kg $CaCO_3$	2 max. (note 2)	
Dissolved oxygen	mg/kg O_2	(notes 3 and 4)	
Total alkalinity to pH 4.5 (M alkalinity)	mg/kg $CaCO_3$	(note 5)	
Oil and grease	mg/kg	1 max. (note 6)	
Boiler water			
Heat flux	**kW/m²**	**<300**	**>300 (note 7)**
pH value @ 25°C	—	10.5 to 12.0 (note 8)	9.5 to 10.5 (note 8)
Total alkalinity (M alkalinity)	mg/kg $CaCO_3$	1000 max.	100 max.
Caustic alkalinity (O or P_2 alkalinity)	mg/kg $CaCO_3$	350 min.	20 min. (note 10)
Oxygen scavenger (note 18) Sodium sulfite *or* Hydrazine *or* Tannin *or* Isoascorbic acid *or* DEHA	 mg/kg mg/kg mg/kg mg/kg mg/kg	In feedwater 30 to 70 0.1 to 1.0 120 to 160 15 to 30 0.1 to 1.0	In feedwater (note 12) 0.1 to 1.0 (note 12) (note 12) 0.1 to 1.0
Phosphate	mg/kg PO_4 (notes 11, 13)	30 to 60 (notes 11,13)	10 to 30
Silica	mg/kg SiO_2	150 max. (note 14)	5 max. (note 14)
Suspended solids	mg/kg	200 max.	20 max.
Dissolved solids	mg/kg (notes 16,17)	3500 max. (notes 16,17)	1000 max.
Electrical conductivity at 25°C, on un-neutralized sample (note 15)	μS/cm	7000 max. (notes 16, 17)	2000 max. (notes 16, 17)

2. The value for *total hardness* is achieved only by the use of suitable external pretreatment plants. It is essential that such plants be properly maintained. It is also recommended that a suitable polymer dispersant be used to ensure clean heat-transfer surfaces.
3. Dissolved oxygen (DO) should be reduced to the lowest practical level, which is achieved by the use of a properly designed feed tank or deaerator.
4. An oxygen scavenger should be used and should be added at the outlet of the feed tank or the deaerator in sufficient quantity to reduce the DO to zero before the FW enters the boiler or the economizer (where fitted).
5. It is recommended that the FW alkalinity be reduced below 25 mg/kg. Alkalinity of 25 mg/kg and above results in 10 mg/kg of carbon dioxide in the steam. This level of carbon dioxide can be economically controlled by the use of a neutralizing amine. If this FW alkalinity cannot be achieved, it is recommended that dealkalization of the MU water be carried out.
6. Standard test methods for oil and grease may not be available, and alternative tests may not be particularly accurate. Nevertheless, any positive oil and grease test result is potentially troublesome and should be investigated.
7. At heat fluxes greater than 300 kW/m^2 (52,832 Btu/h/ft^2/°F) the use of demineralized water is essential.
8. Corrosion of boiler internals may occur if the BW pH is outside the values stated in the table.
9. At heat fluxes greater than or equal to 300 kW/m^2 it is recommended that caustic alkalinity be maintained at 10 to 15% of the TDS concentration, if **phosphate conditioning** is practiced. If **carbonate conditioning** is practiced, see note 11.
10. At heat fluxes greater than 300 kW/m^2 the caustic alkalinity value depends on the silica concentration in the BW and also the pH level requirement.
11. Maintenance of a phosphate reserve is not essential provided that a minimum *carbonate alkalinity* of 250 mg/kg can be maintained, depending on the alkalinity of the FW and the working pressure of the boiler, or that an appropriate program of transporting polymers is employed.

    It is important to ensure that magnesium phosphate is not precipitated in the boiler water because it may cause sludges to adhere

and form hard scales on heat transfer surfaces. Experience has shown that this is unlikely if the phosphate does not exceed 10% of the minimum caustic alkalinity specified in the tables.

As an additional safeguard, it is common practice to use an appropriate polymeric sludge conditioner, which will maintain precipitates in suspension for removal with the BD.

12. Oxygen scavenger substances may, in some high heat flux and high pressure applications, decompose to yield corrosive components. Applications should be individually assessed with the supplier concerned.
13. The use of solubilizing treatments employing chelants (EDTA, NTA, etc.) is permissible provided that a maximum of 10 mg/kg (ppm) is not exceeded at any time. Complete removal of oxygen should have been achieved prior to injection of the chelant. In boilers having heat fluxes greater than 300 kW/m^2 (52,832 $Btu/h/ft^2/°F$) the use of chelants should be avoided because they can decompose to form acidic residues.

NOTE: This guideline refers to 100% chelant present in the boiler. Where, for example, 38% EDTA solution is used, the maximum permitted chelant product concentration is 26.3 ppm (mg/kg). If the cycles of concentration in the boiler is 20x, the product is injected, proportional to FW demand, at a feed rate of approximately 1.3 ppm, direct to the boiler.

14. Silicate scales can form readily in all boilers. Maintenance of a **silica content to caustic alkalinity ratio** of less than 0.4:1 prevents this.
15. With regard to TDS and conductivity, only one of these parameters must be measured.
16. Values for BW dissolved solids are for guidance only. It might be found from experience that lower values are necessary to avoid surging, priming, or carryover.
17. The maximum values for BW dissolved solids are based on fully softened FW in accordance with the table. If, for whatever reason, FW with a significant hardness must be used, then the TDS and conductivity level should be reduced to achieve the SS limit.

    At 20 mg/kg (ppm) FW hardness the upper conductivity limit should be reduced to 6,000 μS/cm (unneutralized sample).

    At 40 mg/kg FW hardness, the upper conductivity limit should be further reduced to 4,000 μS/cm.

18. A wide variety of oxygen scavengers are available; the control levels of these should be as recommended by the supplier of the treatment chemical.

12.2.11 Notes and Comments to Table 12.11

1. The values for pressure at the boiler outlet given in the BSI table of **recommended water characteristics for fired water tube boilers** applies to boilers of modern design and heat flux rating. Boilers of low heat flux may tolerate higher concentrations of solids.

   Boilers operating up to 40 bar (580 psig), but which have a local heat flux density greater than 300 kW/m^2 should be treated as those in the column 41 to 60 bar.

   Boilers operating up to 120 bar (1740 psig), but which have a local heat flux density greater than 300 kW/m^2 should be treated as for the column > 121 bar.

2. Plants containing copper alloys in either the feed or condensate system should have the pH of the FW limited to 8.5 to 9.2. If the feed system is completely ferrous, the pH should be limited to 9.2 to 9.5. For plants utilizing the FW for **spray attemperation** or **desuperheating**, the pH should be controlled with volatile alkalis only.

3. The oxygen limits given are those that should be targeted after mechanical deaeration. In addition, it is recommended that a catalyzed chemical oxygen scavenger be used. It is feasible to use **oxygen control (oxygen treatment, OT)** to produce a stable protective film in the boiler, but this is a highly specialized approach, requiring FW of extreme purity and a very high level of specialist supervision; as such, it is outside the consideration of this standard. The table gives values for five common chemical oxygen scavengers. Where FW is used for *spray attemperation* or *desuperheating,* sodium sulfite should not be used.

4. The proportions of iron, copper, and nickel in the FW depend on the materials of construction, the operating age of the plant, and the WT employed. The maxima given relate to normal steady-state operation; they will be exceeded during startup and also possibly during significant load changes. The *weighted mean metal content* should not exceed the figures in the table during the 24 hours following startup and 1 hour following a greater than 20% load change.

Table 12.11 (BS 2486: 1997 table 3): Recommended water characteristics for fired water tube boilers

Pressure at boiler outlet: bar (note 1)	**0 to 20**	**21 to 40**	**41 to 60**	**61 to 80**	**81 to 100**	**101 to 120**	**.121 (11)**
Feed water at economizer inlet							
Total hardness as mg/kg $CaCO_3$ max.	2	1	ND	ND	ND	ND	ND
pH value at 25°C (note 2)	8.5 to 9.5	8.5 to 9.5	8.5 to 9.5	8.5 to 9.5	8.5 to 9.5	8.5 to 9.5	8.5 to 9.5
Oxygen mg/kg as O_2 max. (note 3)	0.02	0.02	0.01	0.005	0.005	0.005	0.005
Fe and Cu and Ni, mg/kg max. (4)	0.05	0.05	0.03	0.02	0.02	0.02	0.02
Total solids, alkalinity, silica	note 5	note 5	note 5	note 5	note 5	note 5	note 5
Organic carbon	note 6	note 6	note 6	note 6	note 6	note 6	note 6
Boiler water							
Phosphate mg/kg PO_4 (note 7)	30 to 70	20 to 50	20 to 40	15 to 30	10 to 20	3 to 10	3 to 5
Caustic alkalinity mg/kg $CaCO_3$	50 to 300	50 to 150	25 to 50	10 to 20	5 to 10	2 to 5	1 to 5
Silica as mg/kg SiO_2 (note 8)	<0.4x OH Alk.	<0.4x OH Alk.	20 max.	5 max.	2 max.	1.5 max.	0.5 max.
Sulfite as mg/kg Na_2SO_3 *or* Hydrazine as mg/kg N_2H_4 *or* DEHA in feed water as mg/kg *or* Tannin mg/kg *or* Isoascorbic acid mg/kg	30 to 50 0.1 to 1.0 0.1 to 0.25 120 to 160 15 to 30	20 to 40 0.1 to 0.5 0.1 to 0.25 NR 15 to 30	15 to 20 0.1 to 0.2 0.1 to 0.25 NR 15 to 30	NR 0.05 to 0.1 0.1 to 0.25 NR NR	NR 0.05 to 0.1 0.1 to 0.25 NR NR	NR 0.05 to 0.1 0.1 to 0.25 NR NR	NR 0.05 to 0.1 0.1 to 0.25 NR NR
Chloride mg/kg C1 (note 9) NVAT (coal) NVAT (oil) AVT (coal) AVT (oil)	—	—	—	 <8 <8 <0.2 <0.2	 <4 <4 <0.2 <0.02	 <2 <0.5 <0.02 NR	 <2 <0.5 <0.02 NR
Dissolved solids mg/kg max.	3000	2500	1000	200	50	20	10
Conductivity at 25°C µS/cm (note 10)	6000	5000	2000	450	150	60	35

NOTE: NVAT = Non-volatile alkali treatment, AVT = all-volatile treatment, ND = not detectable, NR = not recommended.

5. The level of solids in FW depends on the level of BD required to maintain the specified BW conditions. For FW used in *spray attemperation* or *desuperheating,* the solids content should not exceed 1 mg/kg. Modern steam turbines often have strict limits on sodium and other alkali metals (e.g., less than 0.005 mg/kg Na).
6. In general, oil and organic matter that degrade or deposit will produce undesirable effects in boilers. The levels of these contaminants in FW should be minimized. Oils that do not volatilize at the operating pressure should be eliminated from the FW (e.g., steam condensate that could be contaminated with these low volatility materials should not be used in FW).
7. Phosphate need not be used in boilers where hardness can be eliminated from the FW at all times. Its use is not recommended for boilers that may exhibit severe **hideout** (see the section on *coordinated phosphate treatment*). In these circumstances, sodium hydroxide is the preferred **alkalizing agent** and should be dosed to a maximum of 1.5*x* the sodium chloride content.
8. **Silica limits** are based on the avoidance of silicate scale deposition and the limitation of silica solubility in steam.

   NOTE: The usual standard for ***maximum silica in steam*** *used for modern turbines is 0.002 mg/kg. To ensure that this limit is not exceeded, the* ***maximum concentrations of silica in BW*** *is as follows:*

   - *At 50 bar (725 psig), the maximum is 22 ppm SiO_2 at pH 11, 18 ppm at pH 10, and 15 ppm at pH 9*
   - *At 100 bar (1,450 psig), the maximum is 3.5 ppm SiO_2 at pH 11, 2.6 ppm at pH 10, and 2.3 ppm at pH 9*
   - *At 150 bar (2,175 psig), the maximum is 0.7 ppm SiO_2 at pH 11, 0.6 ppm at pH 10, and 0.5 ppm at pH 9*
   - *At 200 bar (2,900 psig), the maximum is below 0.15 ppm SiO_2, irrespective of pH*

9. **Chloride attack** in high pressure, highly rated WT boilers. The ingress of chloride ions can constitute a hazard. The chloride ions can penetrate deposits and hydrolyze to form hydrochloric acid, which then attacks the tube metal. In severe cases, the hydrogen formed in this corrosion process diffuses into the metal. The hydrogen reacts with carbon in the metal, and methane is produced under extreme pressure, thus destroying the metal structure. Failures by this mechanism, known as **hydrogen embrittlement,** are often violent and may cause sections of the tube to blow out.

It is important that the tube surfaces be kept clean to avoid the initiation of corrosion. Regular waterside inspections and, if necessary, chemical cleaning of high-pressure equipment is recommended. The level of chloride that may be tolerated in such boilers during steady operation depends on the type of treatment employed. Where **all-volatile alkaline treatments** (AVT) are used, then the chloride levels should be lower than where **nonvolatile alkalis** (NVAT), such as sodium hydroxide and sodium phosphate, are used. The value may vary, depending on whether the boiler is coal-fired or oil-fired.

10. Conductivities are determined on unneutralized samples without cation exchange at 25 °C.
11. At pressures above 121 bar (1,755 psig), control valves should be agreed on between the boiler manufacturer and the operator. Values given in the table are for guidance only.

12.2.12 Notes and Comments to Table 12.12

1. In the table of **recommended water characteristics for nonfired water tube boilers,** BSI proposes that plants containing copper alloys in either the feed or condensate system should have a FW pH limited to 8.5 to 9.2. If the feed system is completely ferrous, the pH should be limited to 9.2 to 9.5. For plants utilizing the FW for **spray attemperation** or **desuperheating**, the pH should be controlled with volatile alkalis only.
2. The oxygen limits are those that should be measured before the addition of a chemical oxygen scavenger.
3. The proportions of iron, copper and nickel in the FW depend on the materials of construction, the operating age of the plant, and the WT employed. The maxima given relate to normal steady-state operation, and they will be exceeded during startup and also possibly during significant load changes. The *weighted mean metal content* should not exceed the values in the table.
4. Phosphate need not be used in boilers where hardness can be eliminated from the FW at all times. Its use is not recommended for boilers that may exhibit severe **hideout** (see the section on *coordinated phosphate treatment*).
5. **Silica limits** are based on the avoidance of silicate scale deposition and the limitation of silica solubility in steam. The BW silica levels in this table have been set to achieve a level of 0.002 mg/kg in the steam, the normal level specified for modern steam turbines.

Table 12.12 (BS 2486: 1997 table 4): Recommended water characteristics for non-fired water tube boilers

Pressure at boiler outlet: bar (note 14)	**0 to 40**	**41 to 80**	**Above 80**
Feed water at economizer inlet (notes 10 and 11)			
Total hardness mg/kg $CaCO_3$ max.	ND	ND	ND
pH value at 25°C (note 1)	9.3 to 9.9	9.3 to 9.8	9.3 to 9.8
Oxygen mg/kg as O_2 max. (note 2)	0.02	0.01	0.005
Fe and Cu and Ni, mg/kg max. (notes 3 and 8)	0.05	0.03	0.02
Boiler water			
Phosphate mg/kg PO_4 (note 4)	20 to 40	15 to 30	3 to 10
Caustic alkalinity mg/kg $CaCO_3$	25 to 50	10 to 50	2 to 5
Silica mg/kg SiO_2 (note 8)	20	5	1 to 5
Oxygen scavenger (see notes 6 and 7) Sodium Sulfite mg/kg Na_2SO_3 *or* Hydrazine mg/kg N_2H_4 *or* DEHA in feed water mg/kg *or* Tannin mg/kg (note 12) *or* Isoascorbic acid mg/kg (note 12)	 15 to 20 0.1 to 5.0 0.1 to 0.25 120 to 160 15 to 30	 — 0.05 to 0.1 0.1 to 0.25 NR 15 to 30	 — 0.05 to 0.1 0.1 to 0.25 NR 15 to 30
Dissolved solids mg/kg max. (notes 8, 9 and 13)	1000	200	50
Conductivity at 25°C µS/cm (note 13)	2000	400	100

ND = not detectable, NR = not recommended.

NOTE: See Section 12.2.11.8 for more details.

6. The oxygen limits are those that should be targeted after mechanical deaeration. In addition, it is recommended that a catalyzed chemical oxygen scavenger be used. It is feasible to use **oxygen control (oxygen treatment, OT)** to produce a stable protective film in the boiler, but this is a highly specialized approach, requiring FW of extreme purity and a very high level of specialist supervision; as such, it is outside the consideration of this standard. The table gives values for five common chemical oxygen scavengers.

7. Sodium sulfite decomposes at pressures higher than 50 bar and gives rise to sulfur dioxide or hydrogen sulfide in the steam.
8. In systems where the steam and condensate systems are extensive, it is important that any contamination of returned condensate be controlled either by monitoring and dumping or by **condensate polishing**.
9. Many of these boilers provide steam for turbines, and it is important that good quality steam be produced. This requires the correct installation of drum internals and selection of the appropriate boiler water conditions. Boilers with only rudimentary drum internals require lower concentrations to be maintained and/or further mechanical separation equipment installed.
10. The level of solids in FW depends on the level of BD required to maintain the specified BW conditions. For FW used in *spray attemperation* or *desuperheating,* the solids content should not exceed 1 mg/kg. Modern steam turbines often have strict limits on sodium and other alkali metals (e.g., less than 0.005 mg/kg Na). In this case, the recommendations of the boiler supplier should be sought.
11. In general, oil and organic matter that degrade or deposit will produce undesirable effects in boilers. The levels of these contaminants in FW should be minimized. Oils that do not volatilize at the operating pressure should be eliminated from the FW (e.g., steam condensate that could be contaminated with these low volatility materials should not be used in FW).
12. Because of thermal decomposition, the use of **tannin** above 20 bar (290 psig) or **isoascorbic acid** above 60 bar (870 psig) is not recommended.

NOTE: Tannin blends have been used entirely satisfactorily in lower heat-flux, fired WT sugar mill boilers, operating at 650 psig (44.8 bar), using bagasse as the fuel.

13. With regard to TDS and conductivity, only one of these parameters must be measured.
14. Nonfired boilers operating at more than one pressure should be treated so that conditions are consistent with the highest operating pressure.

12.2.13 Notes and Comments to Table 12.13

Table 12.13 (BS 2486: 1997 table 5): Recommended water characteristics of feed water at economizer inlet for once-through boilers

Feed water at economizer inlet (note 1)		
Parameter	**Units**	**Values**
Conductivity at 25°C, after cation exchange	μS/cm	0.2 max.
Oxygen (note 3)	mg/kg as O_2	0.01
Silica	mg/kg SiO_2	0.02 max.
Iron	mg/kg Fe	0.01 max.
Copper and nickel	mg/kg Cu + Ni	0.005 max.
pH (note 2)		8.5 to 9.5
Start up/load charge weighted mean iron	mg/kg Fe	0.1 max.
Start up/load charge weighted mean copper and nickel	mg/kg Cu + Ni	0.03 max.

1. Because there is no opportunity to blow down or remove solids from these boilers, it is necessary that the solids in the FW be kept to a minimum and that any treatment chemicals used be volatile in nature.
2. If copper or copper alloys are used in either the feed or condensate system, the FW pH should be limited to 8.5 to 9.2; otherwise it should be 9.2 to 9.5.
3. The oxygen limit given is measured after mechanical deaeration. In addition, it is recommended that a volatile chemical scavenger be used.
4. The proportions of iron, copper, and nickel in the FW depend on the materials of construction, the operating age of the plant, and the WT employed. The maxima given relate to normal steady-state operation, and they will be exceeded during startup and also possibly during significant load changes. The *weighted mean metal content* should not exceed the values in the table over any 4-hour period.

12.2.14 Notes and Comments to Table 12.14

Table 12.14 (BS 2486: 1997 table 6): Recommended water characteristics for coil boilers

Type of boiler	Low pressure (<40 bar) integral recycle	Low pressure (<40 bar) external recycle	High pressure (<40 bar)
Feed water at coil inlet			
Total hardness mg/kg $CaCO_3$ max.	1.0	1.0	Not detectable
pH value at 25°C	8.5 to 9.5	8.5 to 9.5	8.5 to 9.5
Oxygen scavenger (note 1) Sodium Sulfite mg/kg Na_2SO_3 *or* Hydrazine mg/kg N_2H_4 *or* DEHA mg/kg	 10 to 20 0.05 to 0.1 0.025 to 0.1	 10 to 20 0.05 to 0.1 0.025 to 0.1	 (note 1) 0.02 to 0.05 0.02 to 0.05
Iron, copper and nickel (each of) mg/kg max.			0.02
Coil exit water			
Phosphate mg/kg PO_4	30 to 70	10 max.	3 to 5
Caustic alkalinity mg/kg $CaCO_3$	300 min.	300 min.	150 min.
Silica mg/kg SiO_2 (note 2)	<0.4*x* caustic alkalinity	<0.4*x* caustic alkalinity	<0.4*x* caustic alkalinity
Dissolved solids mg/kg (note 2)	8000	8000	5000

NOTE: ***LP coil boilers with integral recycle*** *are designed with the drain from the water-steam separator recycled within the boiler feed circuits.* ***LP coil boilers with external recycle*** *are designed with the drain from the water-steam separator either being dumped or recycled to the FW tank.*

1. BSI ***recommended water characteristics for coil boilers*** note that it is imperative that the oxygen scavenger used in coil boilers remove all the oxygen in the FW, so the use of a proportionally dosed, fully catalyzed chemical scavenger is essential. Sulfite may decompose at pressures higher than 50 bar and produce hydrogen sulfide or sulfure dioxide in the steam.

2. The required silica and dissolved solids contents of the FW and BW of high pressure coil boilers depends on the steam purity requirements. If a steam turbine is used, steam control elements may suffer from deposition. The silica and solids levels of the equivalent duty WT boiler should be adhered to.

12.2.15 Notes and Comments to Table 12.15

Table 12.15 (BS 2486: 1997 table 7): Recommended water characteristics for electrode boilers

Parameter	Units	Value
Feed water quality		
Hardness (note 1)	mg/kg $CaCO_3$	2 max.
pH		7.5 to 9.5
Iron (note 2)	mg/kg Fe	0.2 max.
Conductivity	μS/cm	400 max.
Boiler water quality		
Hardness	mg/kg $CaCO_3$	0 to 10
Alkalinity Total (note 3) Caustic	 mg/kg $CaCO_3$ mg/kg $CaCO_3$	 600 max. 300 min.
pH value at 25°C		9.5 min.
Conductivity (notes 4 and 5)	μS/cm	400 to 2000
Dissolved oxygen	mg/kg O_2	Nil
Sulfite (note 6)	mg/kg Na_2SO_3	50 to 100

1. BSI **recommended water characteristics for electrode boilers** note that external pretreatment may be required to achieve a FW hardness quality of 2 mg/kg max.
2. Low iron levels in the feed are essential to avoid damage to the electrode from iron deposition. This is achieved only by correct condensate line corrosion treatment. Polymer dispersants should be fed direct to the feed line and boiler to ensure particulate iron is effectively removed with the BD.
3. When **porcelain insulators** are used, an M alkalinity of less than 400 mg/kg should be maintained.
4. For conductivity, refer to the manufacturers' instructions.

5. Optimum boiler conductivity should be maintained using **sodium nitrate** or **sodium sulfite**. If sodium sulfite is used, the conductivity should be maintained within the specified range, irrespective of whether the sulfite reserve is excessive.

NOTE: If nitrate is used, refer to the ***sodium nitrate conductivity guide*** *below:*

- *250 ppm sodium nitrate = conductivity of 345 μS/cm*
- *500 ppm sodium nitrate = conductivity of 685 μS/cm*
- *750 ppm sodium nitrate = conductivity of 1,025 μS/cm*
- *1,000 ppm sodium nitrate = conductivity of 1,375 μS/cm*
- *1,250 ppm sodium nitrate = conductivity of 1,715 μS/cm*
- *1,500 ppm sodium nitrate = conductivity of 2,050 μS/cm*
- *1,750 ppm sodium nitrate = conductivity of 2,400 μS/cm*

6. Some boilers demand the use of volatile oxygen scavengers (VOS) and neutralizing amines to maintain pH levels. The recommendations of the suppliers of VOS should be followed.

12.2.16 Notes and Comments to Table 12.16

1. In the **recommendations for very high pressure and supercritical boilers**, McCoy notes that because only volatile chemicals can be used for water treatment above 2,500 psi, hydrazine alone is added to the FW at 150 to 200% of the concentration of oxygen, which should be less than 5 ppb.

Table 12.16 (McCoy BW table 6.10 and 6.11): Recommended boiler water operating conditions for very-high pressure and supercritical boilers

Components in water and steam. ***Volatile treatments only***	**Suitable concentrations for very-high pressure boiler (2000-3000 psi)**	**Suitable concentrations for supercritical boilers (>3203.6 psi)**
Hydrazine (ppb N_2H_4) FW		10 to 15
Hydrazine (ppb N_2H_4) BW	20 to 30	
pH BW	8.5 to 9.5	9.3 to 9.5
Ammonia (ppb NH_3) BW		250 to 400
Total dissolved solids (ppb) BW	2000	20 max.
Silica (ppb SiO_2) BW	500	20 max.
Sodium (ppb Na) BW		1 max.
Iron (ppb Na) Steam		10 max.
Copper (ppb Cu) Steam		5 max.

At above the critical pressure of 3,203.6 psi, virtually no solids can be tolerated in boiler FW because all of the water is converted to steam, which passes through the turbine. Copper corrosion products tend to be the most troublesome contaminant in supercritical boilers, consequently all efforts must be made to prevent copper and other metallic oxides from entering the boiler. FW quality guidelines include:

- Total iron: 3 to 4 ppb Fe max
- Total copper: 1 to 2 ppb Cu max
- Conductivity: 0.1 μS/cm max

12.2.17 Notes and Comments to Table 12.17

1. In the **recommended feed water quality guidelines,** McCoy notes that for modern industrial boilers, which have extremely high rates of heat transfer, the concentrations for iron should be essentially zero. Similarly, total hardness should not exceed 0.3 ppm $CaCO_3$, even at the lowest pressures; suspended solids in the feed water should be zero, if possible.
2. The tables for *feed water quality* and *boiler salines* were prepared as guidelines only. Values shown reflect the assumption that boilers operated at low pressure can use poorer quality FW than those operated at higher pressures. Thus, FW softened by the hot-lime process contains 15 to 20 ppm $CaCO_3$. This would be satisfactory for an older boiler generating process steam at 200 psi, but it would be unusable at the same pressure for a modern packaged boiler, in which high concentrations of SS are intolerable. Similarly, modern marine boilers have very little tolerance for SS; for these applications, the values given in table 12.17 (boiler salines) are too high.

12.2.18 Notes and Comments to Table 12.18

1. In the McCoy table of **recommended concentrations of boiler salines,** the guidelines for pressures from 100 to 900 psi apply to conventional field-erected boilers with moderate rates of heat transfer, say, 50,000 Btu/hr/ft^2. At high rates characteristic of packaged boilers, large amounts of insoluble material cannot be managed effectively by any dispersant presently available.
2. In the total alkalinity column, zero alkalinity refers to hydroxide ion (i.e., 2P–M). There is always some alkalinity produced by ammonia, hydrazine, morpholine, or other bases.

Table 12.17 (McCoy BW table 6.11): Recommended feed water quality

Pressure (psi)	Silica range (ppm)	Total hardness	*Maximum (ppm)*		
			Oxygen	Iron (note 1)	Copper (note 1)
100	15 to 25	75	—	—	—
200	10 to 20	20	—	—	—
300	7.5 to 15	2	—	—	—
500	2.5 to 5.0	2	0.03	—	—
600	1.3 to 2.5	0.2	0.03	—	—
750	1.3 to 2.5	0.1	0.03	0.05	0.02
900	0.8 to 1.5	0.05	0.007	0.02	0.015
1000	0.2 to 0.3	0.05	0.007	0.02	0.015
1500	0.3 max.	0	0.005	0.01	0.01
2000	0.1 max.	0	0.005	0.01	0.01
2500	0.05 max.	0	0.003	0.003	0.002
3200+	0.02 max.	0	0.002	0.002	0.001

Table 12.18 (McCoy BW table 6.12): Recommended concentrations of boiler salines

		Maximum (ppm)						*Range (ppm)*		
						Sludge conditioners				
Pressure (psi)	**Saturation temperature (°F)**	**Dissolved solids**	**Suspended solids** (note 1)	**Total alkalinity** (note 2)	**Silica**	**Natural**	**Synthetic**	**Residual phosphate**	**Residual sulfite**	**Residual hydrazine**
100	328	5000	500	900	250	150	15	NR†	90 to 100	NR
200	382	4000	350	800	200	150	15	40 to 50	80 to 90	NR
300	417	3500	300	700	175	100	15	30 to 40	60 to 70	NR
500	467	3000	60	600	40	70	15	25 to 30	45 to 60	NR
600	486	2500	50	500	35	70	10	20 to 25	30 to 45	NR
750	510	2000	40	300	30	NR	10	15 to 20	25 to 30	NR
900	532	1000	20	200	20	NR	5	10 to 15	15 to 20	0.1 to 0.15
1000	545	500	10	50	10	NR	3	5 to 10	NR	0.1 to 0.15
1500	596	150	3	0	3	NR	NR	3 to 6	NR	0.05 to 0.1
2000	636	50	1	0	1	NR	NR	1 to 3	NR	0.05 to 0.1
2500	668	10	0	0	0.5	NR	NR	NR	NR	0.02 to 0.03
3200+	705	0.02	0	0	0.02	NR	NR	NR	NR	0.01 to 0.02

† *NR = not recommended.*

13

OPERATIONAL CONTROL OF WATERSIDE SURFACES

Chemical treatment programs are designed to promote clean internal waterside surfaces, but continuous freedom from deposition and corrosion requires excellent operational control. Application of products, regular monitoring, and comparison of analytical results with recognized standards and interpretation of data are all important components of the program.

In addition, a variety of cleaning, inspection, and planned maintenance work is also required, including *boil outs, lay ups, protection of idle boilers* and *nondestructive testing*. Some of these many ancillary tasks are discussed in the following sections.

13.1 SAMPLING AND TESTING STEAM AND CONDENSATE

NOTE: Sampling steam and condensate lines in large process plants such as smelters, pulp and paper plants, steel mills, and the like is potentially dangerous. Site rules must be followed and the use of proper safety equipment employed (safety equipment includes helmet, gloves, goggles, and occasionally a respirator). Under certain operating conditions, ***confined space permits*** *and* ***tag-out or lock-out rules*** *may be necessary and a minimum of two persons required before work begins.*

Water and steam sampling procedures should follow the **American Society for Testing and Materials** method, **ASTM D-1066; British**

Standard guidance on sampling, **BS 6068: Section 6,7: 1994,** or the equivalent. Reliable information starts with reliable sampling, and thus cooling coils are necessary to aid in this quest, no matter the size or design of boiler. Unfortunately only the largest boiler plants tend to be fitted with cooling coils as a matter of course. Probably in excess of 60% of all steam generators and more than 95% of hot water boilers do *not* have cooling coils available. This is a shortsighted design measure and does a disservice to owners and operators who seek to optimize their boiler operations.

Typically, the collected condensed steam should have a temperature of below 90 to 100 °F (approx. 32–38 °C) and for some tests, ideally it should be 77 °F (25 °C).

When starting a new water treatment program, both baseline and operational information regarding levels of steam and condensate contamination generally are required. It may take several weeks of sampling work to fine-tune the program and determine any limitations with regard to steam purity and quality. Thereafter, individual control parameters such as *sodium limits* or *antifoam concentration* may need to be selectively raised or lowered in the BW and the effects tested for in the steam.

As a consequence, good, safe, steam-sampling points are required, and automatic, real-time **continuous analyzer** systems for monitoring of steam and condensate quality are very useful. These requirements usually are not a problem in larger power and process HP boiler plants. Here, each facility tends to have a unique combination of operating conditions and waterside chemistry circumstances that necessitate the provision of a steady stream of reliable operational data, and this can be obtained realistically only from continuous, real-time analysis.

13.1.1 Sampling Steam and Condensate in Higher Pressure Boiler Systems

For larger boiler operators, proper steam sampling points are almost always available using engineered sampling nozzles. Steam sampling is most usually for **saturated steam** and is therefore taken from locations before the superheater. The sample point must be as close to the boiler steam drum as possible, before any contaminants have the opportunity to drop out, or before any condensate film develops on the wall of the steampipe. A **single-port sampling nozzle** is typically employed, made of a piece of pipe inserted through the tube wall with the port centered and opposing the direction of flow. Where sampling of large pipes is

required, **multiport nozzles** generally are used. The nozzle is inserted through the steampipe wall and extends across the steampipe diameter. It provides equidistant, cleanly drilled ports that face upstream to the steam flow.

For **superheated steam,** the sample points should be designed and installed to permit correct **isokinetic sampling.** A modified **multiport nozzle** design ensures that the velocity of the steam entering the sample nozzle is the same as the velocity of steam in the header. The design incorporates a small, high-quality water delivery tube, used to inject water and remove superheat before sample extraction.

If the temperature of the superheated steam exceeds the saturation temperature by 28 to 30 °C (50–54 °F), a *thermal sleeve* is used to attach the nozzle to the steam line and reduce thermal stresses on the nozzle. Isokinetic sampling is especially important where the steam may contain suspended particles.

Grab samples, taken when the sample flow is turned off and on between samples, is one of the most frequent causes of inaccuracies in high-purity BW samples. Fluid and thermal stresses caused by opening and closing samples lines may result in deposits sloughing off lines and aggravate localized sample line corrosion. Samples lines ideally should be run for one or two days prior to the collection of grab samples to avoid inaccuracies. In practice, most high pressure plants have continuously running sample lines, with the water running to a save-all tank for return to the FW system.

In the highest pressure boilers, where online measurement equipment is installed, steam and condensate sampling is taken from the following points, as a minimum:

- Top drum, steam header, or saturated steam line
- Superheated steam
- Condensate piping and/or receivers, after traps
- Primary condensing/ pressure reducing stations

It is preferable to sample vertical pipelines rather than horizontal lines (ideally when the flow of steam is downward rather than rising). Sampling in the vicinity of bends, elbows, and valves should be avoided. At the sample point, the *multiport valve* should be installed perpendicular to the flow of steam.

13.1.2 Sampling Steam and Condensate in Lower Pressure Boilers

For smaller and lower pressure plants, sampling steam and condensate to obtain reliable information may be a problem. Careful inspection may reveal a point in a line where a live steam sample can be directly obtained. But this point may prove to be of little value unless there is a means of connecting a **temporary sample cooler** (such as a *stainless steel coil* in a bucket of cold water).

Often steam sampling is ignored and condensate sampling is taken irregularly from a common condensate receiver. This is seldom entirely satisfactory, but there generally is little incentive to improve the situation until something goes wrong. Ideally, both steam and condensate samples should be taken from each of the main post-boiler loops on a regular basis (even if regular means only once every three months).

When sampling condensate, ensure that the line is thoroughly flushed and use a container that can be quickly capped. Where a sample cooler is not available, fill the container to the top, apply the cap loosely, and keep it closed while cooling the sample. This minimizes the absorption or evolution of carbon dioxide, which can cause distortions of the true pH level. The collection of condensate (as for BW) should be done prior to BD or the addition of treatment, if this is added on a periodic shot basis.

13.1.3 Sampling for Carryover and Steam Purity Tests

In large boiler plants, **carryover** is measured by employing a **single-port sampling nozzle** connected to a steam supply line between the *top drum* and the *superheater*. Sampling from superheaters is difficult, however, because a pump is needed to inject "cool" condensate water into a **double-walled sample probe** (via an **attemperating nozzle**). This is to remove the *degrees of superheat* and thus reduce the tendency for any contaminants to deposit in or on the sample probe, rather than be collected with the steam.

Load swings, water levels, soot blowing, BW total dissolved solids, BW alkalinity and other factors all affect steam purity.

Conductivity, sodium, pH level, silica, ammonia, hydrogen, carbon dioxide, iron, copper and other parameters are typically measured, with alarms and other devices fitted to warn if the steam or water purity goes out of specification.

- Testing for *steam quality* measures the amount of entrained water in dry steam on a weight/weight basis. (Hence the effectiveness of steam separators and reduction in theoretical heat content can be identified.)
- Testing for *steam purity* measures the degree of carryover (typically indicated by an increase in electrical conductivity) and provides a starting point for evaluations into specific types of contaminants such as **iron, silica,** and **sodium**.

NOTE: Pure condensate, for all practical purposes, does not conduct electricity (very pure condensate has an electrical conductivity of perhaps 0.1 to 0.05 μS/cm), and any impurities in the steam are reflected in an increase in conductivity. For the highest precision conductivity measurement testing, any volatile materials present such as ***ammonia*** *(NH_3) and* ***carbon dioxide*** *(CO_2) must be removed. Equipment such as a* ***Larson-Lane Analyzer*** *(which condenses the steam and passes it through an acid-regenerated cation resin) is employed to remove NH_3, while CO_2 is removed by reboiling.*

- Testing for *sodium* (Na) is particularly useful because almost without exception all BW contains sodium. Methods employ either **sodium ion-selective electrodes** or a **flame photometer**, and although both types of equipment have their devotees and disadvantages, they generally can detect down to 0.1 to 0.2 ppb Na. *Sodium ion-selective electrodes* exhibit interference caused by *hydrogen ion activity.* This interference usually is eliminated by raising the pH level to 10.5 by using either **dimethylamine** (DMA) or by passively diffusing **ammonium hydroxide** into the sample.

NOTE: Sodium in the steam is proportional to TDS in the steam. The same is true for BW, and the typical ratio of BW sodium to BW TDS is 1:3.

- At Na levels of 3.0 to 3.5 ppb (TDS of 10 ppb) in the steam deposition in turbines or superheaters is most unlikely.
- At Na levels of 3.5 to 35 ppb (TDS of 10 to 100 ppb) deposition in turbines is possible but unlikely in superheaters.
- At Na levels of 35 to 350 ppb (TDS of 100 to 1,000 ppb) deposition in turbines is quite likely and possible in superheaters.
- At Na levels in excess of 350 ppb (TDS >1,000 ppb) deposition is most likely in both turbines and superheaters.

Steam quality *(degree of wetness/dryness)* and **purity** *(degree of carryover)* limits vary considerably, depending on boiler design, pressure, drum sizes, and a host of other factors discussed elsewhere in this book. Typically, however, steam containing less than 1 ppm of total solids is acceptable in boiler plants operating below 400 psig, whereas this limit is reduced to 0.3 to 0.4 ppm in boilers operating up to 600 psig, and perhaps only 60 ppb in boilers operating at 900 to 1,200 psig.

NOTE: It is important to distinguish between water in steam resulting from ***partial condensation of steam*** *and that resulting from carryover of* ***entrained BW****. Even where steam does not contain measurable carryover from mechanical action, it may still contain volatile amines, ammonia, carbon dioxide, oxygen, sulfur gases, and silica.*

Where sampling indicates that steam purity has been compromised, the first suspects include:

- High and low water levels in the steam drum
- Very variable and rapid load swings, often taking place when the boiler is on manual
- Very high cycles of concentration (high BW conductivity)

NOTE: Soot blowing or operation of the bottom BD may adversely affect steam sampling studies.

13.1.4 Further Notes on Steam Quality and Purity and General Sampling Requirements

- Ensuring superheated steam quality and purity is clearly essential where it is employed in **prime movers** (steam turbines) to prevent downstream units from corrosion and physical damage. For example, where **coil boilers** are employed to drive steam turbines, it should be noted that the steam produced at the coil exit may have between 10 and 30% wetness, and therefore the steam generally is passed through a separator and perhaps a superheater.
- The quality of steam produced in **electrode boilers** is greatly affected by the quality of the electrolyte. For **jet steam boilers,** the BW should be demineralized water, with conductivity provided by adding an electrolyte. For other types of electrode boilers, the FW supplied should be fully softened, as a minimum.

- During commissioning and the early operation of **WT boilers,** the condensate usually is heavily contaminated with *mill scale, oil, particulate iron* and other debris, which can rapidly increase the rate of boiler waterside corrosion. During *boiler startup programs,* the condensate also can be likewise contaminated and may need to be dumped or otherwise rejected, which increases the MU water requirements and creates a higher demand for mechanical oxygen scavenging and internal chemical treatments.
- In **once-through boilers,** intensive steam sampling during the commissioning phase is critical, and the commissioning may be impaired due to the transport of *mill scale* into the boiler. This in turn causes severe pressure drops and a high degree of steam contamination. Considerable BD usually is required to deal with this, and where silica in the FW is high, the BD demand may be even higher.
- When testing BW, the sample should represent the maximum concentration of dissolved and suspended solids in the boiler. The most suitable point for taking the sample is the **continuous BD line.** (Continuous BD lines are specifically designed and located to extract BW from the point of highest solids concentration in the boiler.)
- As an alternative, sampling BW from a point just below the **extra-low-level alarm point** usually is also suitable. However, the BW is not always at its most concentrated point at the water column connection. A sample taken from this point may contain a mix of BW and steam, which leads to errors in sampling and hence, testing, reporting, interpretation, and subsequent actions.
- If a sample cooler has not been fitted, **steam flashing** will occur because the pressurized BW is at a higher temperature than the atmospheric boiling point. Flash samples are overly concentrated compared with samples drawn from the same point via a sample cooler. Also, collecting flash steam samples is hazardous and may lead to burns.
- Samples containing *residual sulfite* or other oxygen scavengers must have minimal contact with air and should be tested without delay. The sample discharge line should be long enough to dispense the sample into the bottom of the sample container without foaming, frothing, or agitation of the sample.

13.2 MANAGING STANDBY AND IDLE BOILERS

It is difficult and generally impractical to store steam for any length of time, and therefore it is generated as and when needed. As a result, boilers may be kept idle for short durations or taken completely out of service for prolonged periods.

Insurance inspections and cleaning programs further add to the frequency at which a boiler may be out of service. During these outages and offline periods, the boiler metal waterside surfaces are especially susceptible to rapid corrosive attack and damage. Consequently, various protection protocols are employed to stave off this risk. The primary factors responsible for downtime corrosion are:

- Warm moist conditions
- The presence of oxygen (air)
- Low pH levels (below pH 8–8.5)

Programs for controlling high corrosion risk are therefore based on excluding all oxygen and, where standing water or moisture is present, by raising the pH to some point above 9.0, depending on the types of metal employed.

13.2.1 Protection of Standby Boilers (Short-Term Offline)

In common parlance, there is no difference between a **standby boiler** and an **idle boiler,** but where any distinction is drawn, it usually is based on the out-of-service time involved. Where the shutdown period is short, perhaps 2 to 3 days or less, boilers may be described as *on standby,* whereas *idle* boilers are shut down for prolonged periods.

Standby boilers should always be stored wet, (i.e., *completely* full of treated water) especially in situations where immediate availability may be required.

Wet lay-up programs are therefore used to protect standby boilers. These are essentially the same programs used to protect idle boilers that may be out of service for perhaps 30 days. (Boilers having outages of longer than 30-day periods generally are subjected to **dry lay-up programs**.)

- The choice of nonvolatile or volatile chemical treatment depends on the design and pressure of the boiler. Typically, an **alkalinity boost-**

er is used to elevate the pH to 10.0 (either *sodium hydroxide, ammonia, morpholine* or *cyclohexylamine*), and a free reserve of 200 ppm of **oxygen scavenger** is maintained using either *tannin, sodium sulfite, sodium erythorbate, hydrazine, carbohydrazide* or *hydroquinone.*

Tannins are particularly suitable for protecting lower pressure boilers (up to 650 psig) because they tend to persist longer than sulfite.

Nonvolatile chemicals are normally only suitable for boiler plant systems that do not contain superheaters or reheaters.

Other chemical sources that give rise to both boiler and steam system alkalinity include **dicyclohexylammonium nitrate** and **diisobutylammonium sulfate**.

Dispersants are often also specified, depending on the level of iron and BW sludge present. *Iron transport polymers* such as acrylic **acid/sodium 3-allyloxy-2-hydropropane (AA/COPS)** and **phosphinocarboxylic acid** (PCA) usually are the most suitable.

- **Emergency standby** or **backup boilers** should be completely filled with *hot water.* Chemically treated, deaerated FW or condensates are suitable water sources for this purpose. **Hot standby** of **LP boilers** can be achieved by installing steam heaters in the offline boiler. Chemicals required are 3 lb of *caustic soda* and 3 lb of *sodium sulfite* per 1,000 gallons (0.4 kg of each per m^3) to achieve 400 ppm P alkalinity as $CaCO_3$ and 200 ppm sulfite as SO_3 in the BW. After filling the boiler, a *surge tank* containing a double strength of chemical treatment should be connected to the steam vent. For temporary situations a 55-gallon drum normally suffices as a surge tank. Alternatively a nitrogen tank supplying gas at 5 psig is suitable.
- If the boiler is on load, this should be backed off at a rate that allows the boiler to cool gradually and avoids the risk of damage caused by high temperature differentials. Sometimes **draw-and-fill cooling** is used to increase the rate of cooling (cooling normally is never more than 100 °F per hour). When the boiler pressure has been reduced to 5 to 10 psig, the steam vent is opened to avoid creating a vacuum.
- The highest quality of water possible should be used when refilling a boiler. Softened water usually is only suitable for LP boilers. For a boiler already online and being taken out of service, a program of additional BD is provided beginning at least 2 to 3 days prior to the standby, to remove BW sludges and minimize the risk of deposition problems during the offline period.

- Wet storage of LP boilers, FT boilers, and WT boilers, either without *superheaters* or with *fully drainable superheaters,* is achieved by being filled to overflowing with hot, treated water and a very small but continuous overflow maintained during the idle period.
- This procedure does not apply to higher pressure boilers having *nondrainable superheaters* or *reheaters.* Here, **steam blanketing** or **nitrogen blanketing** (nitrogen pressurization) at between 5 and 25 psig is employed. First, however, the tubes are backfilled with high-quality condensate or demineralized water and treated with hydrazine (or suitable alternatives) and amine. The boiler is then completely filled with treated deaerated water.

13.2.2 Protection of Idle Boilers (Longer-Term Offline)

Where the offline period is prolonged, the boiler may be stored using either a wet lay-up or dry lay-up program.

13.2.2.1 Waterside Wet Lay-Up

The procedure for wet lay-up of idle boilers over a longer term is the same as for short-term standby; high-quality water is required, the pH is raised to 10.0, and a 200 ppm reserve of oxygen scavenger is provided.

- Testing should be provided each week for pH, OH alkalinity, and oxygen scavenger to ensure that the proper levels are maintained.
- Boilers with superheaters and reheaters should use only volatile organic chemicals.
- Boilers should be effectively sealed and all connections blanked off to prevent air in-leakage. A nitrogen blanket is then provided to cap the system and its auxiliaries.
- The highest possible quality of water should be used for nondrainable superheaters and reheaters to prevent the risk of solids deposition in the units.
- For boilers coming offline, flooding should take place as the unit cools but before the pressure drops to zero.
- Where boilers are filled with water, the treatment solution may need to be made up in a day tank before addition. The floodwater is then circulated via a pump located between the BD line and the FW line to ensure an even distribution of the chemical program.

- In multiple boiler installations, an alternative to nitrogen blanketing is by **wet lay-up by cascading BD.** Here, continuous BD from online boilers is treated with an oxygen scavenger and pH booster and fed into the bottom BD connection of the idle boiler. The hot treated water circulates through the boiler and overflows through the steam vent. This method of storage, apart from protecting the boiler, keeps the fireside dry. This kind of storage is best suited to boiler plants employing *chelant-type solubilizing programs,* rather than *phosphate precipitation programs,* because little or no sludge is transferred to the stored boiler.

A further longer term wet lay-up alternative is through the use of **volatile corrosion inhibitors** (VCIs) such as dicyclohexylamine acetate. These are dissolved in the water at a temperature below 60 °C, and the water is circulated for 4 to 5 hours. The boiler does not need to be completely filled because the VCI migrates to all parts of the boiler and reaches equilibrium in each of the void spaces. With traditional lay-up chemicals, the oxygen scavenger may become depleted easily (which is why the reserve usually is so high) and corrosion protection is quickly lost; however, with VCI programs, there is always a volatile buffer available that maintains equilibrium and hence corrosion protection.

- The proper procedures for **wet lay-up of boiler auxiliaries** are equally important and tend to parallel those methods used for storing boilers.

  Idle FW heaters need special attention because air ingress on the hot shellside tubes during shutdown periods causes oxidation and **exfoliation corrosion.** *Spalling* or *flaking effects* may also occur in intermittently loaded FW heaters (although never in base-load stage heater units) and generally are limited to 70/30 and 80/20 Cu/Ni alloys. Control is by steam blanketing (usually the best practice), nitrogen blanketing, or an *octadecylamine* feed.

  Flooded superheaters are treated with amine to raise the pH of the floodwater to 8.8 to 9.2.
- Where an idle boiler is also subject to cleaning and inspection before going back online, these procedures usually are carried out at the end of the idle period to avoid the risk of corrosion to a clean boiler.

13.2.2.2 Waterside Dry Lay-Up

Boilers having outages of longer than 30 days generally are subjected to **dry lay-up programs** on both the waterside and the fireside. Idle boilers and auxiliaries may be stored either open-and-dry or closed-and-dry. In both programs, the objective is to keep all waterside components completely dry.

- **Open-and dry lay-up programs** generally are suitable only under low humidity atmospheric conditions (<30–40% humidity), and then only for lower pressure boilers. The boiler is drained, washed down, cleaned if necessary, inspected, and then thoroughly dried. Compressed air is used to blow out water from nondrainable and horizontal tubes. Drying is aided by blowing warm air through the boiler. Heaters are placed inside the FT boiler drum or WT steam and mud drums. All apertures including manholes, handholes, furnace door spaces, and stack dampers are left open to ensure a free flow of air. This type of storage is unsuitable if valves leak.
- **Closed-and-dry lay-up programs** are employed under naturally high-humidity conditions. Again, the boiler is drained, washed down, cleaned if necessary, inspected, and then thoroughly dried. Valves must not leak, and seals must be airtight, which is not always possible, especially if maintenance work or periodic inspections are required.

  Moisture absorbents or *desiccants* are required. These are spread on trays and distributed throughout the boiler, so that circulating air passes over them. **Quick lime** (CaO) is used at 8 to 10 lb for every 1,000 lb/hr of steaming capacity. Alternatively, **silica gel** is used at 4 to 6 lb per 1,000 lb of steaming capacity.

  Quicklime should be replaced every two months. Silica gel can be either replaced or regenerated on a similar basis. Silica gel usually is supplied *pink* (due to the presence of $CoCl_2$) and changes to *blue* with moisture saturation. Heating in a ventilated oven at 325 to 350 °F (163–177 °C) regenerates it. **Activated alumina** (*bauxite* containing 75% Al_2O_3) is an alternative to silica gel but is not so effective for this application.
- An alternative to traditional chemicals is the use of VCI materials, such as **Boiler Lizard™** from the **Cortec Corporation**. This product is a VCI powder contained in an inner, water-soluble **polyvinyl alcohol** (PVA) bag and outer wrapping. The wrapping is removed, the inner lining slit open, and the bag left in a suitable place within

the boiler. The VCI volatilizes, protecting all parts of the boiler internals. At the end of the idle period, the boiler is simply refilled and the bag dissolves.

- A further options is to fill the dry, sealed boiler with nitrogen at 3 to 5 psig or dry steam at 5 to 15 psig. If steam is employed, traps on the mud drum or other lowest point remove the condensate. Steam storage has the benefit of keeping the boiler warm, which limits the risk of fireside dampness.
- Idle deaerators or FW heaters usually are isolated from the boiler section and subjected to steam or nitrogen blanketing.

13.2.3 Fireside Protection of Idle Boilers

The combustion process creates deposits that stick to all fireside surfaces. These deposits contain carbonaceous materials and often voluminous quantities of ash, slag, sulfur, and vanadium residues, especially when lower grade fuels are used.

Lay-ups provide an opportunity to remove these deposits; indeed, they must be removed because they attract moisture and promote fireside corrosion. Also, when the temperature of the boiler falls below the **dewpoint,** very corrosive sulfuric acid is formed (the pH of the deposit frequently falls below 3.0).

Prior to shut down, switching to higher grade fuels for a week or so and increasing the use of soot blowers helps remove deposits from fireside surfaces. Additionally, **fuel treatments** such as *combustion additives, slag modifiers,* and *anticaking agents* may prove very useful.

Cleaning procedures include an internal washdown with a 0.5 to 2% soda ash solution, using a high-pressure jet. All wash water must be drained and deposits removed from the boiler. Usually, all external surfaces of the boiler are cleaned as well, in addition to the flue gas side of the *economizer, air heater,* and *ID fans.*

13.2.3.1 Fireside Hot Lay-Up

Hot lay-up is most suited for standby and for short outages for minor repairs. Here, the metal surfaces are maintained at 170 °F (77 °C) or higher by an auxiliary heat source, such as a gas air heater, to deter moisture. Typically, *magnesium-based* treatments are employed at the rate of 1 lb per 1,000 lb/hr of steaming capacity to absorb and neutralize sulfuric acid vapor. These products are blown through the fireside using the FD fan.

13.2.3.2 Fireside Cold Lay-Up

Cold lay-up is most suited for longer term idling and extended outage periods. Again, magnesium-based treatments are employed at rates similar to those used in fireside hot lay-up to absorb and neutralize sulfuric acid vapor.

The risk of corrosion is high with cold lay-up, and all efforts should be made to minimize humidity through the use of desiccants and heaters. Additionally, *film formers* and *temporary coatings* may be applied using spray equipment.

13.3 BOILER INSPECTIONS

Boilers and other pressure vessels (PVs) and associated appurtenances and auxiliaries are comprehensively inspected on a regular basis. Inspection usually occur annually, although for many commercial and light industrial applications, a variance may be issued to permit a temporary extension of a further 6 or 12 months.

Heavy industrial boilers operating in "continuous" processes may be online for perhaps four or even five years before shutting down for maintenance and inspection. Here, correct boiler plant materials selection is critical, and the quality of the various utility support functions must be outstanding if **forced outages** are to be avoided. A heavy industrial or utility boiler that is unintentionally offline may cost $1 million a day in lost production or electricity generation.

The inspection is undertaken primarily to ensure the continuous safe operation of the equipment and to direct repairs or changes in operation if questions of safety or adequacy for service arise. To be of significant value, an inspection must be carried out thoroughly and the results and conclusions compared with those of previous inspections. Local or state authorities may demand annual inspection and provide for penalties if a violation of the appropriate industrial pressure vessel or administrative code is found.

When a boiler is shut down for inspection and maintenance, there may be three levels of inspectors present on site:

- **Authorized or regulatory inspectors,** who operate within a specific jurisdiction and have legal or similar powers to prohibit the use of the equipment or direct repairs where deemed necessary.
- **Plant inspectors,** who are sufficiently experienced and knowledgeable to advise the owners on various aspects of the boiler, such as

its structural integrity, continued safe operation, quality of maintenance, waterside and fireside cleanliness, and likely operating efficiency. Such inspections tend to be semiformal and support rather than supplant the role of the authorized inspector.

- **Informal inspectors,** who have no significant authority and most usually represent the water treatment company. It is always advantageous to permit water treatment technical representatives to inspect the boilers for which they provide programs and support services because they can observe firsthand the results of their efforts during the prior 12-month period (assuming of course, that they are sufficiently experienced to recognizie chemical and mechanical problems). In addition, their relationship with the authorized boiler inspector tends to be mutually beneficial. The representative can provide useful information on the type of water treatment employed, the rationale for program selection, and its operational history, while the inspector draws attention to areas requiring improvement and gives credit when programs contribute to particularly clean and unblemished boiler waterside surfaces.

In the following sections, the informal inspection process is discussed, rather than the more exhaustive and time-consuming regulatory or plant inspection processes.

13.3.1 Preparing for Boiler Inspections

Prior to an inspection, the frequency of boiler BD is increased significantly (often by 50% or more) for two or three days to decrease the level of sludge in the unit. Chemical treatment reserves should be maintained and additional dispersant may be required. MU water should be of the highest quality and deaerated. The increase in BD should be via the manual BD valve where possible. This may prove difficult on very large utility or industrial WT boilers, but when the load is finally dropped, the mud drum and headers should be thoroughly blown down. Also, the *water column, gauge glasses,* and *FW regulator* should be blown down while pressure remains in the boiler.

The rate of *boiler cooling* should be set within the manufacturer's parameters, and the boiler should be drained only when sufficiently cool to avoid the risk of **baked-on sludge**.

Under most normal circumstances, the boiler should be washed out with a hose line during the draining process to further avoid the risk of baked-on sludge. If the potential for boiler sludge is high, however, it

is often useful to provide both *pre-* and *post-wash inspections* as an aid to determining the extent of sludging.

Boiler *fireside walls, baffles, tubesheets, tubes* and *drums* should be cleaned to remove ash and soot before examination. Where soot blowers are installed, they should be utilized as a means of cleaning fireside surfaces before the boiler load has dropped to 50% and should not be operated again, especially if the fire has been extinguished because a risk of explosion exists.

13.3.1.1 Inspection Safety

Safety is the first priority of any inspection program, and appropriate precautions must be taken. Boiler inspections are vitally important and often technically rewarding, but the process usually is dirty, exhausting, hot, and sometimes wet work.

All fires should be extinguished, fuel lines isolated, valves closed, and **lock out/tag out programs** implemented to prevent accidents through the sudden release of some form of energy.

- All **confined space entry permits procedures** and other safety regulations must be followed.
- The inspector should personally examine the safety precautions before entering a boiler. ***He or she should not work in isolation*** (an *inspection attendant* should be available, who has a means of summoning assistance and facilitating a rescue without personally entering the boiler), ***or under particularly hot or poorly ventilated conditions*** (pockets of nitrogen or volatile amine can be dangerous).
- Coveralls, hard hat, gloves, goggles, safety shoes, a good flash lamp, and low-voltage emergency lighting are basic requirements.
- Additionally, a good scraping tool, such as a putty knife or wide-blade screwdriver, plus a small hammer, deposit sample bags, and a camera (if allowed) are also required.

13.3.2 Scope of Inspection Work

A boiler inspection includes a thorough examination of all waterside and fireside surfaces, plus the *permanent boiler log, daily log,* and other water treatment and maintenance records. Any *economizers, attemperators, FW heaters,* and other associated equipment may also be inspected.

Evidence of *waterside deposits, plugging, pitting,* and other forms of *corrosion,* plus *leaks, cracks, bulges, blisters, overheating, surging,*

carryover, staining, and *damage to staybars* and other supports are all recorded.

Where problems are identified, the causes should be determined together with possible remedies and future prevention strategies. If problems are identified, it is likely that the water treatment representative will be called on to explain the causes and provide answers.

More formal inspections also verify the operation of safety and other controls such as *low water and fuel cutoffs, level controls, fusible plugs, pressure gauges, water glasses, gage cocks, stop valves, safety/relief valves, and BD valves and lines.* Also, *FW pumps, flue and damper arrangements, combustion safeguards, name plate specifications, set pressures, boiler connections, floats, mercury switches, bellows,* and other components may be inspected.

13.3.3 Inspecting Boiler Pretreatment Plant

- **Ion exchange plant** should be put into regeneration and inspected for *correct sequence timing, backwash rate, regenerant draw, rinse times,* and *slippage from the service valve.*

  NOTE: Inadequate rinsing may lead to excess chlorides or other regenerants entering the boiler with the MU water, causing surging, carryover, and possible corrosion. Deposits on the seating of the service valve may cause hardness or other contaminant slippage.

- A full bed-depth, core sample should be taken of **ion-exchange resin** and checked for *cracked and broken beads, iron fouling,* and *loss of capacity.* The bed should be checked for loss of volume.
- **Filters** should be inspected for *loss of media and agglomerated or blinded media.* Media support and water distribution systems should be checked for fouling and mechanical soundness.
- **Deaerator spray heads and trays** are subject to oxygen corrosion and erosion damage. The *FW storage area* is also subject to risks of oxygen corrosion. The deaerator *venting system* may block with corrosion debris.

13.3.4 Inspecting FT Boilers

13.3.4.1 FT Waterside Inspections

- Larger FT boilers are internally inspected by entering them from the top manhole, but the waterside of smaller HW heating boilers may

be inspected only through the top manhole and front, back, and side handholds (where fitted). Under these circumstances, plenty of light is needed to be able to examine tubes, especially in small horizontal FT boilers.

- **Tube deterioration** occurs more quickly at the ends closest to the burner and leads to leaks.

NOTE: A tube leak may quickly lead to erosion of adjacent tubes, and prompt action is therefore required to rectify the situation.

- **Tube surfaces** should be inspected for *oxygen corrosion, pitting, bulges, cracks,* or *erosion impingement,* especially at the FW entry point (this may occur even if baffles are present). If there is any doubt about tube wall thickness, tapping with a hammer may help determine areas where a serious reduction has taken place. Where **oxygen damage** occurs, the pitting and tuberculation generally is most prevalent at or just below the waterline, often forming a line along the top surface of each tube. Where **general corrosion damage** is evident, check for an improperly balanced chelant program or previous acid cleanings and compare the results with those of previous inspections.
- **Tubes** should be inspected for *oil or organics filming, sludging and scaling,* or other *deposition.* In severe cases of scaling, *tube bridging* occurs, which affects not only heat transfer rates but also water circulation. Tubes should be clean; claims that an **"egg-shell" thickness of scale** is desirable because it provides protection against corrosion are spurious.
- Where scaling is evident, inspect tubes for signs of **under-deposit corrosion** and the shell floor for **excessive sludge**. A high volume of scale and sludge found on the shell floor may reflect both a scaling problem and incorrect BD procedures. Long BD periods (say, over 10–15 seconds) are ineffective at removing boiler sludge. Shorter, more frequent BD programs are preferable. Also, the boiler floor may not be sufficiently angled to permit sludge to fall easily to the bottom BD area.
- In lower pressure boilers, some *"dusting"* of tubes may be acceptable where softening is not carried out and MU water volumes are high. It is always preferable to treat the cause of the sludge and deposit (via a softener), however, rather than minimize the effect.

NOTE: Dropping a light between the tubes aids identification of any tube bridging. Where some limited tube deposition occurs, a modification of the treatment program to perhaps incorporate a chelant may prove useful in providing an online clean-up program. If so, ensure that oxygen in the FW is always removed and good scavenger residuals are present.

- Along with the tubes, tube sheet, and manhole and handhold flanges, the **boiler shell** also should be inspected for corrosion and grooving. Corrosion along welded seams is more serious than general corrosion of the shell plate and indicates a highly stressed area. Entry points for gauge glasses, BD lines, and other tight areas should be inspected for fouling or blockages. The amount of sludge, old tube scale, and other debris accumulating on the shell floor should be noted. The waterline of both the shell and the tube sheets should be inspected for effects of **surging** and **pitting corrosion**.

NOTE: A wavy waterline incorporating some deposition is a good indication of surging. Where oxygen is present, metal surface pitting corrosion occurs readily at the steam-water interface or waterline.

- Inspect the tube sheet for any signs of cracking (especially around the points of tube insertion) or leaking (perhaps from **tube thinning** caused by excessive, repeated, or poor tube-end rolling).

13.3.4.2 FT Fireside Inspections

- Inspect for *slag* or *deposit formations* and heavy *sooting,* noting the location and quantities found. Inspect the *integrity of refractory.* Inspect the burner area for evidence of *flame misalignment* or other localized heat problems that may cause overheating.
- Inspect both the front and the rear fireside internals to determine if any **leaks** have occurred.

NOTE: When a boiler first starts up from cold, there is always some initial condensation arising from combustion (which generally falls to the rear of the boiler and may form a pool of water). This quickly evaporates and should not be confused with tube leaks that leave evaporated solids behind.

- **High gas velocity** may cause *flame impingement* and *impingement erosion,* generally within the second- and third-pass tubes or at the back arch of **return tubes**. The tubes may *blister* and *deform* through overheating (but rarely collapse).

NOTE: Signs of overheating in the furnace tube are indicated by discoloration or shiny areas.

13.3.5 Inspecting WT Boilers

13.3.5.1 WT Waterside Inspections

- **Economizers** are often vulnerable to active corrosion and deposition on the waterside, resulting in leaking or plugged tubes. This generally is caused by residual oxygen released from heated FW becoming trapped within the economizer. Unfortunately, it often is difficult to inspect economizers internally without cutting away a tube. Some designs have headers with integral handholds that provide for some measure of inspection.
- **Steam drums (top drums)** often are difficult to enter or move around in because of the fixed mechanical equipment contained within the confined space. It should not be assumed that this equipment has always been correctly reinstalled after any previous inspection or maintenance programs. Consequently, steam drums should first be inspected for proper location, orientation, and anchoring of *steam separators, FW lines, baffles, continuous BD lines, and chemical injection lines.*

NOTE: Drum internals should be designed so that thorough mixing of FW and BW occurs, the most concentrated BW is blown down, steam is effectively separated with due regard to quality and purity, and chemicals are properly introduced into an area of rapid mixing. Thus:

- *The continuous BD line should be found in the drum above the first gas pass (the hottest part of the boiler), at a point before the BW mixes with FW, but away from the FW line to avoid short circuiting.*
- *The chemical injection line should be found in the drum at a point after BW and FW mixing and before the downcomers (the coldest point of the boiler), to minimize adherence of precipitating sludges onto tube walls.*

- **Steam drums** and **water-wall headers** should be inspected for evidence of *pitting corrosion, chelant corrosion, cracks, erosion, thinning, sludge fouling,* and *scale deposition.* Also, the waterline should be checked for *surging* and *priming* problems.

- **Generating tubes** and **downcomers** entering and leaving the top drum should be inspected either visibly or via the use of an optical fiber camera or video device (fiberscope, e.g., **Boroscope™**) for signs of *corrosion* or *deposition.*

NOTE: Sometimes it is difficult to inspect generating tubes because of baffling. Time constraints may mean that the baffles are not always removed, although wherever possible at least some of the baffling should be removed. Unfortunately, however, bends generally restrict visual inspections to only a few feet of internal surface, which is why optical devices are popular for inspecting critical areas of large boilers.

- All tubes entering the top and bottom drums are highly stressed and should be inspected for *undercutting* of rolled ends or *cracking* where the tube is flared.
- As the lowest point of supply vessels for *furnace-wall generating tubes,* **headers** are particularly susceptible to fouling by the settlement of suspended solids. Also, headers are not always blown down according to schedule in base-load boilers, and this may add to their potential for sludge deposition. Headers usually have removable end caps that enable an inspection to be carried out, although mirrors and a light source are required to facilitate this.
- Many types of WT boiler are of a one-drum design, but where **mud drums** are fitted, these should also be inspected. As its name suggests, much of the mud, sludge, dislodged scale particles, and other general debris in the boiler ends up in the *bottom* or *mud drum.* This material should be removed and the drum inspected for *under-deposit corrosion, wall thinning, erosion,* and other problems.

NOTE: Mud drums usually are free of fixed mechanical obstacles, but may contain considerable sticky mud, It may be necessary to wear high rubber boots rather than regular leather work boots. Where sludging problems have been experienced, it may be useful to inspect the mud drum both before and after cleaning. If the volume of mud collected is significant, it should be quantified (e.g., a bucket, barrel, or barrow-full) and related to the MU water quality and treatment consumption because a change in pre-treatment or internal treatment may be advantageous. It also may be necessary to provide some form of angled steel sheet to permit boiler sludges to fall more easily to the manual BD valve and thus ensure their removal.

13.3.5.2 WT Fireside Inspections

- **Oil preheaters, burners, stokers, primary and secondary air ports**, and **burner control linkages** should be inspected for fouling or wear.
- Both the **ID** and **FD fans** should be examined for fouling, erosion, and mechanical soundness.
- The gas side of **air preheaters** should be inspected for corrosion and fouling.
- Excessive soot or deposit buildup and *acidic cold-end corrosion* may occur on the fireside of **economizers**. **Soot blowers** can fail due to mechanical wear.
- In the **combustion area**, *heavy slag* and *ash* may form, preventing the passage of flue gas and blinding tubes. Locations should be precisely noted to provide fireside adjustments or to implement a *fuel treatment program.* In coal-fired boilers, drums, tubes, and headers should be inspected for abrasion from *clinker* and *fly ash.*
- **Baffles** and combustion area **tile**, **brickwork**, and **other refractory surfaces** are subject to risks of *thermal breakdown* perhaps as a result of severe local overheating caused by poor flame control. Where baffles are missing or broken, this adds to the risk of local overheating (especially of superheater tubes) due to excessive gas combustion temperatures. As a result, intact baffles and fireside boiler-metal surfaces may suffer from *spalling.* Check for missing or broken **tube hangers** and unsupported tubes.
- *Front and rear walls* should be inspected to ensure that **header bottoms** and **top** and **bottom drum plates** are properly protected and not exposed to direct heat.

NOTE: Where wall fabric is damaged or insulation missing, this usually is evident by the appearance of hot spots on the boiler's outer casing.

- **Steam generating tube banks** may exhibit signs of overheating. This may include combustion area *blistering* or *bulging,* which indicates waterside deposits. *Breakout* of tubes from refractory or tube banks also may occur.
- Misaligned **soot blowers** may cause cutting or erosion of tubes.

NOTE: Blistering (and small bulges) are identified by directing a beam of light close to and parallel to a tube, as the blister stands out in the beam.

Missing or damaged refractory may permit short circuiting of flue gases and overheating.

- The **flue gas exit stack** should be checked for *cold-end sulfuric acid attack, fouling from ash* and *expansion joint cracking.*

13.3.6 Inspecting Steam and Condensate Equipment

- **Blowdown and heat recovery system** (BDHR) *flash tanks* and *heat exchangers* are potential candidates for sludging, leading to restrictions in the drain line or heat transfer surfaces. Deposits in the BDHR heat exchanger may lead to *under-deposit corrosion* and leaks.
- **Steam traps** cannot be inspected during boiler shutdowns. They must be inspected during actual operation and, if suspect, be repaired or replaced at some later stage.
- **Condensate return pumps** and **condensate receivers** are likely candidates for mechanical malfunction, especially in vacuum systems.
- **Condensate lines** and **vented receivers** are vulnerable to *oxygen* and *carbonic acid corrosion.*
- **Pressure-reducing stations, orifice plates, pitot tubes,** and **steam meters** may all suffer from excessive mechanical wear and may therefore malfunction.

13.3.7 Additional Inspection Notes

Inspection protocols become more detailed and exhaustive with increase in boiler size and operating pressure; likewise, larger and higher pressure boilers tend to require cleaning at more frequent intervals than do smaller units. The increased inspection and cleaning demands are required because the monetary loss due to reductions in efficiency may become extremely significant. The effects of fouling and loss of heat transfer in a large utility boiler or turbine unit operating on a knife-edge optimization program may easily cost $100,000 in additional fuel and resources per day.

This level of financial impact is clearly not of same order for operators of small HW boilers, LP steam units, or light industrial firebox boilers, but the principle remains the same. Consequently, boiler operating practice should be designed to enable units to remain as clean as possible, for as long as possible. But where the boiler is dirty or shows

some level of deposition, samples of the debris should always be taken for analysis.

13.3.7.1 Deposit Analysis

When sampling sludges and deposits (waterside and fireside), the *precise* location, quantity estimate, and any deposit accumulation pattern should be noted and, where possible, compared with previous inspections. The color should also be identified at the time of sampling (deposits commonly are *white, yellow, gray, blue-green, brown, or black*).

Analyses performed may include conventional **wet chemistry**, coupled with **atomic absorption spectroscopy** or other **metal-scan techniques** to provide a quantitative elemental assay, plus **X-ray diffraction** to determine the major crystalline constituents.

13.3.7.2 Nondestructive Testing (NDT)

To obtain a clear picture of larger, more complex, offline WT boilers, in addition to visual inspections, it is common practice to trepan or cut sections out of some of the tubes. The deposits found are weighed, reported as a weight per unit surface area, and analyzed. Repairs are then made to the tubes.

This type of work is not an exact science. Consequently, other inspection and measurement methods are employed as an aid in identifying corrosion, deposition buildup, structural integrity flaws, and other types of problems. Methods employed generally are various types of NDT, and the protocols are widely used in preventive or predictive PV maintenance programs, especially for boiler plants used in continuous process applications, where a shutdown may be several years hence. Nevertheless, there is a drawback to the use of some types of NDT programs in that lengthy downtimes may be necessary to complete the testing work. Clearly, these can be cost-prohibitive.

Additionally, and despite its name, NDT may in fact still require boiler components to be drilled or cut in order to install monitoring devices prior to using the test equipment.

Some types of inspection and monitoring equipment include:

- **Ultrasonic testing (UT)**, including **B-scan ultrasonic testing**, employs a *pulse echo pitch catch* technique to determine the integrity of pressure vessels.

- **Radiography** often is used in conjunction with UT, wherein the latter technology identifies an area of fault and the former produces a radiographic map of the precise point of damage.
- **Infrared thermometry** is to identify the *maximum permissible temperature of tube alloys,* to determine *furnace heat flux, scale heat conductivity,* and *tube heat transfer rates.*
- **Chordal thermocouples** are special sections of boiler tube containing thermocouples that are used to monitor increases in tube wall temperature due to the buildup of deposit. Calibration relating to the quantification of deposit rate buildup may be difficult
- **Optical fiber cameras** *(fiberscopes)* are employed to view inaccessible parts of the boiler.
- **Turner gauges** may be used to determine scale thickness in situ. These are *Wheatstone bridge* circuit devices that have proved very useful for 40 years or so. As with chloral thermocouples, calibration may be difficult, and the level of magnetic iron content (magnetite) in the deposit may affect the readings. More modern electronic versions, similar to paint thickness testers, are now available.

Despite the usefulness of this equipment, the devices are not without their difficulties in practical situations. The net result is that there is no single technique that can convincingly, economically, or simply provide all the answers needed to determine the rate of deposit buildup or metal wastage.

The degree of inspection and monitoring work employed must be tailored to the types of boiler units under consideration. For the smallest boilers, this tends to be minimal, but it is extremely comprehensive for the largest industrial power, cogeneration, and utility plants. The only commonality is the need to ensure continuous operational safety.

13.4 BOILER CLEANING

New boilers and other equipment must always be cleaned before being put into service, and existing equipment must be cleaned if it becomes dirty. This applies to both waterside and fireside. There are three different mechanisms that may be employed to clean a boiler:

- **Mechanical cleaning**, including *turbining, drilling, hammering, brushing,* and *scraping.* Mechanical cleaning is very labor-inten-

sive, and this may prove to be prohibitively expensive in some marketplaces. Mechanical cleaning programs do not reach inaccessible parts of the boiler and may cause physical damage to the metal. Mechanical cleaning is commonly employed for removing *fireside deposits,* but also heavy *carbonate* or *phosphate scales* in FT shells and WT drums, where acid soaking might prove less than totally successful.

- **Jetting**, a less labor-intensive mechanical cleaning method, is safe and works on accessible deposits that defeat other methods. It is also quick, although setting up may take some time. Methods include *high-pressure water jetting, sand* or *abrasive grit blasting,* and very sophisticated processes such as **dry ice blasting** and **sponge ball blasting.** Jetting makes sense when trying to remove deposits on generator tubes in the cathedral-like firesides of large WT boilers. *Dry ice blasting,* as provided by **Ultraclean Technology** with its **Cryojet™** process, blasts small pellets of dry ice (at –110 °F or -78.8 °C) in a propellant stream. **Sponge Ball, Inc.** employs sponge balls variously impregnated with *carborundum, glass beads,* and other grits to clean all manner of surfaces without causing mechanical damage. These newer techniques have a number of advantages over traditional methods, including the fact that they are nonhazardous, are nonconductive, and generally either leave no secondary waste or can be recycled. There also is considerably less metal degradation than with, say, acid cleaning.
- **Chemical** remains the most widely used method because it is fast, reaches all parts of the boiler waterside surfaces, usually is low-cost (unless very specialized chemical protocols are necessary), and generally very predictable. However, it is not particularly safe in unskilled hands and does not always respond to all types of deposit. Chemical methods seldom fully dissolve deposits; rather, they tend to break up deposits and detach them from metal surfaces. Chemical cleaning methods almost always produce some level of corrosion during the cleaning program, despite the presence of inhibitors, and although the corrosion rate may be high, this is only for a very limited period.

The following sections are primarily concerned with waterside chemical cleaning and fireside mechanical cleaning.

13.4.1 Chemical Cleaning Basics

Chemically cleaning new boilers before they are put into service is termed **preoperational cleaning** (POC), **precommission cleaning**, (PCC), or sometimes simply a **boil-out.**

Acid washing, alkaline boil-outs, and **online cleaning** programs are commonly provided to existing equipment if it becomes dirty.

A failure to carry out these programs where and when necessary results in reduced heat transfer rates, higher energy costs, corrosion, a lowering of equipment life, and probably operational safety issues.

The scope of work for each of these processes varies enormously with the various types and designs of boiler, with, not unexpectedly, the largest and highest pressure boilers requiring the most comprehensive protocols.

For example, with small commercial **LP steam generators** operating seasonally, an annual **boil-out** usually is provided to remove settled sludge. The procedure may simply require the addition of a **hot alkaline wash** (3–5% *alkaline phosphate/caustic* or *carbonate* solution for 3–4 hours), followed by a thorough rinsing, refilling, and the addition of a passivating treatment (*nitrite-, phosphate-,* or *tannin-based* program, as appropriate). For small, new boilers, a *PCC program* is employed to remove **mill-scale** and **grease** before boiler startup, and this is likely to require precisely the same type of program as an annual boil-out.

In comparison, a large, fossil-fuel **cyclone-fired, once-through, subcritical utility steam generator,** operating as a *peak-load boiler,* may require very frequent planned *outages* for maintenance and cleaning. These offline programs may be scheduled as frequently as every eighteen months to two years to clean away deposits that would otherwise cause *overheating* or *blisters* and ultimate failure if the **creep temperature** were exceeded. The **iron oxides removal cleaning solution** here is likely to be a complex mixture, such as 4 to 5% *hydroxyacetic acid and formic acid*, together with 0.5 to 1.0% *ammonium bifluoride,* and possibly supported by **copper oxides removal** using a *copper-complexing agent.* Following the *acid soak* and *flushing* stages, a **neutralization-passivation program** is likely, using an *ammonia-hydrazine mix.* This full cleaning program may then need to be supplemented at some intermediate period by a cleaning program for **restrictor** and **cyclone tubes,** using 3 to 4% hydrochloric acid and 0.5% ammonium bifluoride.

Within these two extremes comes a wide range of cleaning programs that generally must be tailored specifically to the individual boilers and boiler components in question, after taking into consideration the types and volume of scales and deposits or corrosion products that must be removed.

13.4.1.1 Online Cleaning Basics

When an infrequent upset occurs and boiler surfaces become fouled, it is common practice to undertake some form of boiler *online cleaning program.* Under most circumstances, cleaning is quicker, more successful, and more thorough if conducted *offline.* Although this may be appropriate for utility operators having sufficient installed capacity and planned outages or for very small facilities operating seasonally, it often is simply not a practical proposition for many larger industrial concerns, which may need to operate continuously for several years before shutdown. Here, **online cleaning** is the only option.

This is not simply a matter of adding a *chelant, caustic,* and additional *dispersant* for a few weeks, however. The online cleaning program must be properly planned and measured against timeline expectations. *(Is the rate of cleanup taking place within the anticipated time-scale?)* Also, not all online cleaning programs are particularly well thought out with regard to the cost of the program, the cleaning efficiency, or the time taken to produce the desired results. All too often, expectations are optimistically high, and the result is that the length of time taken, the sometimes significant increase in cost, and the dubious results disappoint the boiler owner and operators.

Online cleaning programs can, in fact, produce excellent results, but only if the nature of the foulant is known by conducting an analysis. Only when this information is available can the correct type of program be selected.

Typically, online cleaning must be carried out fairly slowly and carefully, so that the programs may take 3 to 6 months, perhaps longer, before particularly satisfactory results are achieved. If the boiler is particularly dirty before an online clean is considered necessary, then the combustion efficiency will be lower than desirable. It consequently will take some time before this reduced efficiency improves significantly, and therefore there is an additional fuel cost that must be considered, as well as the cost of the online cleaning program.

Also, corrosion may continue to take place under deposits, or the rate of cleaning may be so slow that some level of damage occurs during the process, either *overheating* or possibly *corrosion* as a result of the cleaning solvent.

In addition to the above considerations, a protocol for online cleaning must identify:

- The monitoring work to be performed (such as measuring the rate of dirt pickup), the frequency of testing, and the sampling points
- Chelant, dispersant, or other cleaner reserves to be maintained
- Mechanisms for carrying out BD and the recommended frequency required to flush debris from the boiler
- The point at which the online clean is deemed to have been completed, the criteria for success, and a review of the process for carrying out the program

13.4.1.2 Online Cleaning Formulations

There are two main routes for online cleaning, either *adjuncts* or *standalone programs.* Within each route, corrective programs are available based on either *high polymer content* or *high chelant content* formulations. The polymer-based products tend to dislodge and disperse foulants, while the chelant-based products dissolve and sequester the deposits. In addition to the formulations described in Section 10.7, some other online cleaners are discussed in the following sections.

1. **Adjunct online cleaning programs.** Here, the primary water treatment program continues to be provided and a supplementary product or formulation is added temporarily, specifically to remove the foulant.

   Here are several adjunct cleaner formulations, typical of what are available in the market.

Adjunct Cleaner Formulation "A"

Materials

Sodium hydroxide 45%	18.00%
PCA	25.00%
HEDP	10.00%
Ucon-lubricant antifoam	0.02%
Water	46.98%
	100.00%

NOTE: This formula is designed for removing calcium and iron foulants. Use at 300 ppm in the boiler. This produces 37 ppm of active polymer for dispersancy and 18 ppm active phosphonate for threshold stabilization.

Adjunct Cleaner Formulation "B"
Materials

Sodium hydroxide 45%	5.00%
SSMA 25%	16.00%
PAA	10.00%
ATMP	5.00%
Ucon-lubricant antifoam	0.02%
Water	63.98%
	100.00%

NOTE: This formula is appropriate for applications requiring enhanced dispersancy of phosphate precipitates and sludges. Use at 300 ppm in the boiler. This produces 12 ppm of active SSMA for phosphate dispersancy.

Adjunct Cleaner Formulation "C"
Materials

Sodium hydroxide 45%	8.00%
EDTA 38% solution	20.00%
PCA	8.00%
HEDP	5.00%
Ucon-lubricant antifoam	0.02%
Water	58.98%
	100.00%

NOTE: This uses a chelant cleaner for phosphate-based programs. Although the feed rate is theoretically based on meeting the chelant demand, in practice, however, much of the demand is satisfied by the existing phosphate precipitant. The bulk of the EDTA is available to strip off old calcium deposits. Cycles of concentration should be limited. Use this formulation at 300 to 400 ppm in the boiler. At 400 ppm product, 30 ppm chelant is provided.

2. **Stand-alone online cleaning programs.** The primary water treatment program is discontinued for a period until the foulant has been removed, after which the original program or a modification is reinstituted.

   Where, for example, a chelant program is employed, the online cleaner will tend to have a *high chelant–low phosphate ratio*, but when this has done its work, it may then be substituted with a *low chelant–high phosphate ratio* material for maintenance duty. The

various stand-alone programs tend to be very comprehensive and, when produced for small boiler applications, may be *multiblend formulations* supplied in one drum.

Here is a typical example of a stand-alone cleaner that temporarily supplants the existing deposit control product. The program still demands the use of an oxygen scavenger and condensate line treatment.

Stand-Alone Cleaner Formulation "D"
Materials

Sodium hydroxide 45%	2.00%
EDTA 38% solution	20.00%
Terpolymer	5.00%
SSMA	5.00%
PAA	15.00%
SHMP 33%	10.00%
Ucon-lubricant antifoam	0.02%
Water	42.98%
	100.00%

NOTE: This is a chelant cleaner with added phosphate. It is necessary to attempt some precision in calculating the chelant demand to ensure adequate excess for online cleaning. Minimum level of 300 to 400 ppm is maintained in the boiler, with low cycles of concentration. The additional BD reduces the risk of simple transport and redeposition of old deposits. At 400 ppm, this product provides 30 ppm of EDTA and 13 ppm of SHMP.

13.4.1.3 Offline Cleaning Basics

Offline cleaning can, and should, be entirely successful, with the simplest methods requiring, say, a 10 or 15% inhibited *hydrochloric (muriatic) acid* solution that is allowed to soak for some hours before neutralization, flushing, and refilling. Where the waterside deposit analysis reveals complex scales, however, it may be necessary to employ several different cleaning solvents. These solvents are added in a multistep process.

The fundamental technology for cleaning has changed little over the years (especially for smaller, lower pressure boilers), but irrespective of the degree of sophistication or the specific equipment to be cleaned,

there is always a step-by-step procedure required, and these steps must be followed precisely (although solvent mixes are available that are designed to limit the number of steps required and thus shorten the offline period). If a step is missed, shortened, or lengthened, or if the cleaning solution is too weak or too strong, too hot or too cold, then the clean will not be entirely successful and problems will soon develop.

Cleaning a boiler offline is unlike online cleaning. Ensuring operator safety is essential because the process generally involves using potentially dangerous acids, sometimes at temperatures of 200 to 300 °F.

Also, localized, short-term corrosion rates may be several hundred mils per year (MPY) and very much higher if suitable inhibitors are not included. Consequently, it is vital to employ only well-trained and experienced personnel and to ensure that the appropriate equipment is available on site and is properly used.

Equally important is consideration for the environment and abiding by the local or statutory regulations. It could be expensive if the rules are not met.

Additionally, it is important to know the true volume of the boiler and to ensure that adequate cleaning solvent and other chemicals are made available before the work begins. For most cleaning programs, the basic steps involve:

1. Preparing the boiler by removing or blanking-off components that may be damaged by the cleaning solution. Also, removing sludges and any loose scale from the tubes, shell, or drum floor (to avoid plugging tubes, the bottom BD valve, or flexible hoses).
2. Filling up the boiler with hot water, adding the appropriate amount of inhibited cleaning solution, and either letting it soak for a time or recirculating the solution via an external pump. Some additional heat may be required to maintain the deposit removal process. For larger WT steam generators, natural circulation methods may be employed by indirectly applying heat to various zones of the boiler.
3. Neutralizing, rinsing, and draining or continuously flushing the boiler until all traces of the cleaning solvent are removed. A passivation stage then follows prior to returning the boiler to service.

NOTE: See also Section 13.4.5 Supplementary Cleaning Notes.

13.4.2 Determining When a Boiler Needs Cleaning

The inspection process is the precursor to determining when a boiler needs cleaning. Visual inspections; cutting out tubes; and the use of *chipping hammers, fiberscopes, Turner gauges,* and other aids are employed, together with a full and representative deposit analysis to assess the requirement for cleaning.

Additionally, comparison of *MU water usage* and *steam production* with *chemical treatment supplied, fuel consumption records,* and *flue gas analysis* will provides early warning signs of **deposit formation**. *Water analysis records* can indicate problems of **process contamination, BW carryover**, and inadequate oxygen scavenging (and therefore the potential for corrosion).

It should not come as a surprise during the inspection that a boiler needs cleaning. Unfortunately, for the owners and operators of many smaller plants, it can be just that, simply because there are no MU water meters or steam charts installed, fuel consumption records are not studied, and water analysis sheets are not properly interpreted and proactive steps taken.

13.4.2.1 Dirt Loading

Heat exchange surfaces must be kept clean; deposits reduce heat transfer efficiency and promote various forms of under-deposit corrosion. *It also is easier to keep a clean system clean than to prevent a dirty system from getting dirtier,* so measurement of the dirt loading or deposit loading on a heat transfer surface is an important part of determining when a boiler needs cleaning.

All deposits contain various ratios of scale and corrosion products, but often one material predominates, such as **calcite** or **magnetite**. These materials have different densities and thermal factors that influence the allowable deposit thickness or weight per unit area before cleaning becomes necessary. Practical allowances usually are between the limitations for each of these two materials. These allowances may be perhaps 50 to 100 mg/cm^2 of surface area for lower pressure boilers and 25 to 50 mg/cm^2 of surface area for higher pressure boilers. (For a more precise allowance, see the information below.)

Referring to Table 4.2 (boiler heat transfer surface cleanliness) and the supporting italicized notes in Chapter 4 concerning **tolerance for deposit thickness**, it can be seen that:

- **For a boiler of pressure rating below 300 psig**, a dirty condition is 10 to 15 mil of dirt thickness, which for *calcite* equates to between 68.8 and 103.3 mg/cm^2 of surface area, and for *magnetite* is between 131.4 and 197.3 mg/cm^2.
- **For a boiler of pressure rating 300 to 1,500 psig**, a dirty condition is 5 to 10 mil of dirt thickness, which for *calcite* equates to between 34.4 and 68.8 mg/cm^2 of surface area, and for *magnetite* is between 65.7 and 131.4 mg/cm^2.
- **For a boiler of pressure rating 1,500 to 3,000 psig**, a dirty condition is 2.5 to 5 mil of dirt thickness, which for *calcite* equates to between 17.2 and 34.4 mg/cm^2 of surface area, and for *magnetite* is between 32.9 and 65.7 mg/cm^2.
- **For a boiler of pressure rating above 3,000 psig**, a dirty condition is more than 2.0 mil of dirt thickness, which for *calcite* equates to a maximum of 13.8 mg/cm^2 of surface area, and for *magnetite* a maximum of 26.3 mg/cm^2.

NOTE: 1 mil = one thousandth of an inch, 10 mil = 0.25 mm.
Very approximately: Eggshell thickness = 1/32 in, or 31 mil.
10 mil = 100 mg/cm^2 deposit, or 93g/ft^2, or 3.3 oz/ft^2.
Thus: a dirt loading of, say, 50 mg/cm^2 equates to approximately 1.65 oz/ft^2.

In a large steam generator, with many thousands of square feet of boiler surfaces, the physical amount of deposit to be removed can be formidable. Even for a modest FT boiler, the amount can be significant, as shown in the following example.

Example of boiler dirt loading:
Assume a FT boiler of, say, 500 HP, having 2,500 sq ft of heat generating surfaces (and 225 sq ft of internal shell below the waterline, which becomes hot and to which scale can adhere). If we also assume that the boiler has a uniform deposit of scale and corrosion debris on all waterside surfaces to an eggshell thickness (31 mil), then the total mass of dirt equates to:

$$(3.1 \times 3.3 \text{ oz/sq ft}) \times 2{,}725 = 27{,}877 \text{ oz, or } 1{,}742 \text{ lb of dirt}$$

13.4.3 Boiler Scales and Deposits

A laboratory analysis of most boiler scales and other types of deposits typically shows the presence of a mixture of several minerals and other

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materials. The major components are almost always a **calcium salt,** such as *carbonate, phosphate, or sulfate* and **iron oxides.** *Copper, nickel, magnesium, silica* and *"organics"* also are normally present as either major or minor constituents.

Common constituents include the following:

13.4.3.1 Carbonates

Carbonate in boilers usually is present as a hard, dense, white to tan or brown **calcite** scale ($CaCO_3$). A tan to brown color usually indicates the presence of iron. Samples of scales and deposits normally "fizz" when tested with concentrated *muriatic acid (hydrochloric acid,* HCl) if carbonate is present, although some preliminary heating may be required.

13.4.3.2 Copper Salts

Copper salts usually are the result of corrosion in the post-boiler section and may be present as red **cuprous oxide** (Cu_2O), black **cupric oxide** (CuO), or blue-green **copper sulfate** ($CuSO_4$). Mostly, copper salts are mixed with *hematite* and *magnetite* and take on a black color.

When a deposit is tested with concentrated HCl, then made alkaline to precipitate iron, and finally the solution is filtered, the presence of copper is indicated by a clear blue color in the filtrate. Also, if a lightly sanded nail is inserted into the acid test solution, any copper present will plate out on the nail.

13.4.3.3 Iron Oxides

Iron oxides are complex corrosion deposits of variable composition that originate from anywhere in the boiler plant system and then are transported to some other location (usually back to the boiler). The most common sources of iron oxide are the **economizer** (pre-boiler section), **boiler tubes** (boiler section) and the **condensate system** (post-boiler section).

When present as a minor constituent, iron oxides typically impart a tan to brown color to the overall deposit. When iron oxides are present as a major constituent, the color is red-brown to black. Where iron oxides are found, *copper oxides* usually are also present (typically at 10–15% of the amount of iron oxide concentration).

If the deposit is tested with concentrated HCl, some of the iron oxides generally dissolve quite easily. If the acid solution is then made

alkaline, the iron precipitates as a brown, lightly flocculating sludge of **hydrated ferric hydroxide** [$Fe(OH)_2$].

Iron in boiler section deposits can also be present as the *phosphate, hydroxide,* or *silicate.*

Mill scale is a three-layer structure, typically with Fe_2O_3 (1–5%) at the atmospheric surface, Fe_3O_4 (10–15%) in the middle, and FeO (80–85%) at the metal surface.

Ordinary **rust** typically is primarily non-ferromagnetic Fe_2O_3 (**ferric oxide**, or **hematite**). It is often red in color and can be found variously as a light and "fluffy" material or as a hard and dense tubercle or other type of deposit.

Magnetite (**ferrous-ferric oxide**, Fe_3O_4, or FeO/Fe_2O_3) is black and magnetic. Magnetite usually is desirable as a *passivating film.* It is found in conjunction with other passivating agents, such as *phosphate* and *tannin*, as a fine, black powder or deposit on flat steel surfaces. The thickness of the deposit often increases with an increase in boiler steel operating temperature. Under less than ideal BW conditions, magnetite may form as a porous, friable deposit (coarse magnetite).

Ferrous oxide (FeO) and **hydrated iron oxide** (FeOOH) can be found as a bright red to red-brown, light and "fluffy" deposits under various conditions, such as in cold FW tanks and freshly acid-washed or wet laid-up boilers.

13.4.3.4 Magnesium

Magnesium typically is present as the *phosphate* [**magnesium hydroxyphosphate**, $3Mg_3(PO_4)_2{\cdot}Mg(OH)_2$] or the *hydroxide* [**brucite**, $Mg(OH)_2$] in boiler section soft sludges, and in hard deposits as the *silicate* (**serpentine**, $2MgO{\cdot}2SiO_2{\cdot}2H_2O$).

13.4.3.5 Nickel

Nickel is sometimes found in boiler deposits as **nickel oxide**, either in the gray-black *nickel (-ous, -ic) oxide* Ni_3O_4 form, or the black *nickel sequioxide* Ni_2O_3. Where present in the boiler, it usually originates from corrosion of **condenser** or **preheater tubes.**

13.4.3.6 Organics

Organics such as *oil* or *grease* occasionally are present in process boilers as a result of either improper precommission cleaning procedures or

online process contamination. The deposit may have a greasy, waxy, charred, or tarlike texture, but more usually is found as a black, highly carbonized, friable material.

Tannins may be found bound up with magnetite in waterside tube deposits. Degradation products of amines, glycols, polymeric dispersants, chelants, and other organics may also be found and usually are reported in the deposit analysis as a **loss on ignition**.

13.4.3.7 Phosphates

Phosphates typically are found as tan to brown boiler tube deposits but also are often present as sludge in the FT shell or WT mud drum. They almost always are found in combination with *carbonate,* and some *silicate* most usually is present as well.

Phosphate-based sludges and deposits such as **hydroxyapatite** [$Ca_{10}(OH)_2(PO_4)_6$] and **tricalcium phosphate** [$Ca_3(PO_4)_2$] usually dissolve to some degree when tested with concentrated HCl, but there is no "fizz".

13.4.3.8 Silicates

Silicates produce hard, dense, gray to grayish brown scales of variable composition. Silicates are complex materials and usually are associated with several cations, including *sodium, magnesium, iron,* and *calcium.*

Most common silicate deposits, such as **analcite** ($Na_2O{\cdot}Al_2O_3{\cdot}4SiO_2{\cdot}2H_2O$), do not dissolve when tested with concentrated HCl.

13.4.3.9 Sulfates

Sulfates typically are found as a hard, dense, white deposit (occasionally in a thin, needle-like crystal form) of **anhydrite** ($CaSO_4$).

Sulfates do not dissolve when tested with concentrated HCl.

13.4.4 Cleaning Solutions and Inhibitors

NOTE: All cleaning solvents are dangerous. They may be strongly acidic or caustic. Additionally, they are likely to be toxic and may liberate dangerous gases or form explosive mixtures with air. Suitable protective clothing and goggles should be worn. Splashes in the eye should immediately be irrigated using clean, cold water. The working area should be well ventilated.

Beware of ignition. No smoking. Do not light fires in boilers containing cleaning solutions. Always add solvent to water, not water to solvent especially sulfuric acid—add acid to water, very slowly and carefully). Where hydrocarbon process contamination of boilers and heat exchangers occurs, deposits and scales may release deadly poisonous gases such as hydrogen cyanide (HCN) and hydrogen sulfide (H_2S) or, in the presence of cupric ion, cyanogen (C_2N_2).

Cleaning solution formulations may include one or more *deposit removers,* plus an appropriate *corrosion inhibitor* (to protect exposed metal). An *antifoam* and often a *wetting agent* [e.g., an **alkylarylpolyethoxy alcohol** with a 12–15 *hydrophilic-lipophilic balance* (HLB) to improve detergency and solubilization] may also be added.

All cleaning solvents should be slowly recirculated in the boiler unless stated otherwise, or where **soaking** is a suitable option. If soaking is used, a premixed solvent is required. For smaller boilers, **recirculating rigs** are often employed. For larger boilers, both recirculating rigs and **natural circulation** (induced by various strategically located heating sources) have been employed. Cleaning methods include:

- **Dissolution,** using **mineral acids** *(hydrochloric, nitric, sulfuric, phosphoric)* or other strongly dissociated acids. Where, for example, *inhibited hydrochloric acid* is used, various reactions take place, including a strong dissolution reaction with **ferric oxide** (Fe_2O_3), a slower reaction with **ferrous oxide** (FeO), and the (hopefully, very limited) corrosion of exposed steel. Although both ferric and ferrous ions are produced, as the combination of ferric and ferrous oxides comprises **magnetite,** these reactions can be summarized in the equation:

Fe_3O_4	+	Fe	+	$8H^+$	→	$4Fe^{2+}$	+	$4H_2O$
magnetite		exposed steel		hydrogen ions		ferrous ions		water

In practice, much of the action is a combination of dissolution and deposit cracking, which results in lumps of debris that may cause blockages if suitable precautions are not taken, such as blanking off valves, using filters, or maintaining velocities of greater than 1 to 2 fps. Draining and hot water rinsing may be required *under nitrogen* in large industrial WT boilers. Considerable rinsing usually is required to remove all traces of acid.

- **Chelation,** using **ethylenediaminetetraacetic acid** (EDTA), **hydroxyethylenediaminetriacetic** acid (HEDTA), **diethylenetriaminepentacetic acid** (DTPA), phosphonates, and other compounds, together with **organic acids** such as *citric* or *formic acid.* Here, the reaction is:

Fe_3O_4	+	Fe	+	$8H^+$	+	4chelant	→	4Fe(ll)chelant	+	$4H_2O$
magnetite		steel		hydrogen ions				chelated iron		water

Rinsing requirements for chelant cleaners are generally less than with mineral acids.

- **Complexing,** using a **complexing agent** such as *thiourea* or *ammonia,* for example, to remove mixtures of **cuprous oxide**, **cupric oxide**, and **plated copper metal**.
- The removal of organics by *industrial detergent cleaners.* These products employ several mechanisms, depending on the formulation, but tend to include **dissolution** (using nonaqueous solvents such as *kerosene, petroleum spirits,* and *naphtha,* **saponification,** by *caustic,* or **emulsification** by *nonionic detergents.*

13.4.4.1 Solvents for Removing Iron Oxides

A number of solvents are used to dissolve and remove iron oxide deposits. These are detailed in the following sections.

- **Citric acid [2-hydroxy-1,2,3-propanetricarboxylic acid,** $(COOH)CH_2C(OH)$-$(COOH)CH_2COOH$]. Sodium and ammonium salts of citric acid are also used. Citric acid functions by complexing with iron rather than by hydrogen ion activity. If *citric acid* is used at too strong a concentration and the pH falls below 3 to 4, insoluble *iron citrate complexes* may form. This problem is best avoided by raising the pH with *sodium hydroxide* or *ammonia* to form the respective salt, at a pH of 4.0 to 4.2. **Ammoniated citric acid** (approximately **monoammonium citrate**) is commonly employed. Clean at 180 to 200 °F (82–93 °C). The citric acid strength usually is 3 to 5%, and it is circulated at 2 to 3 fps for 6 to 8 hours. Dissolution of iron oxides is slow, but both ferric and ferrous ions are sequestered by the ammoniated citric. This process is also suitable for *austenitic SS, aluminum, cast iron,* and *titanium.*

- **Ditetraammonium-EDTA.** The aggressiveness of this and similar materials (such as **triammonium EDTA**) is dependent on the pH of the cleaning solution and the temperature. Typically, ensure that the pH is approximately 9.0 and the temperature is between 200 and 300 °F (93–149 °C), although **sodium EDTA** at a pH level of 4 to 5 and a temperature of 150 to 200 °F (93 °C) is satisfactory as an iron oxides remover.

  Where an **alkaline EDTA cleaning program** is employed, **hydrazine** sometimes is added to help keep the chelated iron in the ferrous state and prevent corrosion of exposed steel. Under very exacting circumstances, such as removing iron oxides from nuclear powered SGs, **triammonium EDTA** together with 0.5 M *hydrazine* may be employed, at a pH of 7 and a temperature of 200 °F (93 °C).
- **EDTA/organic acid** [e.g., **citric, oxalic** (**ethanedioic acid,** COOH·COOH), or **formic acid**]. These solvent mixes provide a slower and less aggressive cleaning program than, say, **ammoniated EDTA/hydrazine,** although they may not be as effective. Use at 150 to 200 °F (66–93 °C). Also, **HEDTA (sodium salt)/citric** or **formic acid** also may be used. This mix may prove to be more successful because of the higher solubility of **HEDTA** over **EDTA**. Clean at 100 to 150 °F (38–66 °C). The organic acid component typically is only 3 to 5%. **Oxalic acid** is the strongest of the common organic acids but is soluble only to the extent of 8 to 9%.
- **Formic acid** (**methanoic acid**, HCOOH). Use at only 120 °F (49 °C) for cast iron and up to 140 °F for *marstenitic SS* (60 °C). Not suitable for *galvanizing, aluminum,* or *enamels. Formic acid solvents* containing the appropriate corrosion inhibitors and iron stabilizers can be very successful in cleaning larger units, such as once-through boilers.
- **Hydrochloric acid** (**muriatic acid**, HCl). Supplied in concentrated form at approximately 32 to 37% w/v HCl in water. This is the "standard" acidic cleaning solvent, but it is often very corrosive and the spent solution needs considerable rinsing. Very aggressive! Typically, clean at 5 to 20% v/v product/water at 150 to 180 °F (66–82 °C), but up to only 120 °F (49 °C) for cast iron and up to 140 °F for *marstenitic SS* (60 °C).

Where the hot acid is recirculated, a strength of 7.5% and a cleaning time of 4 to 6 hours usually is satisfactory, but HCl is also appropriate

for fill-and-soak methods, although the strength required often is 20% and the time period much longer (perhaps 16–24 hours). Recirculation should be slow, only 1 to 2 fps, because the corrosivity of HCl increases significantly with an increase in velocity.

Where the acid is left in the boiler for this length of time, it must be particularly well inhibited. HCl is essentially nonfoaming, although some low-cost by-product acids, which may have a tendency to foam, are sometimes used. Where concentrated acid and water are mixed together in the boiler vessel (**acid blend-fill arrangement**), this work should be completed within 2 hours.

Hydrochloric acid is not to be used where *austenitic SS, galvanizing, tinning, soft solder,* or *enamels* are present. When properly inhibited, HCl can be used to clean **admiralty brass**, **bronze**, **cupro-nickel**, and **monel**.

At 37%, HCl has a specific gravity (sp. gr.) of 1.184; the sp. gr. of 32% HCl is 1.159; of 10% HCl, 1.047; and of 5% HCl, 1.023.

After cleaning, to neutralize, say, 2% HCl, for every 100 gallons, use 244 lb of *soda ash* or 184 lb of *caustic.*

- **Hydrochloric acid/ammonium bifluoride.** Clean at up to 120 °F (49 °C) for cast iron and up to 140 °F for *marstenitic SS (*60 °C). It is widely used where silicates are present with the iron oxides. Typically, 5 to 7.5% HCl is employed. The ammonium bifluoride normally is present at 0.5%, but it may be increased to a maximum of 1.5% for a boiler that has not been cleaned for many years. The presence of **hydrofluoric acid** (HF), which is formed by the reaction of *ammonium bifluoride* with HCl (see equation), tends to increase the rate of iron oxide dissolution and reduce the corrosion rate of exposed steel, when compared to using HCl alone. This is due to the stability of the **hexafluoroferric ion** (FeF_6^{3-}), which prevents the ferric ion from corroding exposed steel.

NH_4F_2H	+	HCl	→	NH_4Cl	+	2HF
ammonium bifluoride		hydrochloric acid		ammonium chloride		hydrofluoric acid

NOTE: Although the addition of HF to HCl can be beneficial in helping to control the corrosion of steel (because fluoride ions form very stable self-limiting complexes with ferric ions), HF should not be used where significant hardness scales are present because ***calcium*** *and* ***magnesium fluorides*** *(CaF_2, MgF_2) may be precipitated.*

- **Hydrochloric acid/stannous chloride.** Modifications of the standard HCl cleaning program to aid control corrosion of exposed steel include the addition of HF, as discussed earlier, but also *stannous chloride.* Where the cleaning program is likely to remove considerable volumes of **rust** and **magnetite**, even in the presence of a *nitrogen-* and *sulfur-based* proprietary corrosion inhibitor, rapid corrosion of exposed steel may develop. This is because the ferric ions (Fe^{3+}) released from ferric oxide act to reduce the exposed steel to ferrous ions (Fe^{2+}).

  If stannous chloride ($SnCl_2 \cdot 2H_2O$) is added, it preferentially reduces the ferric ion to ferrous ion. Two pounds of stannous chloride will reduce 1 pound of ferric ion:

$2Fe^{3+}$ ferric ion	+	Fe steel	→	$3Fe^{2+}$ ferrous ion		
Sn^{2+} stannous ion	+	$2Fe^{3+}$ ferric ion	→	Sn^{4+} stannic ion	+	$2Fe^{2+}$ ferrous ion

  Under alkaline cleaning conditions, **sodium gluconate** can be used to similar effect because the **gluconate–ferric ion complex** is particularly stable.

- **Hydroxyacetic acid (glycollic acid)/formic acid (HyFor).** Clean at 180 to 200 °F (82–93 °C). Typically, a 2:1 ratio is employed (2% hydroxyacetic, 1% formic) for 4 to 6 hours at 1 to 2 fps. Using these solvents at a 1:1 ratio (1.5% of each) provides for a better controlled, slower, and less aggressive clean than when simply using hydrochloric acid. Here, *formic acid* (available commercially as a 70% solution) is the primary remover of iron deposits, and *hydroxyacetic acid* (available as an 85–90% solution) acts in a secondary chelating role. Consequently, this method may be less successful than HCl at dissolving and removing voluminous, amorphous magnetite deposits. *Hydroxyacetic acid* is sometimes mixed with *citric acid,* but it is not always successful at wholly removing iron oxide deposits; however, when *ammoniated* and suitably inhibited, it can be very suitable for *Fe-Cu sludge mixtures.*
- **Phosphonates.** Various phosphonates, such as **1-Hydroxyethylidine-1,1-diphosphonic acid** (HEDP), have been

used as cleaners, although they tend to be expensive. The phosphonate solution is employed at a pH of 9 (obtained by using *ammonium hydroxide*) and at temperatures of 180 to 200 °F (82–93 °C). They provide a chelating action similar to that of the **aminocarboxylic acids.**

- **Phosphoric acid** (H_3PO_4). Supplied as a 75 to 85% w/v strength product. Clean at only 120 °F (49 °C) for cast iron and up to 140 °F for *marstenitic SS* (60 °C). It is not suitable for *galvanizing, aluminum,* or *titanium.* Following the removal of iron oxides with phosphoric acid, the metal surfaces should be passivated with **sodium nitrite** *(oxidizer)* under alkaline conditions (using **sodium hydroxide**). At 85%, H_3PO_4 has a specific gravity (sp. gr.) of 1.69; the sp. gr. of 75% H_3PO_4 is 1.58; of 10% H_3PO_4, 1.053; and of 5% H_3PO_4, 1.025.

NOTE: Sodium nitrite should never be used under acid conditions because dangerous fumes of ***nitrogen dioxide*** *are released.*

- **Sulfamic acid** ($HO{\cdot}SO_2NH_2$). Clean at only 120 °F (49 °C) for cast iron and up to 140 °F for *marstenitic SS* (60 °C). It is not suitable for *galvanizing* or *aluminum* over 150 °F, but it is suitable for *copper, brass,* and *SS.* Sulfamic acid tends to be used only in small systems because of its relatively high cost. It is a crystalline solid and so is easily transported. Additionally, in the dry form it is relatively safe and has a negligible effect on skin. Typically, it is used at 10% strength, and when 5% sodium chloride is added, it is reasonably successful at dissolving ferric oxide.
- **Sulfuric acid.** As a 10 to 20% v/v solution, sulfuric acid can be used to clean 300 series SS, as well as other steels and metals, but not *galvanized steel* or *magnesium.* The cleaned SS can then be passivated with **nitric acid**. In practice, sulfuric acid is seldom used, except by specialist cleaning companies, because of its high **heat of dilution** and terrible burning effect on skin and other tissues. Add acid to water.

  At 98%, H_2SO_4 (66.4 °Be) has a specific gravity of 1.84; at 15% H_2SO_4, 1.102; at 10% H_2SO_4, 1.066; and at 5% H_2SO_4, 1.032.

13.4.4.2 Removal of Copper/Copper Oxides

Where copper corrosion occurs, some small amounts of copper will redissolve and be transported to the boiler section, where they plate out

onto exposed steel to produce a copper-iron couple, and galvanic corrosion of the anodic steel occurs. (The plated copper usually is present as a discontinuous film, some 10–15μ in thickness.) Consequently, *copper* and *cupric/cuprous oxides* are often present in iron-based boiler deposits. They are indicators of both pre- and post-boiler section corrosion, especially in larger WT boiler systems, where corrosion products may also contain *oxides* and **spinels** of Ni, Zn, and Al.

NOTE: Spinels are very hard metal ***aluminates*** *or* ***ferrates.***

When cleaning boilers containing iron-copper deposits (with, say, *hydrochloric acid*), unless special precautions are taken, the cupric oxide dissolves and the cupric ion is reduced to copper, which then replates onto the steel surface, thus beginning the corrosion cycle again.

CuO	+	$2H^+$	→	Cu^{2+}	+	H_2O
cupric oxide		hydrogen ion		cupric ion		water

Cu^{2+}	+	Fe	→	Cu	+	Fe^{2+}
cupric ion		steel		plated copper		ferrous ion

Although various **alkaline citrates** and **inorganic oxidizing cleaners** are sometimes used, the "standard" procedure, where HCl is employed, is to add **thiourea**. This method circumvents the *copper corrosion cycle* and permits the simultaneous removal of iron and copper deposits.

From the first of the two reactions shown, it can be seen that in the acid cleaning solution the **cupric ion** (Cu^{2+}) is formed from cupric oxide. The *thiourea* component then reduces the cupric ion to the **cuprous ion** (Cu^+) and, in a series of reactions, complexes it, essentially preventing the cupric ion from ultimately plating out as copper.

$2Cu^{2+}$	+	$CS(NH_2)_2$	+	H_2O	→	$2Cu^+$	+	$2H^+$	+	S	+	$CO(NH_2)_2$
cupric ion		thiourea		water		cuprous ion		hydrogen ion		sulfur		urea

Apart from generating the cupric ion, the acidic oxidation reaction *(loss of electrons)* produces *cuprous ion* as an intermediate from any **cuprous oxide** that may be present in the deposit. It is therefore neces-

sary to ensure a sufficient excess of thiourea to prevent any additional cuprous ions from reverting to copper and cupric ion, which simply permits the corrosion cycle to repeat itself.

Ensuring the right balance of HCl and thiourea may be difficult with some cleaning projects because the required ratio changes with the copper content of the deposit.

Localized deposits containing copper and copper oxides demand a high local concentration of thiourea, and if an inadequate excess of thiourea is present to complex the cuprous ion, precipitation of the insoluble, white **copper-thiourea monochloride** salt may occur.

$CS(NH_2)_2$	+	Cu^+	+	Cl^-	→	$CuCS(NH_2)_2Cl$
thiourea		cuprous ion		chloride ion		copper-thiourea monochloride

As the overall concentration of copper and copper oxides in the boiler deposit increases, however, less thiourea is required. This is because, as ferric ions are generated during the iron oxide dissolution process, they oxidize the plated copper, which can then be removed from the boiler by forming a complex with thiourea. Conversely, if ferric ions are not generated, the plated copper remains and no complexing can take place.

Fe^{3+}	+	Cu	+	$4CS(NH_2)_2$	→	Fe^{2+}	+	$[Cu(CH_4N_2S)_4^+]$
ferric ion		copper		thiourea		ferrous ion		copper-thiourea complex

13.4.4.3 Solvents for Removing Copper and Copper Oxides

A number of solvents are used to remove copper and copper oxides. These are described in the following sections.

- **Hydrochloric acid/thiourea** [**thiocarbamide**, $CS(NH_2)_2$]. The procedure for cleaning iron oxides containing copper and copper oxides is the same as for cleaning iron oxides alone. A typical formulation is 5% HCl with 2% thiourea, plus corrosion inhibitor, wetting agent, and antifoam. A complete removal of copper is required because the passivation process otherwise will not be effective.
- **Ammonium bromate** (NH_4BrO_3), **ammonium nitrite** (NH_4NO_2), **ammonium perborate** (NH_4BO_3), **ammonium persulfate** [$(NH_4)_2S_2O_8$]. These are all examples of ***inorganic oxidizing clean-***

ers, used in a two-stage cleaning process, following the use of HCl or other iron-removing solvent. These cleaners stabilize copper in the cupric state rather than complexing it in the cuprous state, as in the thiourea method. The use of inorganic oxidizers has been employed for 50 years and is a good method when the extent of copper deposition is not known.

Typically, HCl is added first, then drained, and the boiler rinsed with hot water. Next, one or another of these cleaners is added at 0.5% strength or 1 lb per lb of copper to be removed, and allowed to soak for 6 hours at 160 to 170 °F (71–77 °C). Draining and rinsing again is necessary, followed by passivation, although the ammonia, which prevents the copper from replating, confers some degree of passivation.

The spent oxidizing solution requires the addition of a reducing agent before it can be discharged to sewer or waste treatment plant.

The downside of the *inorganic oxidizing cleaning method* is that the oxidizers are very aggressive and heavy pitting may occur unless the corrosion inhibitor is particularly effective and is present at the right concentration.

NOTE: Most inhibitors are present to the extent of 0.2 to 0.5 %. Where ***bromate*** *or* ***perborate*** *is used as an oxidizing cleaner or copper passivator, it may be necessary to add 1 to 1.5% inhibitor, to ensure that pitting or gouging does not occur.*

- **Ammonium bicarbonate/ammonium hydroxide/ oxygen.** This method is an improvement on the earlier methods because the degree of oxidation can be regulated. It is tailored for those situations in which large amounts of copper and copper oxides must be removed. Also, there is no need to reduce the spent cleaner before discharge.
- **Ammoniated citric acid (pH 10)/air, sodium nitrite** or **bromate (Citrosolve process).** This is a multiple-step process, first using **ammoniated citric acid** (approximately **monoammonium citrate**) at a pH of 4.0 to 4.2 to remove ferric oxide and magnetite. Clean at 180 to 200 °F (82–93 °C). The citric acid strength usually is 3 to 5%, and it is circulated at 2 to 3 fps for 6 to 8 hours.

  Cooling the solvent to 140 to 150 °F and then raising the pH to 9.5 to 10 with ammonia or triethanolamine (TEA) follows this step.

NOTE: Triethanolamine (TEA) also sequesters iron, is less toxic than ammonia, and reduces the risk of ***copper cracking****.*

The temperature is again raised, *aeration* begins, or 0.5 to 1.0% *sodium nitrite* is added to dissolve the copper, which is then complexed by ammonia to $[Cu(II)(NH_3)_4]$. The solvent is circulated for 2 to 3 hours before draining, and rinsing with hot condensate follows this. Rinsing requirements are minimal because of the passivating effects of the alkaline conditions.

Derivations of the *Citrosolve process* use the addition of **ammonium bifluoride** in the first stage and later the addition of **sodium bromate** as an improvement over *air* or *sodium nitrite.*

- **Triammonium EDTA/oxidizer (alkaline copper removal method).** Similar to the Citrosolve method, this process also has some derivations. It is a multiple-step process, first requiring the dissolution of ferric oxide by the use of a 40% inhibited *triammonium* EDTA solution at a pH of 9.2 and high temperature (approximately 300 °F/100 psig) for 3 to 6 hours. Next, the temperature is lowered to 200 °F and air is injected into the boiler over a 2- to 3-hour period, at a rate of 40 to 80 cu ft per 1,000 gallons of boiler volume. This step oxidizes the *ferrous chelonate*, and the resulting ferric chelonate then oxidizes plated metallic copper. The aeration step also aids circulation and passivation. Finally, the boiler is given a single rinse of hot condensate.

  This process is suitable for direct firing of the boiler. It is much safer than using acids to remove iron oxides, and the aeration step also passivates the boiler.

13.4.4.4 Solvents for Removing Scales

The most common nonferrous or copper scales include:

- **Acmite**, *sodium iron silicate,* $NaFe(SiO_3)_2$
- **Analcite**, *sodium aluminum sulfate,* $NaAlSi_2O_6{\cdot}H_2O$
- **Anhydrite**, *calcium sulfate,* $CaSO_4$
- **Aragonite**, *calcium carbonate,* $CaCO_3$
- **Brucite**, *magnesium hydroxide,* $Mg(OH)_2$
- **Hydroxyapatite**, *calcium phosphate,* $Ca_{10}(OH)_2(PO_4)_6$
- **Quartz**, *silica,* SiO_2

- **Serpentine**, *magnesium silicate,* $Mg_3Si_2O_7 \cdot 2H_2O$

Most scales contain several of these salts, together with iron and some copper. Therefore, the choice of cleaning solvent or mixture must take account of these different constituents. (Refer to the previous sections for more details of many of these solvents.)

- *Calcium/magnesium carbonate/hydroxide* and *calcium phosphate* can be removed by using 5 to 15% **hydrochloric acid** at 140 to 150 °F, by recirculating **tetrasodium EDTA** at 200 to 300 °F, or by 7 to 10% **sulfamic acid** at 140 to 150 °F. The temperature may need to be a little higher to start the dissolution process.
- *Calcium sulfate* cannot be removed by HCl. Suitable solvents include **neutralized** (pH 6.5) **tetrasodium EDTA** at 200 to 300 °F, together with **ammonium carbonate**; **EDTA/organic acids** (*acetic, citric, formic,* etc.) at 140 to 150 °F; or sometimes, 1% NaOH followed by 5% HCl at 140 to 150 °F.
- *Silicates* can sometimes be removed by an **alkaline boil-out** at 50 to 100 psig but more usually require the presence of **hydrofluoric acid**.
- *Sulfides* can be removed by slowly heating with 5 to 10% HCl and scrubbing or flaring the **hydrogen sulfide** (H_2S) generated. The addition of an aldehyde may be required. **Alkaline gluconate programs** comprising 2% *sodium gluconate* [$CH_2OH(CHOH)_4COONa$] in a hot 5% solution of *caustic* is also effective.
- *Disulfides* such as *pyrite* FeS_2, require oxidation with hot, 7 to 10% **chromic acid** (H_2CrO_4).

  Where *silicates* are present and **hydrofluoric acid** is required, the most usual means of addition is through the use of *ammonium bifluoride*. (See Section 13.4.4.1, Solvents for Removing Iron Oxides, Hydrochloric Acid and Ammonium Bifluoride).
- **Hydrofluoric acid** (HF) is a weak acid, so the effect of the hydrogen ion is negligible when dissolving iron oxides. When silicates are present, however, it acts as an intensifier for their dissolution. Normally, the HF concentration required is 0.5% for up to 3% silica. If the silicate concentration in scale is much higher, the HF may be raised to 1 or 1.5%. When the cleaning program is in progress, ammonium bifluoride is added during the last 2 or 3 hours of the process.

NOTE: Extreme care must be taken when HF cleaning programs are undertaken. Do not under any circumstances allow the acid to reach skin or body tissues. Toxic gases may develop. Excellent ventilation is required.

13.4.4.5 Inhibitors for Cleaning Solvents

Without the addition of corrosion inhibitors, acid cleaning or pickling processes to remove oxides and scales would result in severe corrosion of exposed metal surfaces. Acid corrosion is an *electrochemical* or *redox process,* and raising cleaning temperatures or acid strength (lowering the pH) increases the hydrogen ion concentration and consequently the rate of corrosion.

Inhibitors must inhibit the rate of corrosion without diminishing the cleaning of oxides, scales, and general foulants. They do this by the formation of **chemisorption bonds**, generally interacting with cathodic or anodic areas of the metal, although some inhibitors can function in more than one way, depending on their concentration in the cleaning solution.

Cathodic inhibitors are passivating inhibitors; they raise the hydrogen overvoltage, thus impeding the reduction of hydrogen ions at the cathode. They are suitable for inhibiting sulfuric or phosphoric acids. Examples are *benzotriazole* (at low concentrations) and *alkylamines.*

Anodic inhibitors limit the oxidation of iron by sharing the lone pair electrons on the nitrogen with a metal ion or atom and supressing the anodic reaction. Examples are *benzotriazole* (at high concentrations), *pyridines, thiols,* and *quinolines.*

General adsorption inhibitors form a physical barrier over the entire metal surface. Examples are *diphenylamine* and *furfuraldehyde.*

Both anodic and general inhibitors are nonpassivating and are suitable for use with hydrochloric acid–based cleaners. Other inhibitor groups include **filming amines** such as *polymethylimine* and *diamines, the rosin-amine ketones,* and also some of the *imidazoline surfactants.* The imidazolines provide increased protection at levels up to their *critical miscelle concentration* (CMC), above which there is a leveling off as a thick, adherent diffusion barrier is formed.

All modern corrosion inhibitors used for acid cleaning processes are **nitrogen-** or **sulfur-based** organic compounds. Inhibitors containing both nitrogen and sulfur groups tend to be the most effective, not only for mineral acids but also for organic acids and chelating agents. Examples include *thiourea, thiomorpholine,* and *phenolthiazine.*

In practice, although there are many dozens of potentially effective inhibitors that can be called upon, extensive use generally is made of readily available proprietary products. The most common product ranges are the **Armohib® (AKZO Nobel Group)** and **Rodine® (Parker Amchem/Henkel Group)** brands.

The corrosion rate of carbon steel in 10% HCl at 160 °F is approximately 0.6 mils/hr. Obviously, the corrosion rate is more than this level for 15% HCl or at higher temperatures.

As a comparison of corrosion-inhibiting effectiveness, 0.25% **Armohib 28** must meet a performance specification, with 15% HCl at 200 °F, of less than 0.22 lb/ft^2/day. This equates to 0.022 mils/hr or under 4% of the uninhibited acid corrosion rate.

NOTE: 0.022 lb/ft^2/day = 1,075 milligrams per square decimeter per day (mdd).

Given that, mils per year (mpy) = 1.437 × mdd/D, where density D = 7.85 for carbon steel.

Armohib 28 performance specification = 1.437 × 1,075/7.85 × (24 × 365) = 0.022 mils/hr.

- **Inhibitor required for hydrochloric acid** (cleaning grade, non-foaming): **Rodine 52** or **Armohib 28** at 1 to 3 gallons per 1,000 gallons of dilute acid
- **Inhibitor required for organic** or **powdered acids**: **Rodine 85** or **Armohib 31** at 1 to 4 gallons per 100 gallons of concentrated acid, or 1 to 4 gallons per 100 lbs of powdered acid
- **Inhibitor required for hydrofluoric acid in presence of HCl** or for **phosphoric/sulfuric acids**: **Rodine 51** or **Armohib 31** at 1 to 2 gallons per 100 gallons of concentrated acid

13.4.4.6 Passivators for Cleaning Solvents

Passivating agents are chemicals that promote the formation of a passivating film on the surface of a metal or alloy, such that the electrochemical behavior of the metal or alloy then approaches that of an appreciably more noble metal.

For steel, passivation is achieved by the surface formation of a tough, adherent mixture of oxides. The passive film is primarily **gamma-magnetite** (γ-Fe_2O_3) but also contains **gamma-hydrated ferric oxide** (γ-FeOOH). The film thickness is perhaps 15 Å to 30 Å (**angstrom units**).

There are various passivation chemistries commonly available. Some are better than others, but the strongest oxidizers produce the most effective passivation. The addition of air to the boiler during passivation improves weaker passivators such as *ammonia/hydrazine.* Chemistries include:

- **Citrate/iron/nitrite passivator:** The *Citrosolve process* using air or 0.5 to 1.0% $NaNO_2$ or $NaBrO_3$.
- **Phosphate/nitrite passivator:** A combination of 0.25% NaH_2PO_4 (MSP), 0.25% Na_2HPO_4 (DSP), 0.5% $NaNO_2$.
- **Carbonate/nitrite passivator:** Based on 1.0% Na_2CO_3 and 0.5% $NaNO_2$. The carbonate may be replaced by *caustic*, except where there is a risk of **caustic cracking**.
- **Ammonia/hydrazine passivator:** An *alkaline hydrazine* solution (pH over 9.0, 0.5% N_2H_2) provides a useful passivator. If there are concerns over the use of hydrazine, *diethylhydroxylamine* (DEHA), *erythorbate,* or *carbohydrazide* may be substituted. Air blowing improves the passivating effect.
- **Gluconate passivator:** *Sodium gluconate* is an excellent sequestrant of ferric and cupric ions in alkaline solutions. It can be very useful therefore to add sodium gluconate to neutralizing, rinsing, and passivating solutions to prevent the formation of insoluble ferric hydroxide when acidic solutions are diluted. The addition of 0.5 to 1.0% gluconate also prevents **flash rusting** if the passivation step is delayed.

13.4.4.7 Solvents for Removing Organics

A variety of formulations exist for cleaning organics from burners and other fireside areas. **Soot**, **oil**, and **grease** removers are widely available; the formulations are often very specific and can be produced in both aqueous and nonaqueous solvent bases. Nonaqueous solvents commonly include *petroleum spirit, naphtha,* or *odorless kerosene.*

Nonaqueous solvent degreasers tend to work as *cold degreasers,* but where considerable quantities of grease must be removed, aqueous-based **emulsifying degreasers** are employed, and these work best in hot water or steam solution.

The removal of dirt and stubborn grease generally requires the use of aqueous-based, **heavy-duty industrial cleaners**. These cleaners may or may not contain traditional ingredients like *caustic* or *phosphate* (which can be replaced by *silicates* or *organic surfactants*).

All heavy-duty cleaners contain combinations of *alkalinity builders, wetting agents, penetrants, emulsifiers,* and other ingredients. Cleaning methods for using these products may include brushing, soaking, and pressure jetting.

Degreasing small parts can be achieved with solvent sprays. *Chlorinated hydrocarbons* such as **trichloroethylene** (*tricho*) are sometimes used, normally in a heated vapor bath, although special handling, solvent recovery, and disposal methods are required.

Some formulations can be particularly complex, but three examples of basic formulation cleaners are provided here.

Heavy-Duty Multipurpose Cleaner	
Materials	
Potassium hydroxide (50%)	2.0%
Oleic acid HLB 11.2	3.0%
Propylene glycol monobutylether	3.5%
Sodium metasilicate	1.5%
Tridecanol POE 7	5.0%
Pine oil	0.5%
Water	84.5%
	100.0%

Carbon Remover and Oil Penetrant	
Materials	
Cresylic acid	10.0%
Xylene	56.0%
Tridecanol POE 7	5.0%
Propylene glycol monobutylether	15.0%
Potassium hydroxide (50%)	1.5%
Oleic acid HLB 11.2	3.0%
Amphoteric imidazoline	3.0%
Pine oil	0.5%
Water	6.0%
	100.0%

Emulsifiable Oil/Grease Solvent Cleaner	
Materials	
Lauryl alcohol POE 4	7.0%
Lauric diethanolamide	3.0%
Oleic acid HLB 11.2	2.0%
Propylene glycol monobutylether	5.0%
Odorless kerosine	83.0%
	100.0%

Waterside, organic-based process contaminants and deposits, such as polymeric or tarry materials, tend to require a different approach for their effective removal from boilers and heat exchangers.

- **Polymeric sludges and tars** can be removed by heating a 1% **caustic** and 0.7% **potassium permanganate** ($KMnO_4$) solution for 12 to 24 hours at 150 to 175 °F, followed by draining and flushing.
- **Hydrocarbons and carbonized or coke deposits** can be removed by **chromic acid**. The chromic acid oxidizes the binders holding the deposits together. Use a 10 to 20% solution for 12 to 24 hours at 190 to 200 °F. Chromic acid cannot be effectively inhibited and is not suitable for cleaning *copper, brass, aluminum, zinc,* or *cast iron* because these are all rapidly attacked.
- **Asphalts and waxes** can be removed by dissolving in hot naphtha for 3 to 4 hours. The naphtha benefits from the addition of 0.1% of a *water-soluble surfactant* (HLB value of 15–20, such as **polyethylene glycol 600 monolaurate**) and 0.1% of an *oil-soluble surfactant* (HLB value of 0–5, such as **propylene glycol monstearate**). The solution must be circulated; fill-and-soak methods are unsatisfactory.
- **Oily surfaces** can be deoiled by using a high HLB value emulsifier such as *dioctylsulfosuccinate*, together with antifoam, applied either as a hot-water soak or pressure washed.
- **Oily/rusty surfaces** that need cleaning can be simultaneously deoiled and derusted by employing a hot, **alkaline gluconate program** (5% caustic, 2% sodium gluconate) with 0.2% *anionic* or *nonionic surfactant.*

13.4.5 Supplementary Cleaning Notes

Additional information regarding waterside and fireside cleaning programs arae described in this section. (See also Section 13.4.1.3 concerning online cleaning basics.)

13.4.5.1 Precommission Cleaning (PCC) and Alkaline Boil-Outs

New boilers, heat exchangers, and other equipment must be provided with a PCC program to remove *oil, grease, mill scale, pipe-threading compounds, drawing compounds,* and other detritus that otherwise prevent the formation of clean, passivated metal surfaces and encourage

under-deposit corrosion. This type of program is well accepted in larger boiler plants but sometimes is not carried out by the contractors or installers of smaller units. (This is simply due to ignorance of the fundamentals of corrosion and passivation.)

Where equipment has been in operational use for some length of time (say, several years), and despite the use of appropriate internal and external water treatment programs, it may become necessary to provide some form of basic offline cleaning to restore heat-transfer efficiency. For smaller HW and LP steam FT boilers, especially where external water treatment is minimal and internal water treatment is limited by cost considerations, the frequency of offline cleaning may be annual, perhaps at the end of the winter heating season.

In practice, *PCC programs* and *basic offline cleaning programs* are virtually the same. Both types of program rely on providing an **alkaline boil-out**.

These cleanings are relatively simple, but critically important. A boil-out cleaning solution is added (on small boilers it is often pumped in via a *hose cock (hose bibb)* and the boiler is then lightly fired for a period of between 6 hours and 48 hours.

The time required for the PC and boil-out depends on the size of the boiler, the amount of material to be removed, and whether the cleaning is for a new or used boiler.

End-of-season boil-outs for small FT boilers may only take 4 to 6 hours, whereas a PCC program for a large WT steam generator may require 48 to 72 hours or more.

Cleaning solutions also vary in complexity, depending on the ratios of *oil/grease* to *rust/mill scale* and other factors. The most common components include:

- **Trisodium phosphate** (TSP), Na_3PO_4
- **Disodium hydrogen phosphate** (DSP), Na_2HPO_4
- **Sodium hydroxide** (caustic soda), NaOH
- **Sodium carbonate** (soda ash), Na_2CO_3
- **Sodium metasilicate**, Na_2SiO_3, or in the hydrated form, $Na_2SiO_3 \cdot 9H_2O$

Usually, any two of these materials are combined to provide the required degree of causticity, general detergency, and de-oiling abaility; a nonionic wetting agent and perhaps an antifoam may be added.

A typical powdered formulation may be added at 0.5% w/v and require 2,000 to 3,000 ppm of phosphate to be present in the boiler. Half-strength solutions are useful for flushing once-through boilers or for neutralizing acid washes.

13.4.5.2 Outline of Acid Cleaning Procedure for Smaller FT Boilers

- All necessary permissions and standard safety procedures must be complied with before any cleaning work is carried out. This includes locking out the steam header and FW valves with chains and padlocks and attaching safety tags.
- Any brass valves of other components should be removed and blanks installed.
- The circulation pump should be a centrifugal type with a plastic or PVC impellor, or cast iron with adequate corrosion inhibitor. The acid tank, hoses, and other equipment should be connected to and from the boiler using suitable connection points. This usually is the bottom BD connection (with the valve removed) and the open manhole as the top point.
- Acid volume requirements must be established and delivered to site. (Acid can be supplied preinhibited or inhibitor added on site.)
- The boiler should have been previously drained and all sludge removed with a pressure jet. It should be filled with fresh water, then checked for pressure and vacuum and the integrity of the circulation rig and hoses.
- Following this, the top manhole should be knocked in and the boiler fired to raise the water temperature to the appropriate level. The fire should then be extinguished.
- Drop the water level if necessary to allow for the acid and ensure that all hose lines are tied down. Begin full water recirculation.
- Acid should be added, slowly and carefully at first to determine if foaming will take place. Extreme care is required in the first hour while acid is being added because a delayed foaming action can take place, resulting in acid siphoning out of the top manhole. A separate water line and antifoam should be made available to kill foam as it occurs.
- The recirculating cleaning process should be carried out uninterrupted for 4 to 24 hours, depending on the severity of the scales and

deposits. Ammonium bifluoride should be added as needed. If the deposit is very high in iron, then adding it soon after the start of the program aids the dissolution of iron. If the deposit is high in silica, it should be added closer to the end of the program to break up the silica after the iron has been dissolved.

- Upon completion, the spent acid solution should be neutralized and pumped to a suitable disposal point. The boiler should be thoroughly rinsed and all sludge washed out.
- All cleaning rig equipment should be removed and boiler components replaced. The boiler should be refilled with fresh water, a passivation solution added, and the boiler lightly fired for several hours to passivate all internal surfaces.
- When the boiler is brought back into service, the water treatment program should implemented. Higher than normal levels of BD and sludge dispersant should be maintained for the first week to remove all fine sediment.

13.4.5.3 Outline of Acid Cleaning Procedure for Smaller WT Boilers

The procedure is very similar to that for FT boilers except that more preliminary survey and basic engineering work are often necessary.

- WT boilers usually have a manhole door at either end of the top and bottom drums. These are obviously closed during cleaning, so it often is difficult to gauge the effectiveness of the clean.
- The top hose connection point is usually the level controller.
- Calculations are necessary to determine the volume of the drum(s) and by how many inches or centimeters the hot water must be dropped to allow the acid to be injected. This may need to be translated into the number of minutes taken for the required quantity of water to be drained via the bottom BD valve.
- The equipment layout must be devised to ensure proper circulation of acid, not only from drum to drum, but also from the headers. This may require additional pumps, the use of a manifold, or the moving of hoses from one leg to another.
- Similar precautions are required for the neutralization and rinsing stages. Also, the rinse hose must be put down every tube, starting from the end of the drum and working down the line. All traces of

mud and sludge must be moved down to the mud drum, from where it can be easily removed from the boiler.

13.4.5.4 Considerations for Acid Cleaning Larger Industrial WT Boilers

Cleaning large industrial WT boilers generally is a complex program involving considerable preclean planning and engineering work. The amount of scale and deposit to be removed may well be anywhere from 3,000 to 8,000 lb or more.

- The cleaning program usually requires a multiple-step approach, involving the removal of *copper* and *copper oxides* as well as *iron oxides, calcium scales,* and possibly *silicates.* Where copper removal is required, provision must be made for blowing air through the boiler and the tubes. This makes for some difficult site engineering work, but it has the benefit of promoting passivation upon completion of the cleaning and rinsing stages.
- Large industrial boilers are often *natural circulation boilers.* When considering the circulation of the cleaning solvent, this can be achieved by either a forced or natural circulation system. If forced, it is necessary to tie together all bottom drains into a common supply to the circulating pump suction. If natural, a firing plan must be devised to raise the water temperature to 250 to 300 °F in order to permit natural circulation to take place. Circulation is enhanced if cyclic heating and cooling patterns can be established.
- The quantity of solvent required usually is considerable because the boiler volume may be anywhere from, say, 10,000 gallon for a 250,000 lb/hr steam generator to 70,000 gallons for a 3M lb/hr unit.
- Addition of solvent usually is via a **blend-fill station**.
- Additional sampling lines are needed at different points on the boiler to allow the *solvent concentration* and *iron pickup rate* to be checked during the procedure.
- A complete tag list of all valves is required to ensure that all safety rules are complied with. Also some of these valves will be required to operate during the procedure, so the *valve open/close sequencing program* must be recorded.
- Raising the temperature of the water from ambient to working temperature may take 4 to 8 hours. The solvent cleaning period will be

an additional 12 to 24 hours. More solvent additions may be needed during this time to maintain concentration. Also, a period of perhaps 4 to 8 hours is needed at the end of the clean to ensure complete iron pickup and stabilization. *(If this laboratory testing work is not carried out effectively, considerable quantities of iron oxides may remain in the boiler and not be dissolved.)* Air blowing and copper pickup may add an additional 4 to 6 hours. Draining and rinsing with three to four boiler volumes of condensate will take another 12 to 24 hours.

- Next, the boiler must be passivated. The boiler is filled above normal working level and *ammonia/hydrazine* or a similar passivation treatment is added. The boiler is first given a hydrostatic test. Following this, the water level is dropped, and the boiler is lightly fired for 4 to 6 hours to ensure adequate passivation of the boiler surfaces.
- Finally, before going into service, the boiler is partially dropped and the top drum and tubes are inspected to determine the effectiveness of the clean. This is likely to require that some tube sections be cut out for sampling.

13.4.5.5 Fireside Cleaning of Small FT Boilers

Fireside cleaning is essentially a manual labor job that requires brushing, vacuuming, and similar work practices. Close attention to preparatory work, such as installing plastic sheeting to minimize the spread of soot, helps keep the work site clean.

- Technicians must wear suitable safety and protective clothing, including a hard hat, gloves, goggles, and respirator with a HEPA filter.
- No work should be attempted until the boiler has properly cooled down, all safety and shut-off switches are in the off position, and all *lockout* and *tagout* procedures have been followed.
- The burner and associated equipment must be wrapped up or otherwise protected against dirt and soot. The front doors are opened and plastic sheeting is attached to minimize the spread of soot. The tubes are brushed, and the soot and dirt are vacuumed away while brushing takes place. Some contractors have truck-mounted vacuum systems to increase efficiency and minimize post-boiler cleaning work.

- The back doors are opened, and all residuals from front-end cleaning are removed. Any additional rear-end cleaning is carried out. The deposit box at the base of the chimney flue is checked, and all flue soot is vacuumed away.
- The boiler doors and openings are closed, properly gasketed, and sealed. All protective sheets and covers are removed. Lockouts and tagouts are removed, and finally the unit is inspected before firing-up recommences.

13.5 SOME TROUBLESHOOTING NOTES

This section covers some examples and notes on common but unrelated problems, all of which rely in part on the effective observation of boiler plant operating conditions and the interpretation of daily water analysis log sheets.

13.5.1 Managing High Sludge Problems in Lower Pressure Boilers

There can be several reasons for high levels of sludge in the BW, such as insufficient BD, the excessive use of dispersant (which then acts as a flocculant), excess precipitant, or simply hardness leakage through the softener on the MU water line. In many cases, however, high sludge is the result of the production of calcium hardness salts (either phosphate or carbonate) stemming from the use of precipitation programs and unsoftened MU water.

In lower pressure boilers, especially those employed in the myriad of ordinary factories located around the world, high sludge may present a serious problem. Commonly, where boiler designs provide for a significant internal drum or shell volume, the use of *soda ash* and *caustic soda* to prevent calcium and magnesium scales by precipitation reactions (**internal softening**) is employed. This use of soda ash as a reactant for FW contaminants is much rarer today than, say, 25 or 30 years ago in high-efficiency boilers operating in fully industrialized countries, simply because the design and high heat-flux operation of modern boilers cannot tolerate the volumes of sludge produced.

Where **carbonate conditioning** programs are employed, it should be noted that, apart from high sludge volumes, CO_2 also results from the added sodium carbonate and the alkaline earth FW contaminants, as shown here:

$$\underset{\text{soda ash}}{Na_2CO_3} + \underset{\text{water}}{H_2O} \xrightarrow{\textit{heat}} \underset{\text{sodium hydroxide}}{2NaOH} + \underset{\text{carbon dioxide}}{CO_2\uparrow}$$

$$\underset{\text{calcium bicarbonate}}{Ca(HCO_3)_2} + \underset{\text{caustic soda}}{2NaOH} \xrightarrow{\textit{heat}} \underset{\text{calcium carbonate } \textit{sludge}}{CaCO_3} + \underset{\text{sodium carbonate}}{Na_2CO_3} + \underset{\text{water}}{H_2O}$$

The production of carbon dioxide in turn produces a low pH in the condensate system, requiring additional neutralizing amine to compensate.

It is difficult to manage the problem of high sludge production in lower pressure boilers where precipitation programs, especially carbonate conditioning, are used because it has a knock-on effect resulting in condensate line corrosion. The answer is always to install a water softener. The payback time is very short because of the reduced BD necessary as a result of decreased sludge production.

13.5.2 Managing High Silica Levels in Raw Water Makeup

High levels of silica in the raw water supply can lead to serious risks of deposition in boilers, especially if cycles of concentration (COC) also are high. The incoming silica can be reduced by adsorption on **magnesium hydroxide** [$Mg(OH)_2$] precipitate during lime-softening processes, or by the addition of magnesium hydroxide in a reaction tank, followed by filtration.

Where silica removal from raw water is not practiced, it is commonly managed by raising the alkalinity of the FW. However, high alkalinity water may lead to BW carryover, but simply reducing this high alkalinity without concern for silica removal is a recipe for disaster. Glassy silicate scales undoubtedly will occur.

13.5.3 Understanding the Significance of High Iron Levels When Operating a Chelant Program

EDTA and NTA chelant and phosphate-chelant programs are widely used in all types of boilers. Where a stable, passivated magnetite film exists, there is little risk of corrosion when using these products, and under normal alkaline boiler conditions, the chelation of ferric iron [$Fe(OH)_3$, Fe_2O_3, Fe_3O_4] will not occur.

Chelant programs are *solubilizing programs,* and any small level of transported iron present, originating from the condensate system, is generally mopped up.

However, high levels of either chelant or oxygen affect the redox tendencies of iron-oxygen reactions. Consequently, *overdosing chelant in the presence of some oxygen,* or *high DO levels in the presence of chelant,* permits the liberation of Fe^{2+} ions (corrosion) from a metal surface and their subsequent chelation, thus preventing the formation of blanketing oxides or hydroxides. The result, therefore, of excess chelant *and* unscavenged oxygen is corrosion of BW metal surfaces. Consequently, it is essential that if high iron levels are recorded, the source of the iron should be identified before serious problems develop.

In practice, the addition of a small amount of phosphate to a chelant program is recommended as an aid in improving control and reducing the potential impact of chelant corrosion.

13.5.4 Identifying High Water Losses in HW Heating and Other Closed-Loop Systems

Closed-loop systems should lose very little water, perhaps only 5 to 10% of the system volume per year. In practice, however, losses often tend to be much higher than this, perhaps due to unforeseen maintenance work that necessitates a system to be partially drained. A typical loss is more likely to be 50% of the system volume per season. This obviously causes problems with regard to maintaining adequate chemical treatment reserves for effective deposit and corrosion control. In fact, often the first sign that a closed-loop system is losing water is when a periodic test is undertaken and the result indicates a reduced level or complete lack of treatment reserve.

If and when water losses occur, the most usual response is simply to add more chemical; it is only when this exercise is repeated one or two more times that a water loss is considered and checks are carried out to identify the source of the leak. The first step in verifying water losses is to install a water meter on the MU line. The following checklist may also help.

- Check all *circulating pumps* for leaks around packing, glands, or mechanical seals and replace or tighten as necessary.
- Check all *pressure relief valves.* These can open to relieve excess pressure in the system caused by temperature changes or failing pressure regulator on the MU line.

- Check *automatic air vents* for water leaks, especially if they pass directly to a drain.
- Check the *expansion tank.* If it is full of water, there is likely to be insufficient air space for expansion and the relief valve will open.
- Check *backflow preventers* on the system as well as on the city mains supply to the building.
- Check for a malfunctioning *pressure regulator* by installing pressure gauges before and after the regulator. The regulator should be set for 2 psig above the highest head in the system at the normal operating temperature and pump circulation rate.
- Many common closed-loop inhibitors have a colored dye added. If this dye appears on the external face of flanges, pumps, or heat exchangers or in the drain pan of a *fan coil unit* or *humidifier,* this usually is a good indicator of a leak. Most inhibitors are strongly alkaline, however, and the dye may simply indicate minor weeping through a gasket accentuated by the penetrating ability of the alkali. If the closed-loop passes through a leaking heat exchanger, the dye will show in the primary steam, condensate return, or water system. An analysis of the primary steam-water system will reflect changes in the pH level, conductivity, and other parameters.
- If a serious leak is suspected, use a **fluorescent tracer dye** to identify the source of the leak. These dyes can be seen in drains and other dark places with the aid of an ultraviolet lamp at concentrations of below 1 ppm.

If serious water losses occur and action is not taken, the MU will bring oxygen into the system, and pitting corrosion of the boiler of heat exchanger tubes may take place.

13.5.5 Understanding the Significance of Hardness Breakthrough in Lower Pressure Boilers

Under circumstances where water softeners are used to treat the MU water for an industrial boiler plant facility and water analysis periodically shows BW alkalinities that are lower than expected, the first thing to check is the water softener.

Determining calcium levels normally does not identify hardness breakthrough because the calcium salt simply reacts with phosphate precipitant (or similar treatment) and is lost as a sludge. It does, however, produce an immediate and noticeable reduction in alkalinity. *(Calcium bicarbonate* breaks down to *calcium carbonate* and *carbonic acid.)*

If hardness breakthrough occurs and goes undetected for any length of time, the treatment reserve is swamped and quickly becomes depleted. This loss of treatment is serious because **calcium carbonate scaling** can result. The reduction in alkalinity also can permit **silicate scaling** to occur and prevent adequate maintenance of the magnetite film, which protects the waterside metal surfaces from corrosion.

Check the softener for adequate salt and run it through a regeneration cycle to ensure that the correct level of brine is drawn into the resin bed. The resin may lack adequate capacity due to fouling or cracking, or it may have been partially lost down the drain. Alternatively, the softener may be undersized.

Simply checking the treated water for hardness at some time during the working day generally is of little benefit because the softener may operate perfectly satisfactorily for many hours and then become exhausted several hours before the end of its service cycle. This type of problem frequently leads to periodically low BW alkalinities. The treated water must be checked every hour or so until to the *end* of the service cycle. Additionally, samples should be taken immediately after the softener returns to service to ensure that all the excess chloride has been rinsed away. If not, then the boiler suffers from a sudden influx of dissolved solids and **surging** and **BW carryover** results.

13.5.6 Optimizing Treatment Programs and Control Parameters in High-Pressure Industrial Boilers

Large industrial boilers tend to operate at pressures of 950 psig or thereabouts. They use copious quantities of high-quality FW and minimal amounts of chemical treatments, and are often subject to considerable swings in steam loads. In addition, they seldom have the availability of a full spectrum of sophisticated online waterside monitoring equipment that would perhaps be found in a base-load utility boiler plant, and such equipment that is available may be operating at the limits of accuracy. (The larger fossil-fuel and nuclear-powered utility plants tend to have not only very sophisticated skid-mounted chemical injection systems but also comprehensive, online *boiler steam-water analyzer panels,* such as those from **Johnson March Systems, Inc.**). All of these factors make effective monitoring of treatment levels and optimization of waterside control parameters very difficult and time-consuming. If there is not very much to measure and the available measuring devices do not have very low levels of detection, program optimization may be a problem. Nevertheless, there are several tools and techniques that can be

employed, and for the most part, the most useful rely on proven, relatively simple surveillance methods.

13.5.6.1 Monitoring Via Tracer and Tagged Polymer Systems

At the top end of the program monitoring scale is the use of **online fluorescence tracing systems**, whereby *tracer dye polymers* form part of the water treatment program and their concentration can be measured online at various locations throughout the boiler plant system. Much less expensive, handheld *fluorometers* are now available to conduct the same type of analysis at the laboratory bench or on the boiler house firing-floor. These tracer dye polymers can be used to determine:

- The degree of carryover from fluctuating load boilers and the effectiveness of strategies designed to minimize the problem
- Optimum BW cycles of concentration
- Chemical feed requirements and the optimization of proportional dosing control equipment

The most widely known of these tracer polymers are the **Trasar®** products from Nalco, of which the latest offering is **NexGuard®**, a **polyacrylic sulfonate** (PAS) designed for high-pressure operation. Other tracer polymer systems include **Optidose®** (from **Rohm and Haas Company**) and **Bel-Trak®** (Biolab/Water Additives Division of **Great Lakes Chemical Corp.**).

These *tracer* and *tagged polymer* products are very useful for conducting test work such as in the examples given above, but, similar to their application in cooling water, the monitoring system only measures the bulk-water concentration of polymer. This may have little or no relevance to metal surface chemistry and the protective integrity of the magnetite film.

13.5.6.2 Monitoring Iron Oxide Transport

The **transport of iron oxides** throughout the system is a very noticeable effect resulting from less than fully optimized chemical treatment programs and associated control parameters in high-pressure boilers.

A good condensate control program, using the correct mix of different distribution ratio (DR) neutralizing amines, will minimize corrosion and limit iron transport. A "standard" control method is often

simply to measure the pH level at various points throughout the post-boiler section (and sometimes to make residual amine determinations as well). The proof of good control, however, is the demonstration of low levels of *suspended iron* and the conversion of troublesome, yellow or red Fe^{3+} ferric iron (**hematite**) into black **magnetite**. (Almost all **transported iron** is in the *suspended* form rather than *dissolved,* irrespective of the boiler plant design or operating conditions.)

A monitoring program may take several months to complete, but the test procedure is quick and simple. It consists of collecting 1-liter samples of condensate and filtering them through a 0.45μ pore size, **Millipore** or similar standard membrane filter system (a membrane filter housing mounted on a stout glass laboratory water aspirator or conical flask, which is connected by rubber tubing to a vacuum hand pump). The filters holding the trapped iron oxide are then compared to known color standards (see Figure 13.1).

This procedure provides a practical demonstration of the effectiveness or ineffectiveness of the program.

- If the filters are stained with red and yellow, there is inadequate deaeration.
- If the suspended iron is high, there is a pH level and iron corrosion problem.
- Ideally, there should be minimal staining due to trapped suspended iron, and the color should be black.

13.5.6.3 Monitoring Dissolved or Entrained Hydrogen in FW and Steam as an Indicator of Corrosion Rates

Some degree of general corrosion always takes place in utility boilers; even in well-protected units, this may still represent 200 to 300 lb/yr (90–136 kg/yr) or more. Startups tend to produce the highest rates of corrosion, but shutdowns, thermal cycling, and reduced loads also can produce exaggerated corrosion levels. As a result, it is standard practice for many operators of high-pressure steam-generating plants to employ **dissolved hydrogen analyzers** as an aid to understanding the type and degree of various possible corrosion mechanisms that can take place in the various steam-water circuits. This type of equipment measures extremely small levels of entrained hydrogen (< 20 ppb or μg/l) by detecting differences in the *thermal conductivity* of air used to scrub the hydrogen from the sample. (Hydrogen is significantly more thermally conductive than other common gases.)

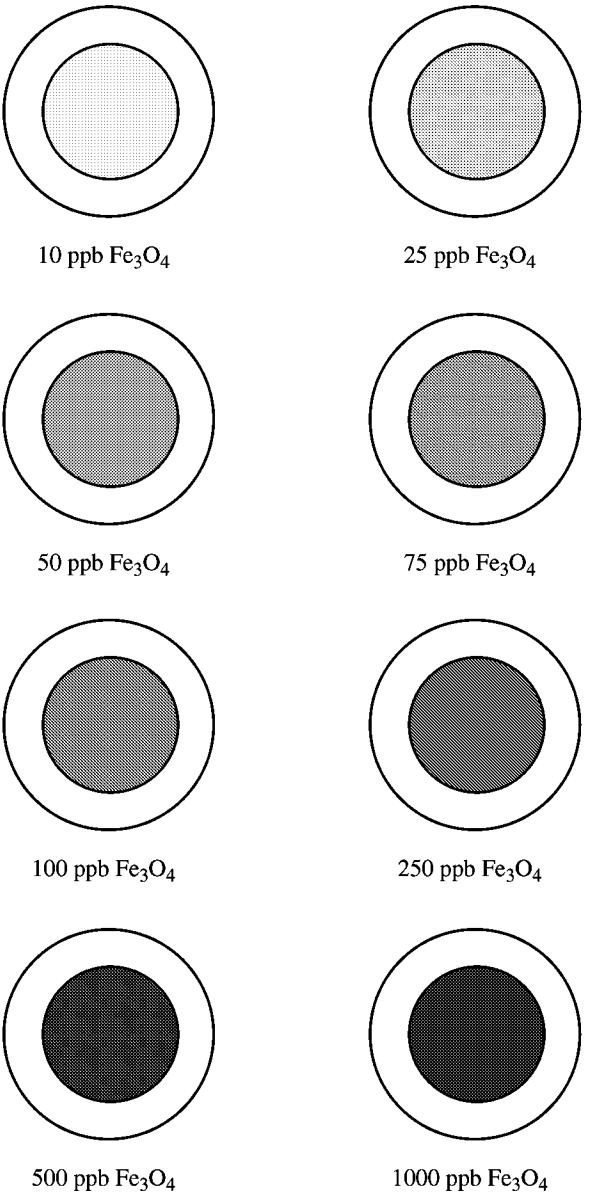


Figure 13.1 Black color comparison standards for the measurement of suspended/transported iron oxide (Fe_3O_4) content in condensate, based on filtering 1 liter samples through a 0.45μ membrane filter.

Hydrogen can be produced as a result of the breakdown of *hydrazine* or *amines, general etch corrosion,* or *localized corrosion* that may, in turn, lead to the development of **hydrogen embrittlement corrosion** *(hydrogen damage).* Depending on the source of hydrogen, the rate of production can be affected by various parameters, such as steam-water flow, load swings *(thermal cycling),* and *heat flux.* Consequently, an accurate interpretation of the results of entrained hydrogen monitoring may be difficult and also tends to be specific for individual boilers.

Nevertheless, extensive studies have shown that, with careful calibration and operation, extremely useful information that helps maintain utility boilers at knife-edge performance levels can be gleaned. Some generalizations resulting from monitoring dissolved or entrained hydrogen in FW and steam are:

- Where AVT programs are employed, maximum protection against boiler waterside corrosion occurs when the FW conductivity is below 3 μS/cm.
- For high-pressure boilers, dissolved hydrogen (H_2) should be limited to < 1 ppb in FW, < 3 ppb in saturated steam, and 10 ppb in superheated steam.
- High levels of hydrogen in steam do not necessarily indicate that *hydrogen damage* will occur.
- Hydrogen evolution resulting from the breakdown of hydrazine or amines is negligible. Typically, 100 ppb of hydrazine produces only 0.4 ppb of hydrogen.
- Where **general corrosion** occurs, the rate of hydrogen production is relatively independent of heat flux. Thus, the concentration of hydrogen is inversely proportional to steam flow.
- Where **localized corrosion** occurs, the rate of hydrogen production grows with increase in heat flux, and the dissolved hydrogen concentration rises with increase in steam flow.
- When the load on a utility boiler changes from a *steady state* to cycling up to a *peak load* or down to a *reduced load,* the concentration of hydrogen in steam can easily triple, indicating a significant increase in corrosion in FW heaters and boiler section components.

13.5.7 Estimating Energy Losses in Low-Pressure Boilers Caused by Deposition

One primary emphasis of this book has been to promote clean waterside surfaces because fouling due to boiler sludge or scaling produces a quantifiable decrease in operating efficiency and a corresponding increase in energy costs. An example of **energy loss estimation,** making use of the heat energy loss chart shown in Chapter 10 (Fig. 10.4) is shown below.

Compare a 400-hp LP steam FT boiler, having clean waterside surfaces, operating at 85% of maximum continuous rating (MCR) for 8,500 hr/year and 78% efficiency, with the same unit having alternately 1/16 inch of sludge deposit and 1/32 inch of iron and silica deposit. Assume No. 2 fuel oil has a heating value of 142,000 Btu/gallon and costs $0.85/gallon.

Note: 1 boiler hp = 33,472 Btu/hr (0.033472 MBtu/hr)
1 lb steam = 970 Btu/hr (from and at 212 °F)
1 boiler hp = 34.5 lb/steam hr

1. **Clean boiler:** Energy input = 400 × 85/100 × 0.033472 × 100/75 × 8500 = 128,979 million Btu per year.
2. **Boiler having 1/16 inch sludge:** This type and thickness of deposit translates into a 5% reduction in heat transfer, or a loss of 6,449 million Btu per year. To produce the same volume of steam requires an additional 45,415 gallon of fuel, at a cost of $38,600 per year.
3. **Boiler having 1/32 inch iron or silica deposit:** This type and thickness of deposit translates into an 8% reduction in heat transfer, or a loss of 10,318 million Btu per year. To produce the same volume of steam requires an additional 72,664 gallon of fuel, at a cost of $61,800 per year.

13.5.8 Estimating Deaerator Steam Demand

Given the importance of deaerators in removing oxygen from FW, it is important to understand the steam-heat energy relationship. The following example uses this relationship and refers to Table 3.2 (Steam Tables Suitable for Pressure Deaerators).

Example: A boiler plant facility is located at an elevation of 5,000 feet. The deaerator processes 50 gpm feedwater at 10 psig with an inlet temperature of 180 °F. How many lb/hr of steam are required?

NOTE: psia = psig + psi atm

It is first necessary to determine the value for psi_{atm} using the following equation:

psi atm = (14.697 − 0.0005 E), where E = elevation in ft

Solving for psi atm = 14.697 − 2.5, thus: psi atm = approx. 12.2
Substituting, psia = 10 + 12.2 = 22.2

Using steam tables provided in Table 3.2, 22.2, psia = approximately 233.5 °F. At this temperature, steam has a latent heat of evaporation of approximately 956.5 Btu/lb (say 957). Thus, 1 lb of steam at 10 psig (22.2 psia) provides 957 Btu energy.

To produce flashing in the deaerator, a temperature of approximately 233 °F is required, but the water entering the unit is at only 180 °F, so that supplementary heat energy is required to provide the 53 °F increase. This equates to 53 Btu per lb of water entering the deaerator.

Given that 1 gallon of water weighs 8.345 lb, the hourly Btu demand = 50 gpm × 8.345 lb × 53 Btu/lb × 60 min = 1,326,855 Btu

The steam demand = 1,326,855/957 = 1386.4 lb/hr
(say 1,386 lb of steam per hr.)

14

CONTROL OF FIRESIDE CONDITIONS AND SURFACES

As with boiler plant waterside functions, a major operational fireside objective is to maximize efficiency and keep maintenance and related costs under close control. This means that all *fuel system components, fireside,* and *heat transfer surfaces* must be kept clean and in good working order. Also, the *fuel delivery, combustion,* and *flue gas emission processes* should run equally perfectly.

The fireside of the boiler can be broken down into five major zones:

- **Preflame zone**
- **Combustion zone**
- **High-temperature zone**
- **Cold-end zone**
- **Emissions zone**

In each of these areas, a combination of sound engineering design and good operating conditions goes a long way to achieving stated objectives. Nevertheless, within these zones it generally is the case that some additional measure, in the form of a **fuel treatment** or **additive program,** can further improve local conditions and effect a measurable degree of improvement in efficiency. The type or types of additives that might prove beneficial are dependent on the specific fuel types employed, together with the boiler design, means of fuel delivery, and other limiting factors.

This chapter discusses the problems associated with each of the zones, the types of fuel treatments available, and benefits to be gained, and provides an outline on the type of formulations employed.

14.1 BASIC FIRESIDE PROBLEMS

14.1.1 Preflame Zone Problems

All fuel types contain some level of impurity or noncombustible component. For all practical purposes, the very low level of impurities found in natural gas fuels can be ignored (although during combustion, gas produces a higher percentage of moisture as compared to, say, fuel oils, and this can cause some problems downstream). For most coals, oils, and combustible process by-product fuels, however, the impact on fuel efficiency and maintenance costs can be significant and warrants the use of additives.

14.1.1.1 Problems with Solid Fuels

The types of problems associated with solid fuels include:

- **Combustion quality characteristics:** Coal, coke lignites, and other solids fuels can be classified by their content of *carbon, total volatiles, water,* and *noncombustible residuals,* as well as their *calorific value* or *Btu heat content, particle size, degree of agglomeration,* and other factors. Lower grade solid fuels have reduced levels of combustibles and increased levels of noncombustibles compared with higher grades. (The noncombustible content consists largely of vanadium and other catalytic metals that contribute significantly to the formation of slags and clinkers.) High levels of noncombustible material increase the tonnage of fuel needed, and this further increases handling requirements. Essentially, the poorer the fuel grade with respect to its combustion quality, the more an additive can help maximize the potential of that fuel.
- **Water content:** As a result of coal washing operations, *small particle size* and *high surface-moisture content* may create problems during transport of the fuel and its storage at the boiler plant facility. Coal normally is cleaned of waste and harmful materials (such as rock, clay, mud, ash, and some sulfur), sorted, and classified before sale. The process usually involves crushing the fuel to a uniform size to aid washing, but small particles and high water content create problems in handling because of agglomeration and resistance to flow when unloading into hoppers and conveyors. Also, in cold weather the fuel may freeze solid.

These problems can be minimized by the use of *polymeric* **flow improvers** and **freeze-point depressants,** similar to those employed in fuel oils.

- **Dust content:** In hot, dry climates the opposite problem occurs. Water evaporates, and the dust and fine particles may blow away, causing pollution and a nuisance hazard. This **"fugitive dust"** is controlled by spraying the fuel pile with water containing a *polymeric* **dust binder** that physically holds the particles together.
- **Storage of bagasse and similar process residues:** Depending on the weather patterns during harvesting, sugarcane bagasse may contain considerable internal and surface moisture. If stored for lengthy periods, a health hazard can be created due to the growth of *microorganisms, malodors,* and *spoilage.* These problems can be controlled by the use of microbiocides, such as **carbamates** and water soluble, *enzyme-based* **reodorants,** or simple, low-cost **deodorants**.

14.1.1.2 Problems with Fuel Oils

The following fuel oil problems are all interrelated. They generally coexist to some degree (less in higher grade oils and more in lower grade oils) and exert a compounding negative impact on each other.

- **Water:** Virtually all fuel oils contain some level of either free or emulsified water, which lowers the calorific value of the fuel, permits microbiological growths to develop, and promotes corrosion of tank bottoms. Where slugs of water are delivered along with the fuel to the combustion chamber, these interfere with the burning process and further increase the risk of corrosion. Therefore, under many circumstances, an *organic* **demulsifier** *(emulsion breaker)* is employed to separate the water from the oil, whereupon it sinks to the bottom of the storage tank and can be drained away. There is an additional benefit because some **sodium,** which originates in the fuel and contributes to slagging, is also removed due to its solubility. Often a **microbiocide** is also added.

  It is not always necessary to *demulsify* the water, however, because when small quantities are present in fine droplet form, the water explodes at the burner firing point, improving atomization of the fuel and providing for more complete combustion. Consequently, a *water-in-oil* **emulsifier** may be used to deliberately retain the water as small, emulsified droplets. The overall effec-

tiveness of this approach must be verified on a case-by-case basis because the increase in burning efficiency may be entirely offset by the decrease in calorific value of the fuel.

- **Asphaltenes:** All lower grade oils resulting from the remaining heavy-end components or residuals after thermal fractionation are subject to *tank sludging, fuel line and filter plugging,* and *combustion problems.* One of the principal contributors is the presence of asphaltenes, which are solid (at atmospheric pressure) organic molecule residuals. They typically contain from 36 to 90 carbon atoms in the molecule and have a boiling point in excess of 875 °F. Polymeric **asphaltene dispersants** are used to combat the risk of asphaltene settlement.
- **Paraffin crystalline waxes:** Apart from *asphaltenes,* a number of differing molecular weight *paraffinic waxes* are also present. These progressively crystallize at lowering temperatures (their respective **pour points**). These waxes increase friction and resistance to flow, so that the *viscosity* of the fuel is raised. This type of problem is controlled by the use of **pour-point depressants** *(viscosity improvers),* which limit the growth of the crystals at their nucleation sites within the fuel. They also have a dispersing effect.
- **Stratification:** Where different fuel grades or heavy-grade fuels of distinct origins are mixed together, there is often an incompatibility resulting in the primary components separating out as stratified layers within the storage tank. If the tank is maintained at too high a temperature, the rate of stratification increases. These bands of fuel have differing calorific values and burning characteristics and need different burner settings to combust efficiently. Also, it should be noted that asphaltenes are insoluble in *paraffinic* and *naphthenic-based fuels* and drop out, thus increasing the degree of stratification.

  The solution to stratification problems is to avoid mixing fuel grades, keep tank temperatures lower rather than higher, provide mechanical agitation where practical, and supplement operational actions with the use of a polymeric **antisettling dispersant**.
- **Oily Sludges:** Tank sludges are common where lower grade fuel oils are burnt, especially if the tank has not been cleaned in many years. The oily sludges may be composed of many materials, including partially emulsified oil, inorganic and organic particulate matter (such as *silt* and *paraffin waxes*), and *microbiological biofilms* and debris.

Apart from physically cleaning tanks periodically, *dispersants* that promote homogeneity are employed. These often take the form of "dispersant packages," which are polymer blends containing asphaltene and wax dispersants and other problem-specific additives. In addition, low-priced general-purpose dispersants, microbiocides, and antioxidants form part of the package.

14.1.2 Combustion Zone Problems

The burning of fuels involves a combination of **thermal decomposition** (dominant when combusting *solid fuels*) and **hydroxylation** (dominant when combusting *gaseous fuels*), as part of the overall process.

Apart from the operational problems associated with closely matching the *fuel* and *excess air* ratio requirements and the *ignition* and *combustion temperatures* for any given steam demand and local atmospheric condition, the composition of the fuel, with all its variables, adds considerably to the puzzle of providing continuously near-perfect combustion.

Inadequate excess air results in:

- Unburned carbon and carbon monoxide
- A significant loss of energy.

Too much of excess air results in:

- A lowering of gas temperatures
- An increase in stack emissions (consisting of *sulfated fly ash*).

The presence of *asphaltenes,* originating in the fuel, acts as a trap for **vanadium**, **nickel**, and **sodium** (which promote *slagging* and *sulfur corrosion*); these asphalthenes often contain **sulfur compounds**, which simply add to the contaminant load. Additionally, asphaltenes act as precursors to spherical stack solids (**cenospheres**), which are exhausted with the flue gases as stack emissions.

Heavy fuel oils may contain a relatively high level of noncombustible materials that result in considerable ash formation. Oils containing more than 0.05% ash are considered **high-ash fuels,** whereas oil containing less than 0.02% ash are considered **low-ash fuels**. *Vanadium, nickel, sodium, iron, a*nd some other catalytic metals form the greatest proportion of the ash content.

The vanadium content of heavy fuel oils (expressed as **vanadium pentoxide**) typically ranges from 50 to 1,000 ppm V_2O_5, although 50 to 300 ppm is more the norm. Sodium content typically varies from 10 to 100 ppm Na, depending on the percentage of salty water present in the oil.

The vanadium-containing ash contributes significantly to the formation of sticky, adherent slags, to the oxygen-induced corrosion of hot-end fireside metals surfaces, and to the acid-induced corrosion of cold-end surfaces.

NOTE: Consider a boiler burning a 1% sulfur, 500 ppm vanadium, 50 ppm sodium, heavy fuel oil at the rate of 25,000 gallons per day. The contaminants produced during combustion include 2,000 lb (900 kg) of sulfur compounds, 100 lb (45 kg) of vanadium, and 20 lb (9 kg) of sodium compounds.

Where combustion is imperfect, ***soot deposition*** *occurs. This, in turn, results in:*

- An insulating layer at heat exchange surfaces
- A disturbance in convection gas currents throughout the combustion path
- An increase in flue gas temperatures
- A loss in sensible heat and a demand for additional fuel

To combat all these combustion-related problems, a wide variety of combustion catalysts and additives are available in the market.

14.1.3 High-Temperature Zone Problems

The primary problems that develop in the high-temperature zone are related to slag deposits on *furnace section waterwall tubes, superheaters,* and *reheaters,* as well as within the general *convection area.* Slagging, of course, significantly reduces heat transfer and operating capacity. It increases maintenance time requirements for cleaning and also may cause overheating and DNB, thereby reduceing the lifespan of the boiler plant equipment.

The degree of slagging, is, in turn, closely related to the concentration of **vanadium**, **nickel**, and **sodium** compounds present in the fuel, and the types of low melting-point oxides and complex sticky deposits formed under specific boiler temperatures and prevailing conditions. These deposits are difficult to remove online with soot blowers, but

they are even more difficult to remove offline because they set hard, forming tough, adherent mineral scales (slags).

Slag components typically include:

- **Gamma sodium vanadyl vanadate** ($\gamma 5Na_2O{\cdot}V_2O_4{\cdot}V_2O_5$), which has a melting point (MP) of approximately 1070 °F (577 °C)
- **Vanadium pentoxide** (V_2O_5), having a MP of approximately 1245 °F (674 °C)
- **Sodium pyrovanadate** ($2Na_2O{\cdot}V_2O_5$), having a MP of approximately 1150 °F (621 °C)
- **Sodium metavanadate** ($Na_2O{\cdot}V_2O_5$), having a MP of approximately 1165 °F (629 °C)

Eutectics of these metal oxides can have MPs of below 1000 °F (538 °C), which further increases the potential for sticky deposits to adhere on high-temperature zone components.

Where additives are employed, they are known as **slag modifiers** or **deposit modifiers** and are designed to raise the MP of the oxides and slag formations, thus resulting in less sticky deposits with a reduced tendency to adhere to walls and tubes.

Magnesium salts have long been employed for this purpose because MgO has a melting point of over 5000 °F (approximately 5070 °F/2800 °C) and forms complex salts with elements, such as vanadium, that have MPs of between 1500 and 2500 °F. **Cerium salts** generally are used in superior products, however, because they are much more efficient than magnesium (perhaps 3–5 times more efficient), but they also are much more expensive.

14.1.4 Cold-End Zone Problems

The term *cold end* commonly refers to the *back-end convection area* of the boiler system where an *economizer, air-heater,* or *ID fan* may be found, together with the *stack* and (with high dust-burden flue gases) possibly a *cyclone scrubber* or *electrostatic precipitator.* Any fuel treatment applied in this area may be considered to act as a **postcombustion additive**.

The primary boiler plant problem here is **cold-end corrosion**, caused by the destructive effects of sulfuric acid produced within the convection area. Further problems include **acid rain**, which occurs when *sulfur gases* are emitted and widely dispersed to eventually produce sulfuric acid in the upper atmosphere, which precipitates as rain.

To some extent, fly ash neutralizes sulfur gases, but with high dust-burdened flue gases, the sulfur gases simply tend to make the ash very sticky, and it forms **sulfurated ash deposits** on the air heater tubes and plugs the path of the gas stream.

Internationally, stringent legislation is in place to severely limit the emission of *sulfur gases* (also NO_x gases and so-called *greenhouse gases*) to provide some degree of protection to the environment. Nevertheless heavier grade fuel oils, many coals, and lower grade fossil fuels still contain some sulfur, and any fuel that contains sulfur will release sulfur gases during the combustion process.

Sufur rapidly oxidizes to **sulfur dioxide** in the combustion chamber, Some of this sulfur dioxide undergoes further oxidation to produce the very corrosive gas **sulfur trioxide.** The conversion rate is fairly low and is dependent on several factors, including:

- *The percentage of sulfur present in the original fuel.*
- *The percentage of excess air.* Where heavy oil is used as a fuel, the conversion reaches approximately 6% when the excess air is approximately 12 to 15%. For coal, the maximum conversion is only 1.5%, at similar levels of excess air.
- *The levels of* ***vanadium pentoxide*** *and* ***vanadate complexes*** *present as fireside deposits.* The higher the level, the greater the catalytic effect. There is also some catalytic effect simply due to the presence of hot steel tubes.

The various boiler sulfur reactions are shown here:

S sulfur	+	O_2 oxygen	→ *combustion*	SO_2 sulfur dioxide
$2SO_2$ sulfur dioxide	+	O_2 oxygen	→ *catalysis*	SO_3 sulfur trioxide
SO_3 sulfur trioxide	+	H_2O water	→ *dew point*	H_2SO_4 sulfuric acid

The production of sulfuric acid from condensing water vapor is dependent upon the **acid dew point temperature**, which varies from

approximately 270 to 330 °F (132–166 °C). In turn, the dew point is dependent on the ash composition and content in the boiler (especially with regard to *vanadates*). Normally, boiler operators run the plant to achieve back-end temperatures of perhaps 20 to 40 °F above the dew point, but it may be almost impossible to consistently maintain this degree of safety margin in industrial applications where steam loads vary, such as in batch-type production programs.

The ultimate answer to cold-end corrosion problems is to totally eliminate sulfur from all fuels used, although from a political or economic standpoint, this is seldom a viable option. At the boiler plant facility itself, more practical options include raising the exit gas temperatures to prevent the dew point from being reached and using selective fuel treatments.

Raising the exit gas temperatures is achieved by installing air preheaters or air heater bypass dampers. Unfortunately, this action also serves to reduce the efficiency of the boiler and thus raise costs.

A further complication is that as exit-gas temperatures rise, the volume of air and flue gas passing through the stack increases, and this can cause load limitations and a further reduction in efficiency.

NOTE: The volume of exit-gas increases proportionally to the increase in temperature, according to the ***ideal gas law****, V = T/P; where V = volume, P = pressure, and T = temperature °K.*

14.1.5 Emissions Zone Problems

Fireside carbon deposits burn off at temperatures in excess of approximately 1100 °F/590 °C, but in boiler plants operating under fluctuating load conditions, this temperature is not maintained and accumulated *unburned carbon* **(soot)** is simply blown out of the stack during every startup cycle. This creates a plume of **high-opacity stack gases,** which often contravenes the emission regulations of industrially developed countries. Colored *sulfur* and *nitrogen gases* may also affect opacity.

NOTE: ***Opacity*** *readings (covering power or reduction in light transmission) may also be high where water vapor in the stack gases condenses in cold weather.*

Similarly, when burning low grade, high-ash fuels, the particulate fly ash is also carried through the flue gas system and into the atmosphere unless precautionary measures are taken. Dust control and desulfurization equipment employed today includes:

- **Hot precipitators:** These are located in front of the *air heaters* and typically operate at between 600 and 800 °F (315–425 °C).
- **Electrostatic precipitators:** These are *cold precipitators,* located after the ID fans. Particularly efficient precipitators (> 99%) often remove the alkaline fly ash before it can react with acids in the flue gas. Where scrubbers are not employed, the acid is ultimately liberated to the atmosphere.
- **Cyclone separators:** Often used as roughing systems in process industries before other forms of emission control equipment, seldom satisfactory as stand-alone equipment.
- **Bag houses:** These are employed to follow dry scrubbers and/or precipitators in coal burning plants.
- **Wet and dry scrubbers:** Dry scrubbers are generally preferred today. Scrubbers can be used for the removal of both particulate matter and toxic sulfur gases (*dry scrubber* or *spray dryer desulfurizers).*

Where stack temperatures are low and sulfur gases are present, problems of *dry soot emissions* give way to *wet* **acid smutting.**

NOTE: Acid smuts can cause severe damage because the pH level is often below 2.0 Where, for example, acid smuts fall on a vehicle, the body paint is likely to be discolored or spotty and may be eaten away. The effect on the environment is even greater.

In any case, whether emissions are wet or dry, the presence of soot in the flue gas effectively means lost Btus. Where fuel treatments are employed, their function is to limit the supply side of flue gas emissions by improving the combustion process.

14.2 FUEL TREATMENTS/ADDITIVES

Fuel treatments have been used for very many years as an aid to improving the combustion efficiency process. Old formulations often used *saw dust, wood flour, common salt, zinc sludge, ground oyster shell,* and similar crude ingredients, but could still provide a dramatic effect when thrown into a fire. The metallic salts present (*sodium* in salt, *zinc* in sludge, and *calcium* in shell) acted as catalysts that dramatically lowered the ignition temperature of soot deposits from around 1100 °F/590 °C to only 600 °C/315 °C; the fire burned vigorously and the soot disappeared.

Today a wide range of inorganic and organic materials are employed, and the applications have become very specific and far-reaching. These fuel treatment products are available in solid, liquid, or emulsion form and are designed to match the physical nature of the fuel. Well-designed, commonly available feed equipment allows for easy injection. Fuel additives are employed in various types of combustion processes, including:

- Fossil-fueled boilers
- Gas turbines
- Black liquor recovery boilers
- Fluidized bed reactors
- Lime and cement kilns
- Refinery crude oil heaters
- Bark burners
- Municipal waste incinerators.

There are a number of major, primary manufacturers of fuel treatments (such as **McDermott-Canning, Inc.** of the United States and **Interplast S.A.** of France), as well as many smaller regional producers. **Gamlen®** is a very well known brand, but the group was split up some years ago and several manufacturers and suppliers around the world (including McDermott-Canning) now share the brand name.

The primary ingredients of most fuel additive formulations almost always include metals such as *iron, copper, manganese, magnesium,* or *cerium.* Depending on the form of the treatment, these metals can be present in several forms, including:

1. A very finely divided *metal oxide* powder or slurry, dispersed in a carrier oil (e.g., 10–55%) **magnesium oxide** of less than 1 micron particle size, in light fuel oil). The shelf life of this kind of product is limited to perhaps 6 to 9 months because of the risk of settlement of the dispersed phase. Formulations using magnesium oxide can be produced using either natural or synthetic MgO. Natural MgO is much less expensive but may contain **quicklime** (CaO), **silica** (SiO_2), or **carborundum** (Al_2O_3), all of which can be very abrasive. To some extent, MgO-based formulations have been replaced by *stabilized* **magnesium hydroxide** [$Mg(OH)_2$] ingredients.
2. A *crystalline salt* or powdered *metal oxide* such as **manganous chloride** or **manganese dioxide.** This kind of ingredient is blended

with other powders or crystalline solids and has a virtually unlimited shelf life. They usually are blown into the furnace area or fed to a fuel conveyor system.

3. A *carboxylate derivative* (e.g., **cerium sulfonate** or **cerium octoate** with 30 to 37.5% Ce content). Formulations made with this type of ingredient usually contain a nonionic or anionic surfactant plus a solvent. Lower cost products are made with *aliphatic solvents* because these are about half the price of the superior *aromatic solvents.* These types of formulations generally are fed to the fuel tank or line, but for special applications, such as a lime kiln, they are sprayed into the furnace through the face plate of the kiln, close to the flame zone, via a lance fed by a metering pump. Feed rates vary, but the more expensive *cerium-based* products are fed at lower dose rates than, say, *magnesium-* or *manganese-based* products. For example, if a cerium-based material is added to coal, it typically may be fed at from one-third to 1 pint per ton of coal (0.33–1 liter per m^3), depending on the grade, whereas the magnesium- or manganese based materials (which may be half the price) are likely to be fed at approximately three times this level.
4. An *emulsified fatty acid soap* (e.g., **magnesium** or **iron tallate**, having between 8 and 18% metal content. This type of product is cationic and may exhibit some partial solubility in both oil and water. It can be fed by pump (usually a progressive cavity pump or a screw pump).

When these metal additives are delivered to the furnace, in whatever form suitable, they become oxides. In this "active" form, they exert a catalytic effect on the fuel combustion process.

Apart from metals, **ammonium chloride, amine**, and **diamine salts**, and various organic **polymeric dispersants** and **surfactants** are employed in fuel treatment additive formulations.

Because there seldom is only one specific problem associated with the fuel being used, most fuel treatments are blends of active agents, such as *combustion improvers* and *slag modifiers.* In addition, fireside problems tend to be interrelated, so that, for example, inefficient fuel combustion leads to heavy **sooting** in the combustion area and **dry smutting** from the exit gases.

Where the fuel contains *sulfur compounds,* **sulfuric acid** is ultimately formed, causing **acid smutting** and both **hot-end** *(high temperature zone)* and **cold-end** *(low temperature zone)* **acid corrosion and fouling,** and adds to the total volume of unwanted furnace area deposits.

- *High temperature corrosion* may occur when superheater temperatures are above 500 to 550 °C and the sodium or vanadium slag is molten.
- Increased thermal efficiency is possible if boiler back-end temperature is reduced. Theoretically, without modifying boiler output, a reduction of 8 °C (14.4 °F) in back-end temperature results in a saving in fuel oil consumption of 0.3%. *Low temperature corrosion* can occur, however, when boilers are operated with back-end temperatures close to the SO_3 dew point.
- *Furnace area* and *superheater slagging* may occur at low furnace or superheater temperatures (below 450–500 °C) due to high *vanadium* content in fuel oil. These high levels of *vanadium* in the fuel reduce the **eutectic temperature** of the noncombustibles, creating a molten deposit that holds unburned carbon and contributes to a thickening of the slag. The trapped carbon is unavailable for combustion, and this process consequently reduces the overall fuel combustion efficiency.

14.2.1 Combustion Catalysts and Improvers

Combustion catalysts are considered chemical transfer agents that increase the kinetics of the combustion oxidizing reaction and effectively reduce the *autoignition temperature* of combustibles. They are based on **manganese**, **iron**, or **copper** and may be present as an **oxide**, **salt**, **carboxylate**, or **soap**. Depending on the fuel source and the associated problems, *combustion improvers* may be formulated to act primarily as **smoke suppressants**, thus producing low carbon–high **opacity** exit gases with little tendency for *smutting*. They also reduce the total amount of acidity in the back end of the boiler.

NOTE: Where smoke suppression is required (e.g., in a boiler fired on poor-quality heavy fuel oil) and a typical liquid combustion improver product is employed, to achieve a 35% reduction in unburned particles may require the addition of 2/3 pint of additive per 2,500 gallons of fuel (approximately 0.33 liters per 10m^3). Doubling the smoke particle reduction to 65%, however, may require triple the feed rate of the additive.

Alternatively, combustion catalysts may be formulated to act primarily as **furnace area catalysts**, in which case they reduce the carbon in *fly ash* and *bottom ash*. This, in turn, lowers the degree of fouling in the boiler convection area and the economizer.

For fluidized bed reactors, special water-soluble, combustion catalyst and slag modifier combination products are available. These products are diluted and typically are fed at rates of from 20 to 60 lb per day for every 10 tons of bed extraction.

14.2.2 Slag Modifiers and Deposit Modifiers

Slag modifiers raise the *fusion point* or *sintering temperature* of the ash and directly neutralize any SO_3 formed. They are based on *alkaline-earth metals* such as **magnesium**, **calcium**, and **strontium,** or *rare-earth metals* such as cerium; they are available as **oxides**, **salts**, or **soaps**.

Magnesium-based additives are commonly employed to treat boiler furnace area fouling and corrosion conditions. They are injected into heavy fuel oil or other combustible material. *Cerium* is superior in action to *magnesium salts,* however, because an equivalent weight of cerium increases the melting point of the deposit more than that of magnesium.

During combustion, the metals revert to oxides and react with **ferric oxide** (Fe_2O_3), **vanadium pentoxide** (V_2O_5), **sulfate** (SO_4), **sodium oxide** (Na_2O), and other slag components to form complex compounds having higher melting points. By increasing the melting point, the continued formation of a molten layer and the trapping of unburned carbon are halted and superheating fouling is stopped. The deposits become more friable and can be removed by *soot blowers* or they may break way to fall to the furnace floor.

If the deposit is allowed to thicken significantly, thermal transfer is reduced and, in extreme cases, steam pressure drops.

Additionally, the vanadium acts as a catalyst for the oxidation of **sulfur dioxide** (SO_2) to **sulfur trioxide** (SO_3). Consequently, the SO_3 content of the furnace gases increases from perhaps 10 ppm to 30 ppm or more. At 30 ppm SO_3, the dew point of the sulfuric acid generated is high enough to saturate the *air heater,* and this unit rapidly corrodes (typically within 1–2 years). To prevent this corrosion, the SO_3 content in the flue gas stream must be below 7 ppm.

The ash produced during combustion is formed in a fine particle size, which further limits slagging in the furnace area and superheater and reduces the total volume of fireside deposits produced. Examples of the actions of slag modifiers are shown here:

Example A: Slag contains approximately 30% Fe_2O_3, 20% SO_4, 30% V_2O_5, 10% Na_2O, and 10% other materials; it has a melting point (MP)

of 700 °C. The addition of sufficient magnesium to the fuel to provide 10% MgO in the slag raises the temperature to 750 °C and 20% MgO to 800 °C. Compare this with cerium, where 10% CeO raises the temperature to 950 °C and 20% to 1000 °C.

Example B: Slag contains approximately 13% Fe_2O_3, 25% SO_4, 45% V_2O_5, 12% Na_2O, and 5% other materials; it has a melting point (MP) of 600 °C. The addition of sufficient magnesium to the fuel to provide 10% MgO in the slag raises the temperature to 650 °C and 20% MgO to 700 °C. Compare this with cerium, where 10% CeO raises the temperature to 750 °C and 20% to 850 °C.

NOTE: For fuel oils where the ash content produced is, say, between 1/3 and 1 lb per 250 gallons (approximately 150–450 gram per m^3) of fuel oil, the typical feed rate of a liquid chemical treatment to provide 10% CeO in the ash is of the order of 3/4 to 2 pints per 2,500 gallons (approximately 0.33–1 liter per 10m^3). The feed rate would be doubled to achieve 20% CeO in the ash.

14.2.3 Clinker Treatments

Clinker treatments are additives designed to reduce the amount of clinkering formations that takes place in boilers fired by **bark, bagasse,** and similar low-calorific-value fuels. These fuels can give rise to considerable amounts of noncombustible deposits that must be continuously or regularly removed from the furnace area. Clinker treatments are formulated for use with various types of furnace, including *slant, pin hole,* and *chain grate furnaces.*

These materials are essentially combustion improvers and tend to have fairly simple formulations (e.g., 3% **copper chloride,** 7% **manganese chloride,** 90% **ammonium chloride**). They are designed to change the crystalline structure within the clinker crystal lattice and raise the clinker eutectic point, thus minimizing the formation of noncombustible clinker, residual ash, and other deposits. Feed rates are approxiimately 0.5 to 2.0 lb per bone-dry ton.

14.2.4 Acid Neutralizers (Fuel Corrosion Inhibitors)

Acid neutralizers are alkaline materials that produce active components designed to absorb and neutralize SO_3 in the gas stream during combustion. The effect is to reduce sulfuric acid corrosion on heat-exchange surfaces (such as *economizers* and *air heaters*), which takes

place when the flue gas temperature falls below the **acid dew point.** The potential for **acid smutting** is also reduced.

Reducing the amount of **vanadium** and **sodium** deposits formed through the use of *slag modifiers* can also effect good control of acid corrosion by SO_3. Vanadium and sodium deposits form low-melting-point slags and are a major contributor to the formation of SO_3.

14.2.5 Emulsion Additives

Stabilized fuel oil emulsion additives have been employed for some years, especially in utility boiler systems, as an aid to significantly improving *fuel oil atomization* at the burner, thus resulting in more complete combustion, a cleaner boiler, and less carbon build-up. The products contain between 7 to 10% water dispersed in light oil, together with suitable emulsifiers and dispersants. The water exists as a droplet and must be greater than 2 μ in diameter to have sufficient mass and energy to explode during atomization.

NOTE: Water-in-oil dispersants have an HLB of between 0 to 5. Examples include ***sorbitan tristearate*** *(HLB = 3.5) and* ***sorbitan monolaurate*** *(HLB = 4.3).*

Improvements in atomization and combustion lead to a reduced requirement for excess air (it can drop to below 1%), resulting in lower back-end temperatures and better fuel efficiency.

Emulsion additives may also incorporate magnesium oxide–hydroxide slurries as part of the product.

14.2.6 NO_x Emission Control Additives

Selective catalytic reduction (SCR) and **selective noncatalytic reduction processes** (SNCR) are widely employed in large industrial and utility boiler plants, as well as in municipal waste incineration plants and other combustion processes. They are used to complement mechanical improvements (such as *low NO_x burners* and *furnace design modifications*) as an aid to reducing the emission levels of NO_x, SO_2, and other noxious gases into the atmosphere.

SNCR programs typically employing liquid additive formulations based on **urea** (**carbamide,** NH_2CONH_2), together with *stabilizers* and *modifiers,* are particularly useful. The additive is sprayed into the combustion area, after the burner. The use of such additives reduces the NO_x level by between 50 and 90% by converting NO_x into harmless nitrogen and water.

Emulsion additives (water droplet emulsions) also aid in the reduction of NO_x gases (by perhaps 15%) by the lowering of excess air requirements.

14.2.7 Fuel Oil Conditioners and Storage Additives

Fuel oil storage additives comprise a number of functionally specific ingredients that usually are blended together to provide a multifunctional product that is dosed to the fuel tank, typically at a rate of 1 gallon per 2,000 to 5,000 gallons (1 liter per 2–5 m^3). They are formulated to improve the handling and combustion characteristics of all types of liquid fuels, especially heavy residual oils and those having high **basic sediment and water (BS&W)** content.

NOTE: Where the fuel tank contains oily water emulsions, sludge, and particulates, the effectiveness of any fuel treatment is directly related to the ability of the additive to penetrate and attack the sludge or emulsion mass. Simply feeding the treatment to the tank does not work. Typically, some form of power-injection equipment is employed to inject the chemical under 100 to 200 psig pressure. Agitation of the entire tank contents also is required and can often be carried out using the same equipment.

Similarly, all lines and tank returns can be purged and cleaned and small amounts of additive injected to provide an unrestricted flow of fuel.

Additive components include:

- **Asphaltene dispersants:** These organic polymeric dispersants are designed to keep the high content of *asphaltenes* found in many *residual oils* held in suspension. They promote homogeneity of the fuel, thus preventing agglomeration of **asphalts** and **waxes** and the resultant problems of tank sludging and plugging of filters and strainers. They also aid in the prevention of *coking* and *polymerization* of heavy fuel oil constituents in the oil heater.
- **Cold flow improvers (pour point depressants):** These **viscosity improvers** are often specified in cold climates for unheated *gas oil* or where existing residual oil heaters are inadequate. The use of these *paraffin crystal modifiers* permits fuel to continue to flow at temperatures of 30 to 40 °F lower than the point at which wax crystallization would normally occur.
- **Emulsion breakers (dewatering agents):** These functional materials are water-in-oil emulsion breakers that permit the separation of emulsified water. The water accumulates in the tank bottom and

should be drained off regularly. The water repelling effect resists the tendency of the emulsion to increase the viscosity of the fuel. Water-in-oil emulsion breakers may be based on, for example, **cationic resins, benzene dicarboxylic polymers,** or **diamines** (also having biocidal properties).

- **Biocides:** Especially for controlling ***Clostridium*** and similar organisms found in water present in *aviation kerosene* and *diesel* tanks. Biocides include special grades of **isothiazolines, polyquats, diamines**, and **sulfones.**
- **Corrosion inhibitors:** These are **amine-** or **diamine-based**, *film-forming corrosion inhibitors* that help protect tank bottoms against **oxygen pitting corrosion** and **microbiologically induced corrosion (MIC).** They also protect against corrosion of tank sides and top caused by the corrosive nature of some **sour fuels** (high-sulfur content fuels).
- **Particulate sludge dispersants:** These materials often dissolve rather than disperse particulate organic sludges that can form during storage; thus, they add to the total combustibles passing through the burner. In heavily sludged storage tanks, treatment should be initiated at a low dose, perhaps 1 gallon per 10,000 (1 liter per $10m^3$), in order not to dislodge the sludge too quickly and risk blocking the filters.

Fuel oil conditioner formulations may use a wide range of dispersants, surfactants, and detergents, blended together in a suitable solvent system.

Generally, the primary solvent is **heavy aromatic naphtha (solvent naphtha,** HAN) at 60 to 85% [e.g., **Aromatic Solvent 110** or **150 (Texaco)**].

Isopropyl alcohol (IPA) or **benzyl alcohol (toluol)** often are used in the formulation (as early components in the *order of addition*) to dissolve the surfactant-detergent base [e.g., **Duomeen OL (Akzo Nobel Chemicals, Inc.)** or **Triton N101 (Union Carbide Corp.)**].

Coupling agents such as **hydroxymethyl benzene** or a **polyoxyethylene-polyoxypropylene ether [polypropylene glycol-polyethylene glycol ether, POE-POP ether, e.g., Ucon®** synthetic lubricant from **Union Carbide Corp.)**] and *hydrotropes,* such as an **imidazoline carboxylate** may also be needed to hold the formulation together.

14.3 FUEL TREATMENT FORMULATIONS

There are hundreds of fuel treatments and additive formulations in commercial use today. Following are five formulations, typical of the types of products commonly available.

14.3.1 Fuel Treatment for Lower Grade Solid Fuels

This formulation is proposed as a complete treatment, comprising powdered and crystalline combustion catalysts and slag modifiers. It is designed for **pulverized fuel** (PF), **brown coal, lignite, peat moss,** and **bark,** and for application with *cyclone burners, chain grates, underfed,* and *spreader stokers.*

Formulation	
Materials	
Manganese dioxide	10.0%
Manganese sulfate	15.0%
Copper chloride	9.0%
Fumed silica	1.0%
Lime	65.0%
	100.0%

NOTE: Where the primary problem is to improve combustion efficiency, the product typically is added to the fuel handling system via an automatic feeder and used continuously at a rate of 0.5 and 1.5 lb per ton of fuel.

Where the primary problem is one of slagging, the product is periodically blown into each side of the boiler or shot-fed onto the fuel delivery belt to achieve repeated higher dose rates.

14.3.2 Liquid, Oil-Soluble Combustion Catalyst and Slag Modifier

This formulation is designed to control combustion and slagging problems associated with vanadium, sodium, and sulfur in heavy residual fuel oils.

Formulation	
Materials	
Manganese tallate	10.0%
Magnesium sulfonate	10.0%
Light petroleum solvent	40.0%
HAN	40.0%
	100.0%

This product is added directly to the fuel tank or injected continuously at any point in the fuel system. Feed rates to fuel oil are:

- V and Ni in the range of 100 to 200 ppm, S >1%, Na > 10 ppm. Feed at 1:1,000 to 1:2,000
- V and Ni in the range of 20 to 100 ppm, S >0.2%, Na > 10 ppm. Feed at 1:2,000 to 1:4,000

14.3.3 Liquid Fuel Oil Conditioner/Stabilizer

This formulation is a complex, hydrocarbon-based fuel conditioner for difficult fuel oils containing a high level of asphaltenes, sludges, and waxes.

Formulation	
Materials	
POE-POP ether	2.0%
Imidazoline oleate	10.0%
Polyolefin ester	5.0%
Toluol	5.0%
Light petroleum solvent	10.0%
HAN	68.0%
	100.0%

This product is added directly to the fuel tank at the time of delivery and thoroughly blended (by action of the fuel entering the tank). Feed rates typically are1:3,000, although when starting a new program, initial feed rates should be lower.

14.3.4 Combined Combustion Improver, Sludge Dispersant, and Fuel Stabilizer

This formulation is designed as a complete treatment, providing improved atomization and combustion, sludge dispersancy, demulsification of water from oil, prevention of bacterial slimes at the water-oil interface, reduced cold-end corrosion, and less fuel system deposits.

Formulation	
Materials	
Cerium ethyl hexanoate (in 6% naphtha)	7.5%
Magnesium sulfonate	5.0%
Diamine oleate	5.0%

Cresylic acid	2.5%
Petroleum solvent 140	20.0%
IPA	15.0%
HAN	45.0%
	100.0%

This product is fed directly to the tank at these rates:

- Light and heavy distillates: 1:2,000 to 1:4,000
- Residual fuel oils: 1:1,000 to 1:2,000

14.3.5 Fuel Oil Emulsion Breaker

This product is designed to break water-in-oil emulsions, especially for fuel oils, lubricating oils, or waste oils. This emulsion breaker lowers the surface tension of the oil and, because it is immiscible in water, it is not lost when the water is decanted from the oil.

Feed rates for fuel oil emulsion breakers vary significantly, but a starting point is perhaps 3,000 ppm. Where used to treat oily sludges (by adding to an API separator), the POE-POP ether component in the formulation aids the rejection of greasy soils from the oil and enables the separated oil to be reused as a fuel.

Formulation	
Materials	
POE-POP ether	5.0%
Hydroxypropylethylenediamine	5.0%
Fatty acid distillate	20.0%
Mineral oil	35.0%
HAN	35.0%
	100.0%

14.4 COMBUSTION GAS ANALYSIS

14.4.1 Composition of Air

Dry **air** is a mixture of gases normally containing 78.08% of nitrogen, 20.94% oxygen, 0.04% **carbon dioxide,** plus small amounts of **argon, neon, helium, krypton,** and **xenon** *by volume.*

By weight, the amount of oxygen in air is 23.25%.

Some **water vapor** is also present in air and may be considered to be *low-pressure, low-temperature steam.* Water vapor is assumed to act

as an **ideal gas,** obeying **Boyles' Law of Gases** (for gas analysis calculations, this is generally true to within 1%).

Boyles' Law states: *The volume of a gas is inversely proportional to its absolute pressure, at a constant temperature.* $P_1V_1 = P_2V_2$

The amount of water in dry air required to saturate the air (**specific humidity,** W_{sat}) is dependent on the temperature and certain other factors. Some examples of W_{sat} are shown here *(for a barometric pressure of 29.92 in. Hg):*

- At 30 °F, when dry air becomes fully saturated, it holds 0.3435% water by weight. One lb. of 100% humid air occupies a volume of 12.41 cu ft; 1 lb. of dry air at this temperature occupies a volume of 12.34 cu ft.
- At 50 °F, when dry air becomes fully saturated, it holds 0.7658% water by weight. One lb. of 100% humid air occupies a volume of 13.00 cu ft; 1 lb. of dry air at this temperature occupies a volume of 12.84 cu ft.
- At 70 °F, when dry air becomes fully saturated, it holds 1.5820% water by weight. One lb. of 100% humid air occupies a volume of 13.69 cu ft; 1 lb. of dry air at this temperature occupies a volume of 13.35 cu ft.
- At 90 °F, when dry air becomes fully saturated, it holds 3.1180% water by weight. One lb. of 100% humid air occupies a volume of 14.54 cu ft; 1 lb. of dry air at this temperature occupies a volume of 13.85 cu ft.
- At 110 °F, when dry air becomes fully saturated, it holds 5.9440% water by weight. One lb. of 100% humid air occupies a volume of 15.72 cu ft; 1 lb. of dry air at this temperature occupies a volume of 14.36 cu ft.

Relative humidity (RH) is the degree of saturation (0–100%) at any *dry-bulb temperature.*

14.4.2 Combustion of Fuels

When fuels combust, it is always the *carbon, hydrogen,* or *sulfur* that produces the heat energy chemical reaction by combining with oxygen.

If *flue gas* (exit gas) emerging from a stack is black and smoky, it is an indication of insufficient air. If the gas emerging is a white smoke, it is an indication of a considerable excess of air. Ideally, the gas should be colorless to very slightly brown, with a minimum of haze.

- For **carbon** to fully react, producing *carbon dioxide,* one volume of C requires one volume of O_2, producing one volume of CO_2. One lb. C requires 2.67 lb. O_2 (11.52 lb. of air).
- For **carbon** to react, producing *carbon monoxide,* two volumes of C require one volume of O_2, producing two volumes of CO. One lb. C requires 1.33 lb. O_2 (5.76 lb. of air).
- For **carbon monoxide** to react, producing *carbon dioxide,* two volumes of C require one vol. of O_2, producing two volumes of CO_2. One lb. CO requires 0.57 lb. O_2 (2.47 lb. of air).
- For **hydrogen** to react, producing *water,* two volumes of H_2 require one volume of O_2, producing two volumes of H_2O. One lb. H_2 requires 8 lb. O_2 (34.56 lb. of air).
- For **methane** to react, producing *carbon dioxide and water,* one volume of CH_4 requires two volumes of O_2, producing one volume of CO_2 and two volumes of H_2O. One lb. methane requires 4 lb. O_2 (17.28 lb. of air).
- For **sulfur** to react, producing *sulfur dioxide,* one volume of S requires one volume of O_2, producing one volume of SO_2. One lb. S requires 1.0 lb. O_2 (4.32 lb. of air).

When coal is burned, the amount of excess air required may be as high as 50%. With oil, gas, or pulverized coal fuel (PF), excess air requirements drop to only 10 to 30%, and often much less (perhaps < 5%) with modern burner and furnace designs.

Air contains approximately 21% *oxygen* by volume. When *carbon* fully reacts, it combines with one volume of oxygen to produce one volume of *carbon dioxide,* so the maximum percentage of CO_2 found in flue gas is also 21%. However, the presence of *excess air* in the combustion process will dilute the percentage of CO_2 found in the flue gas.

14.4.3 Analysis of Flue Gas

The analysis of flue gas provides a measure of the efficiency of the combustion process and is given in percentages by volume. Traditionally, flue gas measurements have been taken using an **Orsat apparatus,** although in many industrialized countries this device has long been superseded by a wide variety of very accurate, portable, and precalibrated electronic equipment.

Some examples of the type of results expected when using an Orsat apparatus are shown below.

1. **Analysis of Flue Gas, with 0% Excess Air**

Carbon dioxide	21.0%
Oxygen	0.0%
Nitrogen	78.1%
Other gases	0.9%
	100.0%

Here, the 21% of oxygen originally present in air has reacted on a 1:1 volume basis with carbon to produce one volume of carbon dioxide. The nitrogen content of the air does not take part in the reaction process.

2. **Analysis of Flue Gas, with 50% Excess Air**

Carbon dioxide	14.0%
Oxygen	7.0%
Nitrogen	78.1%
Other gases	0.9%
	100.0%

In this second example, because the nitrogen does not react, the total volume of oxygen and carbon dioxide must still add up to 21%. Because there is 50% excess air, the availability of oxygen to react with carbon is 1.5:1 by volume; thus, the volume of carbon dioxide produced is $1/1.5 \times 21\% = 14\%$.

3. **Analysis of Flue Gas, with 100% Excess Air**

Carbon dioxide	10.5%
Oxygen	10.5%
Nitrogen	78.1%
Other gases	0.9%
	100.0%

In this third example, there is 100% excess air; consequently, the oxygen available to react with carbon is 2:1 by volume; thus, the volume of carbon dioxide ultimately produced is $1/2 \times 21\% = 10.5\%$.

14.4.3.1 Gas Measuring Equipment

The *Orsat apparatus* is a series of glass chambers containing gas-absorbent or reactive chemicals that are connected via a valved glass manifold to a gas measuring burette. The gas in the burette is measured using a leveling bottle containing colored water that is connected to the burette by a rubber hose. A hand-operated, flue-gas sampling pump (rubber bulb) is also connected to the manifold. The entire apparatus is housed within a wooden case with removable sides.

Carbon dioxide is absorbed first using a **potassium hydroxide** solution.

Oxygen is the next gas absorbed, using **pyrogallol** (the same oxygen scavenger produced from *quebracho tannins*). The glass absorption chamber also contains steel wool as a catalyst.

Carbon monoxide is absorbed in a **cuprous chloride** solution that additionally contains copper strips.

In some Orsat apparatus models, *water vapor* may also be determined; hydrogen may also be determined by its oxidation to water vapor.

Modern electronic replacements for the Orsat apparatus include equipment manufactured in the United States by **Bacharach, Inc. (www.bacharach-inc.com)**. This company produces handheld and boxed instruments that can be employed as comprehensive *combustion and environmental analyzers, gas burner combustion testers, single gas analyzers, draft gauges, smoke test sets, sling psychrometers,* and the like.

A comprehensive combustion analyzer typically provides the following levels of information:

- Oxygen, from 0 to 25%
- Carbon dioxide, from 0.1 to 20%
- Carbon monoxide, from 0 to 3,000 ppm
- Oxides of nitrogen, from 0 to 2,000 ppm
- Sulfur dioxide, from 0 to 2000 ppm
- Stack temperature, from 0 to 2000 °F (1093 °C)
- Stack loss from 0.1 to 99.9%
- Primary air temperature, from 0 to 999 °F
- Draft, from –8 to +8 in.
- Excess air, from 1 to 250%

Appendix I

USEFUL DATA

PROPERTIES OF SATURATED STEAM (U.S. AND SI UNITS)

		Volume (v) (cu ft/lb)		*Enthalpy (H) (Btu/lb.)*		
Temp (°F)	*Pressure (psia)*	*Water vfluid*	*Steam vgas*	*Water Hfluid*	*Evap Hf/g*	*Steam Hgas*
100	0.9492	0.01613	350.4	68.0	1037.1	1105.1
150	3.7180	0.01634	97.07	117.95	1008.2	1126.1
200	11.526	0.01664	33.64	168.09	977.9	1146.0
212	14.696	0.01672	26.80	180.17	970.3	1150.5
220	17.186	0.01678	23.15	188.23	965.2	1153.4
240	24.698	0.01693	16.32	208.45	952.1	1160.6
260	35.427	0.01709	11.76	228.76	938.6	1167.4
280	49.200	0.01726	8.644	249.17	924.6	1173.8
300	67.005	0.01745	6.466	269.7	910.0	1179.7
340	117.99	0.01787	3.788	311.3	878.8	1190.1
380	195.73	0.01836	2.335	353.6	844.5	1198.0
400	247.26	0.01864	1.863	375.1	825.9	1201.0
500	680.90	0.0204	0.675	487.9	714.3	1202.2
600	1543.2	0.0236	0.2675	617.1	550.6	1167.7
705.5	3208.2	0.0508	0.0508	906.0	0	906.0

		Volume (v) (m^3/kg)		*Enthalpy (H) (kJ/kg)*		
Temp (°K)	*Pressure (MPa)*	*Water vfluid*	*Steam vgas*	*Water Hfluid*	*Evap Hf/g*	*Steam Hgas*
300	0.003536	0.001004	39.10	111.7	2438.4	2550.1
340	0.02718	0.001021	5.737	280.5	2340.5	2621.0
370	0.09047	0.001041	1.860	406.3	2264.3	2670.6
400	0.2456	0.001067	0.7308	532.7	2182.9	2715.6
450	0.9315	0.001123	0.2080	749.0	2025.9	2774.9
500	2.637	0.001202	0.07585	975.6	1827.5	2803.1
550	6.112	0.001322	0.03179	1219.9	1562.7	2782.6
600	12.33	0.001540	0.01375	1504.6	1172.5	2677.1
647.29	22.089	0.003155	0.003155	2098.8	0	2098.0

PROPERTIES OF GLYCOLS

Properties	*Ethylene glycol*	*Propylene glycol*
Formula	$C_2H_6O_2$	$C_3H_8O_3$
Chemical Service Abstract No.	107–21–1	57–55–6
Molecular weight	62.1	76.1
Boiling point °F/°C	387.3/197.4	369.3/187.4
Vapor Pressure at 77 °F/25 °C	< 0.1 mm Hg	0.13 mm Hg
Wt. per U.S. gal at 77 °F/25 °C	9.26 lb.	8.62 lb.
Freezing point °F/°C	7.9/–13.4	Supercools
Surface tension at 77 °F/25 °C	48 dynes/cm	36 dynes/cm
Thermal conductivity		
(Btu/hr/ft/°F) at 77 °F/25 °C	0.149	0.1191
Acute oral toxicity LD_{50} gm/kg	6.1	33.7
Freeze point of glycol mixtures		
5% by weight °F/°C	28	28
10% by weight °F/°C	25	25
15% by weight °F/°C	21	22
20% by weight °F/°C	17	19
25% by weight °F/°C	12	15
30% by weight °F/°C	6	11
35% by weight °F/°C	–2	2
40% by weight °F/°C	–10	–7

continued on next page

Properties	*Ethylene glycol*	*Propylene glycol*
Freeze point of glycol mixtures (*continued*)		
45% by weight °F/°C	–21	–18
50% by weight °F/°C	-33	-29
55% by weight °F/°C	-51	-43
Refractive index of glycol mixtures at 77 °F/25 °C		
5% by weight	1.337	1.338
10% by weight	1.342	1.344
15% by weight	1.347	1.351
20% by weight	1.352	1.357
25% by weight	1.357	1.362
30% by weight	1.362	1.367
35% by weight	1.367	1.372
40% by weight	1.372	1.377
45% by weight	1.377	1.382
50% by weight	1.382	1.387
55% by weight	1.387	1.392

UNITS IN WATER ANALYSIS

Water analysis samples are normally analyzed by volume rather than by weight and corrections for specific gravity (sp gr) are seldom made, however for all practical purposes, we can regard sp gr as 1.00. Under these circumstance 1 mg/l = 1 ppm.

- **English Degree or Clarks Degree (°E or °Clark):** equal to a concentration of one grain of $CaCO_3$ per Imperial gallon. Thus 1 °E = 14.28 mg/l.
- **Equivalent weight** or ***gram equivalent*:** a mole divided by the valency of the substance. *Example: a mole of sodium chloride = 58.45 g, valency = 1, therefore equiv. wt = 58.45. A mole of calcium carbonate = 100.08 g, valency = 2, therefore equiv. wt. = 50.04.*
- **For $CaCO_3$:** (*MW = 100*): 100 mg/l = 100 g/m^3 = 100 ppm = 2 meq/l = 5.848 grains per U.S. gallon (grpg) = 7.00 °E = 5.559 °D = 10.0 °F = N/500 = 0.84 lb. per 1,000 U.S. gallon = 1 lb. per 1,000 imperial gallon.

- **French Degree: (°F):** equal to one part per hundred thousand. Thus 1 °F = 10.0 mg/l. Also 1 °F is equal to N/5,000.
- **German Degree: (°D):** equal to a concentration of 10 mg/l CaO. Thus *1°D = 17.86 mg/l.*
- **Grain:** one seven thousandth of a lb. Grain per U.S. gallon = 17.1 mg/l.
- **Mass:** the quantity of matter in a body. Equivalent to *weight* in a region with constant gravitational acceleration.
- **Milliequivalent** or **gram milliequivalent (mEq):** unit of mass being one thousandth of a gram equivalent.
- **Milliequivalent per liter (mEq/l):** unit of concentration. Same as N/1,000. 1 meq/l of calcium carbonate = 50 mg/l or 50 ppm.
- **Milligram per liter (mg/l):** equal to g/m^3. Also equal to **part per million** (ppm), on a weight/weight basis for solutions with sp gr. of 1.00. 120 mg/l (ppm) = approx. 1 lb./1,000 U.S. gallon.
- **Molar solution:** one mole of solute dissolved in one liter (normally water). Normally expressed as M/1; examples of dilutions would be M/10, M/20, M/100, etc.
- **Mole:** The molecular weight of an element or compound expressed in grams.
- **Molecule:** the smallest part of an element or compound (pure substance).
- **Molecular weight:** the average weight of a molecule measured in units equivalent to 1/12 of Carbon 12 (^{12}C).
- **Normal solution:** one gram equivalent weight dissolved in one liter (N/1); examples of dilutions are N/10, N/20, N100, N/1,000, etc.

DENSITY OF WATER AT VARIOUS TEMPERATURES

Temperature °C	°F	*Density g/ml*	*Temperature* °C	°F	*Density g/ml*
–20	–4	0.99349	4	39.2	1.000000
–10	14	0.998137	10	50	0.999728
0	32	0.998868	15	59	0.999129
1	33.8	0.999927	20	68	0.998234
2	35.6	0.999968	50	122	0.988066
3	37.4	0.999992	100	212	0.958384

SOLUBILITIES OF SOME COMMON SUBSTANCES

Substance	*Formula*	*Solubility (g/l) at 10 °C*	*20 °C*	*30 °C*
Aluminum sulfate	$Al_2(SO_4)_3.18H_2O$	659	688	728
Calcium hydroxide	$Ca(OH)_2$	1.76	1.65	1.53
Calcium sulfate	$CaSO_4.2H_2O$	2.44	2.58	2.65
Copper sulfate	$CuSO_4.5H_2O$	264	297	340
Ferric chloride	$FeCl_3.6H_2O$	927	1026	—
Potassium permanganate	$KMnO_4$	44	64	90
Sodium chloride	NaCl	358	360	363
Anhydrous TSP	Na_3PO_4	41	110	200
Hydrated TSP	$Na_3PO_4.12H_2O$	257	326	416
Sodium hydroxide	NaOH	515	1090	1190

- **Calcium carbonate:** solubility is 0.014 g per liter (14 ppm) at 60 °F in CO_2-free water.
- **Salt brine:** when regenerating ion-exchange softeners, typically assume a 25% W/V solution and that one U.S. gallon contains 2.5 lb of salt and weighs 10 lb.

ANALYTICAL CONVERSIONS OF SOME COMMON SUBSTANCES

Substance	*Formula*	*Atomic/ Molecular Wt.*	*Valency*	*Gram Equiv. Wt.*	*1 meq/l equals ? ppm*
Aluminum	Al	27.0	3	9.0 g	9.0
Aluminum sulfate	$Al_2(SO_4)_3.18H_2O$	666.4	6	111.1 g	111.1
Ammonia	NH_3	17.0	1	17.0 g	17.0
Barium sulfate	$BaSO_4$	233.4	2	116.7 g	116.7
Bicarbonate	HCO_3	61.0	1	61.0 g	61.0
Calcium	Ca	40.1	2	20.0 g	20.0
Calcium bicarbonate	$Ca(HCO_3)_2$	162.1	2	81.1 g	81.1
Calcium carbonate	$CaCO_3$	100.1	2	50.1 g	50.1
Calcium chloride	$CaCl_2$	111.0	2	55.5 g	55.5
Calcium hydroxide	$Ca(OH)_2$	74.1	2	37.1 g	37.1
Calcium phosphate	$Ca_3(PO_4)_2$	310.3	6	51.7 g	51.1
Calcium sulfate	$CaSO_4$ (anhydrous)	136.1	2	68.1 g	68.1
Carbon	C	12.0	4	3.0 g	3.0
Carbonate	CO_3	60.0	2	30.0 g	30.0
Chloride	Cl^-	35.5	1	35.5 g	35.5
Copper (cupric)	Cu^{2+}	63.6	2	31.8 g	31.8
Copper sulfate	$CuSO_4$	160.0	2	80.0 g	80.0
Iron (Ferrous)	Fe^{2+}	55.8	2	27.9 g	27.9
Iron (Ferric)	Fe^{3+}	55.8	3	18.6 g	18.6
Ferrous hydroxide	$Fe(OH)_2$	89.9	2	44.9 g	44.9
Ferric chloride	$FeCl_3.6H_2O$	270.3	3	90.1 g	90.1
Ferric hydroxide	$Fe(OH)_3$	106.8	3	35.6 g	35.6
Iodide	–	126.9	1	126.9 g	126.9
Magnesium	Mg	24.3	2	24.3 g	24.3
Mag. bicarbonate	$Mg(HCO_3)_2$	146.3	2	73.2 g	73.2
Mag. hydroxide	$Mg(OH)_2$	58.3	2	29.2 g	29.2
Manganese	Mn (manganous)	54.9	2	27.5 g	27.5
Phosphate	PO_4	95.0	3	31.7 g	31.7
Silica	SiO_2	60.1	2	30.0 g	30.0
Sodium	Na	23.0	1	23.0 g	23.0
Sodium chloride	NaCl	58.5	1	58.5 g	58.5

continued on next page

Substance	*Formula*	*Atomic/ Molecular Wt.*	*Valency*	*Gram Equiv. Wt.*	*1 meq/l equals ? ppm*
Sodium nitrite	$NaNO_2$	69.0	2	34.5 g	34.5
Sulfate	SO_4	96.1	2	48.0 g	46.0
TSP	$Na_3PO_4.12H_2O$	380.2	3	126.7 g	126.7
Zinc	Zn	65.4	2	32.7 g	32.7

INTERPRETATION OF "P" AND "M" ALKALINITY TITRATIONS

Ions	*P = 0*	*P < M/2*	*P = M/2*	*P > M/2*	*P = M*
(OH)	0	0	0	2P – M	M
CO_3	0	2P	M	2(M – P)	0
HCO_3	M	M – 2P	0	0	0

- Bicarbonates and hydroxides do not exist together. Carbon dioxide does not exist with carbonates.
- "P" Alkalinity = ½ carbonates and all hydroxides.
- "M" Alkalinity = all hydroxides, carbonates, and bicarbonates.

TEMPERATURE CONVERSIONS

$T\ °F = (t\ °C \times 1.8) + 32$ $T\ °C = (T\ °F - 32)/1.8$

STANDARD SI PREFIXES

10^6 = mega (M) 10^3 = kilo (k) 10^2 = hecto (h) 10^1 = deca (da)
10^{-1} = deci (d) 10^{-2} = centi (c) 10^{-3} = milli (m) 10^{-6} = micro (μ)
10^{-9} = nano (n) 10^{-12} = pico (p)

UNITS OF MEASUREMENT

Length

1 meter (m)	= 3.281 ft	= 39.37 in
1 foot (ft)	= 0.3048 m	= 12 in
1 inch (in)	= 2.54 cm	= 25.4 mm
1 mil	= 0.001 in	= 25.4 micron
1 micron	= 1×10^{-6} meter	

Area

1 m^2	= 10,000 cm^2	= 1.196 yd^2	= 10.76 ft^2
1 ft^2	= 144 in^2	= 00929 m^2	= 0.111 yd^2

Volume

1 m^3	= 1,000 liter	= 35.31 ft^3	= 264.2 U.S. gal
1 U.S. gal	= 3.785 l	= 0.8327 imp. gal	
1 U.S. gal	= 231 in^3	= 0.1337 ft^3	
1 barrel (bbl)	= 42 U.S. gal	= 0.16 m^3	
1 55 U.S. gal drum	= 45.8 imp. gal	= 208 l	

(NOTE: drum size approximations are 55 U.S. gal or 45 imp. gal or 210 l).

Mass

1 kg	= 1,000 g	= 2.205 lb.	= 35.53 oz
1 oz	= 28.35 g	= 437.5 grains	
1 lb	= 435.6 g	= 7,000 grains	
1 tonne	= 1,000 kg	= 0.984 U.K. ton (long ton)	
1 U.K. ton	= 2,240 lb	= 1.120 U.S. ton (short ton)	
1 U.S. ton	= 2,000 lb	= 907.2 kg	

Mass/Volume Relationships For Water, Assuming Sp.Gr. as 1.00

1 UK gal	= 8 pints	= 160 oz	= 10.00 lb
1 US gal	= 8 U.S. pints	= 8.345 lb.	= 3,785 ml
1,000 l	= 2,205 lb.	= 35.31 ft^3	= 220 U.K. gal
1 ft^3	= 28.32 l	= 7.481 U.S. gal.	= 62.4 lb.
1 kg	= 1,000 ml	= 1,000 cm^3	= 1,000 g
1,000 U.S. gal	= 378.5 l	= 0.3785 m^3	= 378.5 kg

Velocity

1 meter/second (m/s) = 3.281 ft/s (fps)
1ft/s = 0.3048 m/s

Flow

1 cubic meter/second (m3/s) or 1 cumec = 35.31 ft^3/s
1 ft3 /s = 0.02832 cumec = 7.481 U.S. gal/s
1 imp. gal/m = 4.546 l/m = 1.20 U.S. gal/m

Pressure

1 standard atmosphere (atm) = 760 mm Hg @ 273 °K (0 °C)
= 1.033 kgf/cm^2
= 14.696 lbf/in^2
= 101 kN/m^2
= 33.92 ft H_2O

1 technical atmosphere (at) = 738 mm Hg @ 273 °K (0 °C)
= 1.000 kgf/cm^2
= 14.2233 lbf/in^2
= 98.07 kN/m^2
= 32.85 ft H_20

1 bar = 753 mm Hg @ 273 °K (0 °C)
= 1.019 kgf/cm^2
= 14.5 lbf/in^2
= 100 kN/m^2
= 10.2 m H_2O
= 33.5 ft H_2O

Energy/Power

1 thousand joule (kJ) = 0.95 Btu
= 0.2388 kcal
= 2.778×10^{-4} kW/hr
= 738 ft-lb

1 ton of refrigeration = 12,000 Btu/hr
= 3.52 kW
= 0.841 kcal/sec
= 4.72 hp

1 horsepower (hp) = 550 ft-lb/s
= 0.746 kW
= 2545 Btu/hr
= 0.212 ton (refrig.)

Concentration

1 part per million = 1 mg/l
= 1 g/m^3
= 8.34 lb/million U.S. gal

Geometric facts

Area of a rectangle:	$A = LW$
Volume of rectangular solid:	$V = LWH$
Circumference of a circle:	$C = 2\pi R$
Area of a circle:	$A = \pi R^2$
Volume of a cylinder:	$V = \pi R^2 H$
Surface area of a cylinder:	$S = 2\pi R^2 + 2\pi RH$

Where: A = area, C = circumference, H = height, L = length, S = surface area, V = volume, W = width, π = pi (3.14159)

Boiler Plant System Calculations

Abbreviations:

Boiler horse power = BHP
Boiler water = BW
Chlorides = Cl^-
Cycles of concentration = COC
Feedwater = FW
Makeup water = MU
Steaming rate = SR
Total dissolved solids = TDS

$$\text{FW COC} = \frac{\text{Cl– in BW}}{\text{Cl}^- \text{ in FW}}$$

$$\% \text{ MU} = \frac{\text{Cl}^- \text{ in FW} \times 100}{\text{Cl}^- \text{ in MU}}$$

$$\% \text{ CR} = \frac{(\text{FW} - \text{MU}) \times 100}{\text{FW}}$$

$$\text{FW} = \text{SR} + \text{BD rate (lb per day)}$$

$$\text{SR} = \text{BHP} \times \% \text{ load} \times 34.5 \text{ (lb/hr)}$$

$$\text{Rate of BD} = \frac{\text{SR (lb./hr)}}{(\text{COC} - 1)}$$

$$\%\ \text{BD} = \frac{\text{FW TDS} \times 100}{\text{BW TDS} - \text{FW TDS}}$$

Basic Boiler Maintenance Check List

Daily or more frequently

Check water levels
Blowdown boiler via bottom blowdown valve
Blowdown water columns
Visually check flame and adjust or report as necessary
Take water samples, analyze, compare with recommendations
Interpret waterside actions necessary
Inspect chemical feed and control system, adjust as necessary
Record feedwater pressure, temperature
Record flue-gas temperature
Record oil pressure and temperature
Record atomizing air pressure
Record makeup water meter, fuel meter, and steam chart readings
Log all events

Monthly or more frequently

Check tight closing of fuel valve
Analyze fuel gas and combustion process efficiency
Check fuel and air linkage
Check indicating lights and alarms
Check low water cutoff and alarm system
Check operating and limit controls
Check safety and interlock controls
Inspect for flue gas leak potential
Check for misaligned firing and hotspots
Check for leaks, vibration, or other conditions warranting attention
Check chemical treatment inventory

Every 6 months or more frequently

Clean low water cutoff and other safety devices
Remove and clean oil preheater
Inspect refractory
Clean oil-pump strainer and replace filter
Clean air-cleaner, replace as necessary
Clean water treatment feed pumps, check-valves, and control system

Every 12 months or more frequently

Clean breeching and fireside surfaces
Inspect all internal waterside surfaces, deaerator, and other auxiliaries

TABLE OF ELEMENTS AND ATOMIC WEIGHTS

		Atomic	
Element	*Symbol*	*Number*	*Weight*
Actinium	Ac	89	227
Aluminum	Al	13	26.98
Americium	Am	95	243
Antimony	Sb	51	121.76
Argon	A	18	39.944
Arsenic	As	33	74.91
Astatine	At	85	210
Barium	Ba	56	137.36
Berkelium	Bk	97	249
Beryllium	Be	4	9.013
Bismuth	Bi	83	209
Bohrium	Bh	107	264
Boron	B	5	10.82
Bromine	Br	35	79.916
Cadmium	Cd	48	112.41
Calcium	Ca	20	40.08
Californium	Cf	98	249
Carbon	C	6	12.011
Cerium	Ce	58	140.13

continued on next page

Element	Symbol	Atomic Number	Atomic Weight
Cesium	Cs	55	132.91
Chlorine	Cl	17	35.457
Chromium	Cr	24	52.01
Cobalt	Co	27	58.94
Copper	Cu	29	63.54
Curium	Cm	96	245
Dubnium	Db	105	262
Dysprosium	Dy	66	162.46
Einsteinium	Es	99	252
Erbium	Er	68	167.2
Europium	Eu	63	152
Fermium	Fm	100	257
Fluorine	F	9	19.0
Francium	Fr	87	223
Gadolinium	Gd	64	156.9
Gallium	Ga	31	69.72
Germanium	Ge	32	72.6
Gold	Au	79	197
Hafnium	Hf	72	178.6
Hassium	Hs	108	265
Helium	He	2	4.003
Holmium	Ho	67	164.94
Hydrogen	H	1	1.008
Indium	In	49	114.76
Iodine	I	53	126.91
Iridium	Ir	77	192.2
Iron	Fe	26	55.85
Krypton	Kr	36	83.8
Lanthanum	La	57	138.92
Lead	Pb	82	207.91
Lithium	Li	3	6.94
Lutetium	Lu	71	174.99
Magnesium	Mg	12	24.32
Manganese	Mn	25	54.94

continued on next page

Element	Symbol	Atomic Number	Atomic Weight
Meiterium	Mt	109	266
Mendelevium	Md	101	258
Mercury	Hg	80	200.62
Molybdenum	Mo	42	95.95
Neodymium	Nd	60	144.27
Neon	Ne	10	20.183
Neptunium	Np	93	237
Nickel	Ni	28	58.69
Niobium	Nb	41	92.91
Nitrogen	N	7	14.008
Nobelium	No	103	259
Osmium	Os	76	190.2
Oxygen	O	8	16.00
Palladium	Pd	46	106.7
Phosphorus	P	15	30.975
Platinum	Pt	78	195.23
Plutonium	Pu	94	239
Polonium	Po	84	210
Potassium	K	19	39.1
Praseodymium	Pr	59	140.92
Promethium	Pm	61	145
Potactinium	Pa	91	231
Radium	Ra	88	226.05
Radon	Rn	86	222
Rhenium	Re	75	186.31
Rhodium	Rh	45	102.91
Rubidium	Rb	37	85.48
Ruthenium	Ru	44	101.1
Samarium	Sm	62	150.43
Scandium	Sc	21	44.96
Seaborgium	Sg	106	263
Selenium	Se	34	78.96
Silicon	Si	14	28.09
Silver	Ag	47	107.88

continued on next page

		Atomic	
Element	*Symbol*	*Number*	*Weight*
Sodium	Na	11	22.991
Strontium	Sr	38	87.63
Sulfur	S	16	32.066
Tantalum	Ta	73	180.95
Technetium	Te	43	99
Tellurium	Te	52	127.61
Terbium	Tb	65	158.93
Thallium	Ti	81	204.39
Thorium	Th	90	232.05
Thulium	Tm	69	168.94
Tin	Sn	50	118.7
Titanium	Ti	22	47.9
Tungsten	W	74	183.92
Uranium	U	92	238.07
Vanadium	V	23	50.95
Xenon	Xe	54	131.3
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.92
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.22

Appendix II

GLOSSARY

The intention of this glossary is to provide a water treatment technology definition that is practical rather than always wholly scientific.

Note: BD = blowdown, BW = boiler water, CR = condensate return, FT = firetube boiler, FW = feedwater, HW = hot water, PF = pulverized fuel, PV = pressure vessel, SV = safety valve, TDS = total dissolved solids, WT = watertube boiler.

Absolute pressure:
The sum of boiler *gauge pressure* and *atmospheric pressur*e (14.696 psia).

Accumulation test:
Test used to determine the relieving capacity of boiler safety valves.

Acid-Base:
Various theoretical definitions. Acid is the opposite of a base. Essentially, an acid is a compound or ion containing hydrogen with a tendency to be a *proton donor* to a base or *electron acceptor* from a base. In practice, an acid dissociates in water (H_2O) to form H_3O^+, not H^+ as generally believed. Some acids accept electrons with the formation of covalent (shared) bonds, stronger acids accept complete transfer of electrons and are thus *oxidizing agents*. Bases and *reducing agents* are forms of electron donor chemicals.

Acidity:
The concentration of acids or acidic salts in solution that can be measured by titration with a standard alkali to a selected pH endpoint.

Acid smutting:
Staining or discoloration (such as to motor vehicle paint-work), as a result of acid fallout. Acid fallout is soot particles containing

adsorbed sulfuric acid, and resulting from incomplete combustion, exiting the flue gas system and falling to earth.

Adiabatic expansion:
The process occurring when steam is expanded by conversion to work without external heat loss or gain. Steam expanding behind the piston of a steam engine after the cutoff point approaches adiabatic expansion.

Admiralty brass or Admiralty metal:
Specific types of brass that resist *de-zincification corrosion* and are widely used in heat exchanger fabrication. Typically, Admiralty brass consists of greater than 70% Cu, 1% Sn, small amounts of either As, Sb or P (to prevent de-zincification), and balance is Zn.

Air:
Dry air has a composition of 20.947% oxygen (O_2), 78.086% nitrogen (N_2), 0.934% argon (Ar) and 0.033% carbon dioxide (CO_2) by volume. However, air usually has some moisture and at 60% relative humidity (RH) and 80 °F (26.7 °C) air contains 2.09% water (H_2O).

Air cock (Boiler vent):
Device used to vent noncondensable gases from a boiler during start-up and shutdown procedures.

Air ejector:
A steam driven device fitted to surface condensers and other items of equipment that removes oxygen and other noncondensable gases, thus maintaining a vacuum.

Air flow switch:
A switch that proves primary air is supplied to a boiler.

Air heater:
An heat exchanger located in the exit-gas system. Air heaters preheat combustion air and may be of several different types including *convection* air heaters of either *tubular* or *plate* design and *regenerative* air heaters.

Air to fuel ratio:
Ratio used to ensure the complete combustion of fuel. The ratio changes over the range of high and low fire.

Alkaline hardness:
Hardness in water (soap-consuming scum and scale-generating salts) is caused by the presence of bicarbonates, carbonates, and

hydroxides, of primarily calcium and magnesium. In natural waters, alkaline hardness is principally bicarbonates.

Alkalinity:
Primarily the sum of carbonate, bicarbonate and hydrate ions in water, but phosphate, silicate etc. may also contribute partially to alkalinity. Normally expressed as ppm (mg/l) $CaCO_3$. Phenolphthalein alkalinity (P Alk.) is that portion of alkalinity titrated with acid to pH 8.2 end-point, while total alkalinity (T Alk. or M Alk.) is that titrated with methyl orange indicator to pH 4.2 end-point.

Alloy:
Metal with additional elements designed to provide beneficial properties, such as brass or stainless steel.

All volatile treatment (AVT):
A form of *low solids treatment* program whereby there is no apparent addition to the total dissolved solids in the BW.

Ambient air:
The atmospheric open air, not in any confined area.

Ambient temperature:
The temperature of the surrounding air.

Amines:
A class of chemicals derived from ammonia employed to treat steam and condensate.

Amphoteric metal:
A metal, such as zinc, that forms salts with potentially weak acidic or basic properties. Limits the applicability of the metal as an inhibitor against water treatment problems. Examples are aluminum salts in water, which produce a weak base [$Al(OH)_3$] and zinc, which may corrode at either low or high pH.

Anhydrous:
Meaning "without water" and describing salts that do not contain any water of crystallization.

Anion:
Negatively charged ion in aqueous solution, e.g., chloride (Cl^-) or sulfate (SO_4^{2-}). Certain chemicals may therefore be *anionic* and exhibit anionic properties.

Anion exchange:
The replacement of negative ions of soluble salts (such as Cl^-) by hydroxyl ions (OH^-) by passage through a basic resin bed (as in one half of the *demineralization* process).

Annunciator:
An audio alarm. The sound is produced electronically.

Anode:
Positive electrode (+) of electrolytic cell where oxidation occurs and electrons are donated.

Anodic inhibitor:
Chemical that reduces the tendency of iron to oxidize (rust) to ferrous ion, such as *chromate* which suppresses that part of the electrolytic corrosion process occurring at the anodic sites on a metal surface.

Anthracite coal:
A hard type of coal with a high calorific value.

Antifoam:
A chemical treatment added to prevent the possibility of foaming occurring in the boiler and reduce the risk of BW carryover. Commonly also known as a **defoamer**, although this type of treatment is designed to stop foaming *after* it has already occurred and may involve different chemistries.

Antiprecipitant:
A chemical that retards the precipitation of insoluble salts. Mechanism is usually by inclusion within the crystal structure.

Appurtenances (fittings):
Equipment fitted directly to a boiler primarily for safety reasons.

Ash:
The powdery residual matter remaining after combustion.

Ash fusion temperature:
The temperature at which ash particles change from a liquid to a solid. A high ash fusion temperature indicates that the ash particle will quickly change to a solid after burning and is less likely to adhere to a boiler fireside surface (as slag).

Ash hopper:
A storage receiver for combustion ash.

ASME code:
One of several codes written by the American Society of Mechanical Engineers. Some codes provide controls for the construction, repairs, and the operation of boilers and other types of PV and boiler appurtenances in the United States.

Atmosphere:
A unit of pressure. 29.92 inches of mercury at sea level at 45° latitude. Equal to 1,000 g/cm^2.

Atmospheric pressure:
The pressure at sea level. Taken to be approximately 14.7 psia.

Atomize:
To convert a liquid into a fine mist by mechanical means.

Attemperator (desuperheater):
An apparatus for reducing and controlling the temperature of superheated steam. Typically, a spray attemperator design is employed.

Attrition:
A form of erosion especially relating to the frictional wear of ion exchange resins, such as that of water softener resin, causing loss of capacity.

Austenitic:
Describes certain types of stainless steels and other metals that consist of nonmagnetic iron containing face-centered cubes of carbon or other elements in solid solution.

Automatic blowdown system:
One of several different types of BW blowdown systems that automatically controls the frequency and duration of the BD period. Some systems provide continuous BD.

Automatic non-return valve:
A type of valve located in the steam line and elsewhere that automatically cuts the boiler in and out, thus providing for online and offline operation. This valve protects the steam system in the event of a loss of pressure from a boiler, caused perhaps by a large steam leak.

Auxiliaries:
Any item of equipment fitted to a boiler to improve control or a major component within one of the many boiler plant systems and sub systems.

Azeotrope:
Two or more compounds that when mixed together provide a constant boiling point, distilling off without decomposition and in a constant ratio (e.g., isopropyl alcohol and water).

Back pressure:
The pressure exerted against a flow.

Backwash:
Part of the operating cycle of water filters or softeners. It involves the upward flow of water to lift up the media bed to release and wash away dirt and other unwanted particulate matter and to reclassify the media.

Baffles:
Equipment located inside the boiler furnace area to direct the path of hot combustion gases and thus gain maximum heat absorption.

Balanced draft:
A system of balancing induced draft and forced draft to a large WT boiler controlled primarily by dampers. In fact, large WT boilers tend to be specifically designed to operate at a slightly *negative* furnace pressure.

Bar:
The cgs system unit of pressure. 1 bar = 1×10^6 dynes/cm^2, = 1×10^5 N/m^2, = 29.531 inches of mercury (Hg), = 753 mm Hg, at 32 °F (0 °C), and at a latitude of 45°.

Base:
Alkaline chemical, opposite of acid, as in the equation: Acid + Base = Salt + Water.

Base exchange softening:
Ion-exchange softening.

Base load boiler:
A utility boiler that operates at constant output in order to generate base-load electricity.

Bed:
The volume of carbon, sand, ion-exchange resin, or other media contained in a pressure tank and used as pre-treatment process for water. Requirements for bed depth, expansion and support, etc. are governed by the design criteria for each process.

Bed volume (BV):
A volume measure of the permitted flow rate of water through ion exchange resins and sometimes other media, such as sand. Typically, ion-exchange resins used for water softening will tolerate 8 to 40 BV/hr.

Bent-tube boiler:
A multiple-drum WT boiler design that allows for more flexibility in the internal arrangement of boiler surfaces.

Bituminous coal:
A soft coal with a high volatile content.

Black liquor:
The liquid remaining from the cooking of pulpwood. It is used as a fuel in specially designed pulp and paper industry WT boilers.

Blowdown:
A portion of the circulating BW that is removed, either intermittently or continuously, to limit the concentration of soluble and insoluble salts in the water.

Blowdown tank:
A PV that receives boiler BD prior to any final discharge to waste.

Blowdown valve:
One of various types of valve employed to enable BD of a boiler. Main BD valves are located at the bottom of all boiler drums, shells, and headers.

Boiler capacity:
The potential output of a boiler, normally given as lbs/hr or kg/hr *maximum continuous rating* (MCR).

Boiler explosion:
A waterside expansive force that can be caused by a sudden drop in steam pressure without a corresponding decrease in temperature (especially in a FT boiler). Or a furnace expansive force due to the ignition of highly inflammable gas, vapor or dust. Minor furnace explosions are called *puffs*, *flarebacks*, or *blowbacks*.

Boiler horsepower:
A boiler steam generating rate of approximately 34.5 lb./hr. *from and at* 212 °F (33,475 Btu per hour) and today, typically provided by 5 sq. ft. of boiler heating surface.

Boiler layup:
The removal of a boiler from service for an extended period. A layup (wet or dry) requires the boiler to be stored under controlled conditions to avoid corrosion.

Boiler room log:
A book into which all notable events, problems, and requirements identified during the operation of a boiler are recorded.

Boiler surfaces:
The various tubes, connecting headers (manifolds), and drums within the *steam/water circulation system* that collectively provide primary heat transfer and steam generation.

Boiler shutdown:
A set of procedures undertaken to remove a boiler from service ("*going off-line*").

Boiler startup:
A set of procedures undertaken to prepare a boiler for service ("*going online*").

Boiler tube:
Any of a number of steel tubes used simultaneously as heat transfer devices for both steam generation and boiler furnace cooling. Boiler tubes may be straight or bent.

Boiler vent (air cock):
Device used to vent non-condensable gases from a boiler during startup and shutdown procedures.

Bottoms:
The portion of petroleum crude left after lighter fractions are distilled. Today, much of the bottoms that goes into residual fuel oil (No. 6 oil) is simply asphalt or asphaltines.

Bourdon tube:
The coiled-tube component of a pressure gauge that coils or uncoils dependent upon pressure inside the tube.

Box header:
A box shaped, steam-water receiving vessel employed in older WT boiler designs. Box headers required *staybolts* to prevent bulging.

Boyles Law:
Under constant temperature conditions, the volume of a gas varies inversely as the pressure: $p_1V_1 = p_2V_2$

Brass:
One of several corrosion resistant *copper/zinc* alloys (e.g. 70% Cu + 30% Zn). See **Admiralty brass**.

Breakthrough (endpoint):
The point reached in the service cycle of an ion exchange resin where the exchange capacity has been exhausted and the ion to be exchanged breaks through the bed.

Breeching:
The exit-gas duct connecting a boiler to its chimney.

Brining:
Part of a softener regeneration process whereby the cation ion exchange resin is converted to the sodium form by the application of a, typically, 10 to 15% W/V strength of brine (sodium chloride).

British thermal unit (Btu):
A measurement of heat energy. One Btu is the quantity of heat required to increase the temperature of one pound of water by one degree Fahrenheit (F). Also, one Btu is lost when one pound of water is reduced by 1 °F.

Brittle fracture:
The separation or cleavage of a metal with little or no resulting *plastic deformation*.

Bronze:
One of several types of high-chloride resistant, copper/tin alloys (e.g. 90% Cu + 10% Sn), usually 11% Sn maximum and also containing small amounts of Zn and P. Also bronze alloys, whereby Sn is replaced by Al, Si, or Be.

Brownian movement:
Movement of colloidal suspended particles due to forces resulting from collision of colloids and molecules of suspended medium (usually water).

BS&W:
Or S&W. Basic sediment and water. The paraffin, sediments, and salt water impurities in crude and oil fuels that need to be removed prior to further processing or use.

Burning in suspension:
The combustion of a fuel in air without visible support. PF coal is burnt in suspension within the boiler combustion chamber.

Butterfly valve:
A balanced valve employed to control gas flow in gas-fired boilers.

Bypass damper:
A type of damper used to control the air temperature in air heaters. It also provides a means of minimizing air heater corrosion.

Bypass line:
A pipeline that passes around an injection point, valve, control point, heater, steam trap, or other device in order that repairs or other work can be carried out on the bypassed item of equipment as and when required.

Calibrate:
To adjust a pressure gauge or other measuring device in order to conform closer to a test gauge or set of standards.

Carbon steel:
A two-phase mixture of *ferrite* and *pearlite*.

Carbonate control:
A virtually defunct form of chemical treatment program employed in older design, low heat-flux boilers, whereby the risk of BW scale formation is managed by means of a controlled reserve of carbonate ions.

Carnot cycle:
An early concept of the cycle of thermodynamic processes as relating to steam engine heat-energy performance.

Carryover:
BW containing some level of contaminant that is entrained and passes with the steam into the main steam-header. Carryover is always detrimental to the steam cycle process and is primarily caused by BW *priming* (*surging*), *gulping*, *misting*, or *foaming*.

Cast iron:
Iron/ carbon alloy, poured as a hot molten liquid into a mold. Usually produced as either *gray iron* (where flakes of graphite are embedded in an iron matrix) or *nodular iron* (spheroids of graphite in the matrix).

Cathode:
Negative electrode (−) of an electrolytic cell where reduction occurs and electrons donated.

Cathodic inhibitor:
Any chemical (such as zinc hydroxide) that suppresses the reduction of oxygen to hydroxyl ion. A cathodic inhibitor suppresses that part of the electrolytic corrosion process at the cathodic sites on a metal surface.

Cathodic protection BW programs:
Cathodic protection equipment has been used very successfully in water tanks and HW and steam boilers as anticorrosion devices for 100 years or more. Such equipment comes in many shapes and sizes, and comprises a sacrificial anode of either zinc or magnesium alloy, either bolted directly to a suitable internal water-wetted (cathodic) metal surface, or self-contained by enclosing the anode with a suitable cathode (such as a silver plated base metal). Usually several devices are required for any boiler, more for larger units and less for smaller ones, and these require replacement every one to two years.

Cathodic protection is a useful supplement to other forms of water treatment, as a general corrosion inhibiting device in HW boilers, or where specific design configurations can lead to inadequately protected localized metal in steam boilers. Where BW makeup demands are minimal and boiler output is fairly constant, cathodic protection devices can also provide some measure of protection against hardness scales. Calcium carbonate salt is formed as a flocculant or soft sludge rather than a hard scale, due to the peptizing effects of a zinc hydroxide complex formed from zinc ions in alkaline BW.

Claims are sometimes made that the use of cathodic protection devices eliminates the need for any type of water treatment chemical, including oxygen scavengers (on the basis that oxygen in the FW increases the rate of zinc anode corrosion, producing both zinc ions and hydroxide ions and resulting in the removal of O_2 from the BW electrolyte). Such claims that corrosion protection devices provide a complete program are spurious.

NOTE: Butler Engineering Associates, Inc. of New Jersey, USA, provide cathodic protection devices suitable for boilers of up to 150 psig, and promotes them as a complete alternative to chemicals with no messy mixing, pouring or testing being required. Nevertheless, it is noted that this com-

pany also markets a liquid, color-coded BW treatment chemical formulation under the brand name COR-EX.

Cation:
Positively charged ion in aqueous solution such as hydrogen (H^+) or calcium (Ca^{2+}) ions. Certain chemicals may therefore be *cationic* and exhibit cationic properties.

Cation exchange:
Replacement of positive ions of a soluble salt by passing sodium through a cation resin (*softening* or *base exchange*) or hydrogen through an acidic resin (as in one half of the *demineralization* process).

Caustic cracking:
A form of boiler waterside, *caustic stress-corrosion cracking corrosion* affecting carbon steels and austenitic stainless steels (300 series). Particularly associated with high localized concentrations of deposited *sodium hydroxide* (caustic soda).

Caustic embrittlement (caustic stress corrosion cracking):
A general term for those types of corrosion induced by caustic and accelerated by stress and moderately high temperatures (200–250 °C).

Caustic gouging (ductile gouging):
A form of corrosive attack on boiler steel by a very high concentration of sodium hydroxide in which hydrogen is evolved and *ferrite* and *hypoferrite* ions are formed.

Cavitation:
Formation of vapor bubbles in rapidly flowing or turbulent water causing risk of pumping failure and erosion and/or corrosion. Due to an increase in velocity at the pump head resulting in a localized pressure reduction and the subsequent collapse of the vapor into *voids* or *cavities*. Where FW temperatures are high (over perhaps 195–205 °F) the pump velocity can reduce FW vapor pressure below that corresponding to the temperature of the liquid and cavitation can occur accompanied by some noise. Warning of severe pump cavitation is often indicated by a heavy noise.

Cementite:
Ferric carbide. A compound of iron and carbon having the approximate formula Fe_3C.

Centrifugal force:
The force created by a rotating impeller that builds up in a centrifugal pump.

Centrifugal pump:
A popular design of boiler FW pump that employs centrifugal force to create pumping pressure.

Chain grate stoker (traveling grate stoker):
A *cross-feed stoker* employed with high capacity boilers because of its ability to feed solid fuel at a faster rate than other stoker designs.

Channeling:
The short-circuiting or taking the least line of pressure resistance of a flow of water in a resin bed.

Check valve:
An automatic valve that controls the flow of a liquid by permitting it to travel only in one direction.

Chelant:
Organic compound (such as ethylenediamine-tetraacetic acid (EDTA) or nitrilo-triacetic acid (NTA) having the ability to take metal ions in water and produce soluble, coordinate-bond complexes. Chelants are commonly used in BW deposit control treatments and various cleaning formulations.

Chelonate:
A coordination complex formed by the chelation of a metallic ion.

Chemical compound:
A chemical formed from a reaction of two or more elements.

Chemical concentration:
The amount of chemical in a given amount of water. Normally given as *parts per million* (ppm), *parts per billion* (ppb), or *milligram per liter* (mg/l).

Chemical mixture:
Two or more chemical compounds or elements mixed together and usually capable of easy separation.

CHEMTREC:
USA Chemical Transportation Emergency System.

Chimney:
The vertical flue part of an exit-gas system. Designed to induce draft in order to exhaust the gases into the atmosphere.

Classes of fire:
The three classes of fire are: **A**: those started from wood paper or rags; **B**: those started from oil, grease, or flammable liquids; **C**: those initiated by electricity.

Classification:
The backwash and rinse cycle part of a filtration or ion exchange process that permits a media bed to resettle in a graduated manner so that the largest grains or beads are at the top and the smallest at the bottom.

Clinker:
Commonly also known as cinder or slag. Clinker is the mass of fused ash that results after the incombustible residual material from combustion cools down from a molten state.

Coagulate:
To bring together small particles into a single larger mass that can be filtered or flocculated and subsequently removed from a water.

Coal bunker:
A storage container for coal, often an overhead hopper.

Coal conveyor:
A continuous rubber belt used to transport coal from the coal yard to a fuel preparation and storage area.

Coalesce:
To bring together small droplets of oil into a larger volume that can then be separated from water.

Coal feeder:
A mechanism used to control the rate of feed to a stoker or pulverizer.

Coal gate:
A device used to control the depth of coal entering the boiler furnace in a stoker feed system.

Coal ram:
A device to evenly distribute the coal into the center retort of an underfeed stoker and force it to the top of the stoker from where it can be fired.

Coal scale:
A coal measuring and recording device for stoker fired or PF fired boilers.

Cocurrent:
A design feature of an ion exchange plant whereby service flow and regenerant flow are in the same direction. The opposite of *countercurrent* (*counterflow*).

Cogeneration (combined cycle):
The production of electricity and industrial process steam in the same boiler plant system.

Cold work:
The permanent deformation of a metal produced by a press, hammer, or other external force.

Colloid:
Extremely small particle, typically 10^{-5} to 10^{-7} cm in diameter. Colloidal solutions or *hydrosols* contain colloidal particles that are electrically negatively charged, which contributes to their fine dispersion and the difficulty of sedimentation and clarification. Coagulation is usually carried out by causing the particles to adsorb positively charged ions, such as aluminum from alum.

Combustible material:
Any material that burns when exposed to oxygen and heat at its ignition temperature.

Combustion:
The rapid *exothermic* (heat generating) chemical process that occurs when oxygen reacts with a fuel.

Combustion control:
The regulation of the combustion process in a boiler furnace. Control takes place by regulating the access of fuel or air.

Complete combustion:
The total burning of a quantity of fuel supplied ideally with the minimum of excess air necessary.

Compressive stress:
The stress that occurs when equal and opposite forces act upon an object. All FT boiler tubes are subject to compressive stress.

Condensate:
Steam that has lost heat and *condensed* (reverted to liquid water).

Condensate polisher:
A type of high-temperature operation, ion-exchange plant. It can remove contaminants from condensate by both exchange and filtration mechanisms.

Condensate tank:
A receiver for the collection of condensate prior to being pumped to an *open FW heater* (deaerator).

Condensing turbine:
A design of turbine whereby the driving force is provided by exhaust steam condensing in a surface condenser.

Conditioning:
The process of adding chemicals to a water to "condition" it, in order prevent any subsequent deposition or corrosion taking place.

Conduction:
The transmission and transfer of heat without bulk motion of the conductor.

Conductivity:
The phenomenon of transmitting electrons through a body (an electric current). Usually associated with the measurement of electrical conductivity through water and measured in *microSiemens per centimeter* (μS/cm) or *micromho per centimeter* (μmho/cm). 1 μS/cm = 1 μmho/cm. The *mho* is equivalent to a *reciprocal ohm* (the unit of resistivity).

Congruent phosphate conditioning:
One of several phosphate-conditioning programs for high pressure WT boilers, (*coordinated* and *equilibrium phosphate conditioning* are others). Congruent phosphate conditioning is used to provide a precisely controlled and limited range of boiler water pH and total phosphate. The program involves the careful blending of various alkaline phosphate buffers with a view to avoiding the formation of free hydroxyl alkalinity.

Contact heater:
A FW heater into which "live" steam is injected.

Convection:
A mechanism of heat transfer in which heat energy is transmitted by convection current motion through gases and liquids. Part of the heat-transfer process in a boiler is by convection whereby the circulation of water carries heat from the tube near the fire to the drum and surrounding areas.

Convection superheater:
A type of superheater that is located within the convective pass section of a boiler and receives heat by convection.

Corrosion:
Oxidation of a metal or alloys to its (lower energy state) oxides or cations. In effect, the wastage or other damage to a metal caused by one or more of several types of chemical or electrochemical reactions. Takes many forms such as galvanic, crevice, pitting, underdeposit, and biologically induced corrosion.

Corrosion current:
Stream of electrons flowing (by convention) from anodic (+) to cathodic (−) areas of a metal. Part of the overall corrosion mechanism.

Corrosion debris:
Corrosion product. Rust, oxide, or other result of corrosion process.
Corrosion fatigue:
A form of corrosion resulting in the *transgranular cracking* of a metal in an corrosive environment under a cyclical pattern of stress.

Countercurrent (counterflow):
A design feature of ion-exchange plant whereby the regeneration flow or backwash flow are in the opposite direction to the service flow. Also, a principle used in heat exchangers whereby the medium being heated flows in the opposite direction to the medium supplying the heat.

Cracking open:
A term meaning to slowly open a valve in order to allow pressure to equalize on both sides of the valve.

Creep:
The high temperature and stress-induced deformation of a metal, the extent of which is time-induced.

Critical pressure:
The pressure at which there is no separation of phase in a liquid. The critical pressure of water is 3203.6 psia.

Cross-linkage:
The tie between polymer chains to link them together, producing added strength and other benefits. As exemplified by *divinylbenzene* (DVB).

Cross "T":
A connection fitted to water columns and other items of equipment permitting easy inspection and cleaning of the equipment.

Cyclone separator:
A steam-water separation device that functions by the use of centrifugal force and changes in direction.

Damper:
A device used to control the flow of air and other gases.

Data plate (name plate):
A plate attached to boilers, valves, and other equipment containing officially required data pertaining to operational rating and safety issues.

Day tanks:
Tanks employed to hold diluted water treatment chemicals or regenerants and used as a reservoir to be pumped or educted into a water system as part of a treatment process.

Deadweight tester:
A device used to test and recalibrate a pressure gauge.

Dealkalization:
Any of various processes for reducing the alkalinity content of water, especially the use of ion-exchange processes for dealkalizing boiler MU water.

Deaerating feedwater heater (deaerator):
A type of steam-heated open FW heater containing a vent and vent condenser and employed for the elimination of non-condensable gases. Depending upon deaerator design and operation, it is sometimes possible to reduce FW dissolved oxygen (DO) levels to below 0.005 cc/l (7.2 ppb).

Dealloying (selective leaching):
A form of corrosion in which of one or more elemental constituents of an alloy is leached, often leaving a porous structure. Examples are *dezincification* of brass and *denickelization* of nickel alloys.

Decarburization:
A form of corrosion induced by the oxidation of carbon in the *ferrite* phase of carbon steel to carbon dioxide.

Defoamer:
See **Antifoam**.

Deionize (DI):
To *demineralize* or remove ions from solution by means of an ion-exchange plant.

Demineralization (deionization):
The process of removal of both cations and anions from waters by ion-exchange, evaporation, or other means.

Density:
The mass of a given volume of matter. The density of water is 1.0 g/cm^3 at 20 °C, or 62.5 lb. per cu ft.

Deposit:
Any of a number of crystalline or non-crystalline scales and other insoluble materials laid down in a boiler system by a variety of mechanisms. Usually on a heat-transfer surface.

Deposit control agent (DCA):
Any of a number of modern, polymer-based chemical formulation additives having one or more deposit-inhibiting effects when applied to water as part of a prescribed treatment program.

Desuperheating:
The process of removing heat from superheated steam in order to control high pressure steam temperature and to tailor the steam for different, lower temperature and/or pressure applications.

Dewpoint:
The temperature at which water vapor (steam) condenses. The dewpoint temperature is important in boiler fuel combustion processes, as whenever a metal surface is cooler than flue gas, condensation occurs. If sulfur gases are present and the acid dewpoint (the tem-

perature at which H_2SO_4 vapor is in equilibrium with liquid H_2SO_4), cold-end corrosion will take place.

Dezincification:
Form of corrosion of brasses whereby the zinc is selectively leached out of the brass. Prevented by either reducing the zinc content to below 15% or by the addition of trace amounts of inhibiting elements, such as arsenic (As).

Discharge pipe:
The piping attached to the outlet side of a BD or safety valve to convey steam/water to an external environment.

Dispersant:
A chemical agent having the ability to lift, separate, and maintain in suspension a variety of mineral particles for a limited period.

Dissociation:
The process of ionization in water of an electrolyte or a salt, whereby cations and anions are formed.

Distribution ratio:
The ratio of a concentration of an amine chemical treatment in steam solution compared to that in condensate solution under a given pressure and temperature.

Divinylbenzene (DVB):
A difunctional monomer commonly employed to cross-link ion-exchange polymers.

Downcomer:
A pipe that transports BW down and away from the top drum, usually to a *waterwall bottom header.*

Draft:
A pressure difference between two points that provides the impetus for air or other gases to flow.

Drip feed:
A means of adding liquid chemical treatment to a FW tank by means of an overhead dripping container rather than by use of a dosing pump. From a control viewpoint, drip feed is most usually unsatisfactory as the feed rate reduces over time with decrease in treatment head pressure, and ultimately the device tends to gum up.

Dry-bulb temperature:
Temperature of ambient air as measured with a dry-bulb thermometer (DB °F or °C).

Dry pipe separator:
A steam-water separation device consisting of a horizontal closed pipe, perforated at the top and with drain holes at the bottom.

Ductile fracture:
A metal fracture characterized by considerable plastic deformation, the tearing of metal and an appreciable expenditure of energy, as occurs with repeated bending of a strip of metal.

Ductility:
The ability of a metal (or other substance) to be drawn by plastic deformation without fracturing.

Economizer:
A type of FW heater located in the exit-gas pass of the boiler system.

Eductor:
A device through which water flows creating a vacuum that is employed to draw a solution (such as a coagulant or flocculant) into the stream of water.

Effluent:
The flow of water out of a tank or water system. The opposite of *influent*. A waste stream.

Electric boiler:
A type of boiler that produces heat via electric resistance coils or electrodes.

Electrostatic precipitator:
A device used to remove *fly-ash* from boiler exit-gases in order to reduce the atmospheric pollution load. It places an electric charge on the dust particle and removes the particle onto a collecting plate.

Emulsion:
A colloidal dispersion of oil-in-water. In BW systems where oil contamination has occurred, emulsifying agents from the oil can produce an emulsion which further adds to the total foulant load and impedes heat-transfer. Specific organic emulsifiers have both *hydrophilic* (water loving) and *lipophilic* (oil loving) groups in the same molecule.

Enthalpy:
The total heat content of a body. The sum of *sensible heat* and *latent heat.*

Entrainment:
The transport of water (and associated TDS) into a gas steam, e.g. *carryover* in a boiler.

Entropy:
Theoretical mathematical expression of energy measurement related to the second law of thermodynamics. Essentially a measurement of relative quantities of energy distribution, and reported in units of Btu/lb. or J/kg.

Equilibrium:
The point of balance at which there is no driving force in a reversible reaction.

Equalizing line:
A steam heating line used to warm up the main steam line and equalize the pressure around the main steam stop valve.

Equivalent mineral acidity:
The total concentration of neutral salts in water, each expressed in terms of calcium carbonate.

Erosion:
A type of metal wastage caused by the mechanical action abrasion of the metal surface by high velocity steam, air bubbles or solid particles. Often part of a larger erosion-corrosion process.

Eutectic mixture:
A mixture of salts having a minimum melting point less than any of the individual constituents.

Eutectic structure:
The microstructure of a metal resulting from the solidification of liquid metal such that two or more distinct solid phases are formed.

Evaporation test:
A test employed to check the effectiveness of the low-water, fuel-cutoff valve.

Excess air:
The amount of air needed for complete combustion over and above the theoretical requirement. In practice, excess air requirements typically may range from 5 to 30%.

Exfoliation
A form of corrosion exhibited by the throwing off of thin slivers or chips from the surface of a metal such as cupro-nickel.

Exhauster:
A device that discharges a mixture of coal and warm air to the burner.

Expansion bends:
A piping design feature that permits the expansion and contraction of lines to occur without risk of damage to the lines, valves, or other system components.

External treatment:
A general description for a wide range of pre-boiler FW and MU water treatment processes.

Extraction steam:
Steam extracted from one or more controlled pressure points on an *extraction steam turbine* and used for various process applications. Extraction steam may be delivered to an *extraction heater.*

Feathering:
The action that may occur at the point when a safety valve is about to lift.

Feedwater:
The water supplied to a boiler by the FW pump and consisting of a combination of CR and MU water.

Feedwater heater:
One of several different types of heater used to raise the FW temperature so as to avoid boiler thermal shock and gain improved efficiency and economic benefit.

Feedwater pump:
One of several different types of pump including turbine and centrifugal pumps used to convey FW to the boiler inlet at the correct pressure.

Feedwater regulator:
A device used to maintain the normal operating water-level (NOWL) in a boiler.

Feedwater treatment:
That part of a chemical treatment program applied directly to the boiler FW. Some chemicals may additionally be applied direct to the BW, steam, condensate, or MU water.

Ferrite:
A term applied to iron in the *alpha state* (αFe) containing approximately 0.2% carbon together with other elements in solid solution.

Ferritic stainless steel:
A magnetic form of stainless steel that contains an αFe microstructure.

Field erected boiler:
A boiler that must be erected in the field rather than supplied as a packaged unit, due to its large size and complexity.

Filming amine:
A long-chain amine usually fed to the steam header and employed to prevent steam and condensate line corrosion by a surface-filming process.

Filtration:
In this context it is the separation of solids from water by forcing the water through a porous filter media. The objective is typically to reduce the level of TDS in the water and often to reduce both the size of the particle remaining and the turbidity of the water. Filtration efficiency and quality is a function of many variable factors, although filtration is usually carried out at relatively low velocities, where velocity and pressure drop are directly related to each other. Typically a sand filter will remove a high percentage of particles above a diameter of 20 to 30 μm, whereas dual or multimedia filtration is required to remove particles down to a diameter of 10 to 20 μm.

Fines:
The debris resulting from the attrition or other breakdown mechanism of filtration or exchange media. Typically, fines are particles of under 50 mesh.

Firebox:
A boiler furnace. The part where fuel is combusted.

Fire point:
The temperature at which a fuel will burn continuously when exposed to a flame, as measured in a *flash-point apparatus*.

Fire tube (FT) boiler:
A design of boiler where BW is on the outside of heat exchange tubes and the hot gases of combustion are on the inside.

Firing rate:
The quantity of fuel that can be burnt per unit time.

Fish-mouth rupture:
The bursting of a boiler tube resulting in a rupture having the appearance of a fish mouth.

Fittings:
Boiler appurtenances.

Flame scanner:
A boiler device that proves the pilot and main flame continuity.

Flareback (puffs or blowbacks):
A boiler explosion of limited intensity. It may still cause flames to be thrown several feet beyond the boiler.

Flash economizer:
The heat exchanger component of a boiler blowdown, flash steam, and heat recovery system (FSHR).

Flash-point:
The temperature at which a fuel emits sufficient vapor to flash when exposed to an open flame.

Flash steam:
Steam generated from HW that is subjected to a sudden pressure drop.

Flash vessel (flash tank):
A PV that permits flash steam from BW blowdown to separate from the hot water.

Flat gauge glass:
A type of glass used for gauge glasses operating at over 250 psig.

Flocculant:
A chemical agent that causes the agglomeration of small, pinhead sized particles to larger flocs for the purposes of settlement and water clarification.

Flue gas analyzer:
One of several different types of flue-gas analysis equipment (such as *electronic*, *Fyrite*, or *Orsat* types). They are used to determine boiler fuel combustion efficiency.

Flux:
A substance (usually liquid) employed to remove surface metal oxides in preparation for soldering, brazing or other metal fusion techniques. Also, the rate of energy transfer across a given surface area.

Fly ash:
Small particles of (mostly combusted) material suspended in the gases of combustion and carried out of the furnace flue with these gases.

Foaming:
The formation of small, stable, non-coalescing bubbles at BW heating surfaces that rise to the steam/water interface. With relatively pure water larger bubbles develop and break easily to release the steam, however, where either excessive suspended solids or excessive TDS are present, the water film around each bubble is toughened and stabilized by the impurities. Smaller bubbles develop and the final eruption of steam (*steam surging*) encourages *priming* (*surging*) and *carryover* to take place.

Forced draft:
Mechanical draft produced by a fan supplying forced air to the furnace.

Fouling:
General term for any impediment to a flow of water in a system. Fouling is caused by insoluble matter.

Fouling factor:
Reciprocal of *heat transfer coefficient* multiplied by 1,000. A term employed when designing *surface condensers*.

Free blowing drain:
A drain line used to remove condensate from the main steam line.

Freeboard:
The space above a media bed in a closed vessel that permits bed expansion and backwashing to take place. The allowance typically is 25 to 60% of the volume occupied by the media.

Free mineral acidity (FMA):
The sum of mineral acids in a solution.

Gagging:
The application of a clamp on a SV spindle to keep the valve in a fully-closed position, especially during a hydrostatic test.

Galvanic corrosion:
A form of corrosion resulting from the presence of two dissimilar metals such as steel and copper in an electrolyte such as water forming a galvanic couple, whereby the less noble *anodic* metal (in this case steel) corrodes.

Galvanic series:
A list of metals and alloys arranged for the purposes of water treatment to show their relative potential for *nobility* or resistance to corrosion.

Gas calorimeter:
An instrument used to determine the heat content of a fuel gas.

Gas cock:
A manual, rapid-action gas shutoff valve.

Gas mixing chamber:
A low-pressure air and fuel gas mixing chamber located prior to the boiler furnace.

Gas porosity:
The development of a porous structure in a solidifying metal caused by the evolution of dissolved or entrapped gases.

Gate valve:
A valve that operates either in the fully open or fully closed mode. Widely used especially as a boiler stop valve.

Gauge glass:
A sight glass to indicate the BW level and capable of being blown down to remove any sludge or sediment that may impair reading the correct level.

Gauge pressure:
The pressure inside a PV. The contribution to *absolute pressure* beyond that provided by atmospheric pressure.

Globe valve:
A type of valve often used to take an item of equipment out of service. An inline globe valve is typically installed with a bypass line and bypass valve.

Grain:
One seven thousandth of a pound. 1 grain per U.S. gallon (grpg) as $CaCO_3$ = 17.1 ppm (mg/l). Also, describes a particulate crystal in a crystalline metal or alloy.

Graphitic corrosion:
Selective form of iron corrosion, primarily in *gray cast iron* but also less commonly in *nodular cast iron*, whereby the (*anodic*) iron matrix converts to *iron oxide* while the (*cathodic*) graphite remains intact. The casting retains it shape but loses all strength and can be cut with a knife.

Graphitization:
High temperature, long-term phenomenon whereby the *iron carbide* component of steel changes to graphite and pure iron.

Grate:
That part of a solid-fuel furnace on which the fuel is held and the combustion process starts.

Gravimetric:
Measurement by weight.

Gulping:
An intermittent form of BW carryover caused by variable water levels. Especially carryover into WT boiler superheaters.

Handhold:
An internally positioned, removable steel cover for boiler shells and other types of PV. It enables inspections and cleaning to take place.

Hardness:
Primarily the sum of Ca and Mg salts in water, although it may include other metal salts such as Al, Mn, Sr, and Zn. *Temporary hardness* (*carbonate hardness*) is that portion of the total hardness that can combine with CO_3 or HCO_3. The balance is *non-carbonate* or *permanent hardness* and is caused by Ca or Mg nitrates/sulfates/chlorides, etc. Permanent hardness is equivalent to the excess of hardness over alkalinity.

HAZMAT:
Hazardous materials and an international coding system for identification. Many water treatment chemical formulations contain hazardous materials, which need special handling and transportation.

Head:
The energy per unit of fluid (e.g. lb.).
Potential head:
Refers to the energy of position, measured by the work possible in dropping a vertical distance.

Static pressure:
Energy per unit of fluid due to pressure, it is the height to which a liquid can be raised by a given pressure.

Velocity:
Refers to the kinetic energy per unit of fluid; it is the vertical distance a liquid would have to fall to acquire the velocity *V*.

Total head:
Refers to the net difference between total suction and discharge heads.

NPSH:
See **Net positive suction head**.

Head loss:
The reduction in driving pressure of a flow of water through a plant due to frictional and fouling losses.

Heat energy:
The energy of a fuel potentially available as heat.

Heat exchanger:
Any of various types of heat transfer equipment, whereby relatively cold water flowing over a surface will, by conduction and convection means, transfer heat away from a process. The most common types of heat exchangers are *plate and frame* and *shell and tube* designs. A boiler is also a type of heat exchanger.

Heat flux:
The rate of flow or transfer of heat in a heat exchanger.

Heat flux density:
The quantity of heat transfer per unit surface area, per unit time.

Heat transfer coefficient: (U).
Rate at which heat is transferred through a heat-exchanger (Btu/sq. ft/hr/°F).

Heat value:
The heat energy potentially available from a unit mass of fuel. Typically measured as Btu/lb coal or Btu/gal oil.

Helmholtz double layer:
The layers of opposite charges formed on the surface of individual electrically-charged particles in water, causing mutual repulsion.

Hematite:
A form of rust. Magnetic, gray-to-red colored iron oxide (Fe_2O_3) offering no protection from further corrosion; usually, red hematite is the first signs of steel corrosion and often followed by the formation of *magnetite*. Hematite occurs in the presence of high levels of oxygen.

Hideout:
The apparent loss of BW phosphate and other salts in high pressure WT boilers operating under high-load conditions. The salts reappear and can be determined when the load is reduced.

High and low water alarm:
A water-level alarm system located inside the BW column.

High fire:
The point of a firing cycle at which the burner is combusting the maximum amount of fuel per unit time.

High pressure boiler:
A legal definition that varies from country to country. In the USA it refers to any boiler generating steam at or above 15 psig. In practice, a boiler is commonly only referred to as "high pressure" if it generates steam at over perhaps 350 to 650 psig.

Horizontal return tubular boiler (HRT boiler):
An early design of FT boiler.

Hot well:
A reservoir to receive recovered condensate, located at the bottom of a surface condenser. Also any other tank or basin that receives water from flash steam recovery.

Huddling chamber:
A design feature on some types of SV that permits steam to collect in a chamber, providing an increased total upward force that causes the valve to pop up.

HVAC:
Acronym for *heating*, *ventilation*, and *air conditioning*.

Hydrogen bond:
A property of water whereby attractive forces cause linking of hydrogen in one molecule to oxygen of another. Due to the energy input required to break the hydrogen bond, steam has a high energy content.

Hydrogen embrittlement:
A form of corrosion whereby cracking of steel occurs, caused by the pressure generated from the reaction of hydrogen (from water) and carbon (from steel) producing hydrocarbons.

Hydrology:
The science dealing with the properties, distribution, and circulation of water.

Hydrolysis:
Any decomposition involving the addition of water. Specifically, a double decomposition reaction between water and another substance.

Hydrometer:
An instrument to measure the specific gravity (SG) of fluids. Typically a small, calibrated, and bottom-weighted glass or metal cylinder that floats to a level indicating the SG.

Hydronic heating system:
A HW heating system whereby heat is typically supplied by pumping HW through pipes at 160 to 200 °F.

Hydrophilic:
Having an affinity for water, such as the sulfonate component of a detergent molecule.

Hydrophobic:
Having no affinity for water (non-water wettable or water soluble).

Hydrostatic pressure:
The water pressure exerted at the base of a water column, equivalent to 0.433 psia per vertical foot.

Hydroxyl ion:
Anionic radical (OH^-) primary contributor to alkalinity of water.

Ideal engine:
A theoretical engine where there is no loss in efficiency due to friction, wiredrawing, leakage, cylinder condensation, or radiation.

Igniter:
A burner device used to ignite a fuel and air mixture.

Impeller:
The rotating part of a centrifugal pump in contact with the water, converts centrifugal force into pressure.

Impingement:
High velocity steam or particles striking a metal surface and causing metal wastage by erosion. Also refers to unburned fuel oil striking a surface and resulting in the formation of carbon deposits and smoke.

Impulse turbine:
A turbine design where the expansion of steam occurs entirely in fixed nozzles. The steam jets from the nozzles are directed into disc-mounted buckets on the rotor forcing the shaft to rotate.

Inclusions:
Foreign, unwanted insoluble contaminants in a metal (or precious stones). Usually *oxides*, *silicates,* or *sulfides*.

Incomplete combustion:
The wastage of fuel caused by an inadequate supply of air, resulting in the formation of soot and smoke, and unburnt particles remaining in the ash.

Induced draft:
Mechanical draft developed by a fan located between the boiler and the chimney.

Inert resin:
Non-reactive ion-exchange resin. Commonly employed at a specific intermediate density to separate cation and anion resins in a mixed-bed demineralization plant, in order to limit contaminant leakage, especially from regenerants.

Infra red:
Light rays situated beyond the red end of the visible spectrum generated during combustion and detected by a flame scanner.

Inherent moisture:
The moisture component of coal and other solid fuels that is not available to bond or freeze to other particles.

Inhibitor:
A type of waterside maintenance chemical treatment. Any of a very wide range of chemicals that prevent or reduce tendencies of deposition, fouling, scaling, corrosion, or other unwanted phenomena to occur in a water system. Typically for smaller boiler plants, individual inhibitors are blended together to produce various *multifunctional* formulations specific for particular water chemistry and/or operating conditions. Larger boiler plants tend to use individual active component inhibitors.

Insulation:
A cladding material applied to boilers, pipes, and all hot surfaces in order to reduce radiant heat energy losses.

Intergranular corrosion:
A form of corrosion occurring at the grain boundaries within a metals microstructure.

Interlock:
A burner safety control system required to ensure proper operating sequences are employed.

Internal FW line:
A perforated pipeline (sparge line) inside a boiler located at the NOWL. It distributes relatively cool FW over a wide area in order to reduce thermal shock and ensure intimate mixing of the FW and chemical treatments with BW.

Internal furnace:
A FT boiler design whereby the furnace is fully located within the boiler shell. All modern FT boilers employ internal furnace designs.

Internal treatment:
Chemical treatment programs based on the direct addition of chemicals to FW or BW in order to prevent subsequent deposition, corrosion, or other problems from occurring. With precipitating types of internal treatments, the boiler waterside space is employed as a reaction vessel and, where a particular boiler design is unsuitable, inadvertent problems of fouling may occur.

Internal treatment:
Chemical inhibitor component of a water treatment program.

Ion:
An electrically charged atom, radical, or molecule.

Ion association:
Concept used in sophisticated scaling models, whereby certain ions in aqueous solution are said to associate in pairs (e.g., $CaSO_4$, $CaHCO_3$-). These ion pairs are then deducted from the total analytical value, to provide an estimate of the free ion content available for seed crystal scaling or growth agglomeration and deposition.

Ion exchange resins:
Hard, attrition-resistant, insoluble synthetic polymers (typically a copolymer of styrene with divinylbenzene). The resins are manufactured in a spherical bead shape that contain either exchangeable anion or cation portions, capable of exchanging with other anions or cations and usually in an aqueous medium. Typically cation resins for water softening will have a practical operating capacity of 20,000 gpg (at 6 lb NaCl per cu ft) rising to 30,000 gpg (at 15 lb NaCl per cu ft).

Jackson turbidity units:
A measure of turbidity of suspended particles. The Jackson turbidity method compares optical obscurity against a series of standards.

Kinetic energy:
The dynamic energy of a body or substance that comes from molecular motion.

Kinetics:
The branch of science dealing with the effects of kinetic energy, especially the speed of reaction.

Laminar flow:
Smooth or streamlined flow of water.

Langelier saturation index (LSI):
A derived expression relating to the saturation point of calcium carbonate solubility in water. Used frequently to interpret various water analyses in order to determine the potential for $CaCO_3$ super-saturation and deposition (*scaling*) and also by inference, but not always correctly, the opposite nonscaling potential (*corrosion risk*). Used more in raw water and cooling water reviews than FW or BW. Although LSI is scaleless, the industry generally accepts and promotes the following:

LSI = 0.0 rising to +3.0: increasing tendency for scaling to occur.
LSI = 0.0 decreasing to −3.0 increasing

tendency of corrosion risk.
LSI = −0.5 to + 0.5: "uncertainty"
zone, some scale and corrosion

Also several other indices, esp. *Ryznar Index* are now used.

Note: LSI and all derivations (such as Ryznar, Puckorius) are simply based on total analytical values rather than free ion species (those ions remaining after ion association pairs are deducted from the total analytical value (TAV).

Laning:
The short circuiting of furnace gases, resulting in a different heat distribution pattern.

Latent heat:
Heat which, when supplied or removed from a substance, produces a change of state without a change in temperature.

Latent heat of fusion of water:
144 Btu/lb. at 32 °F (0 °C)

Latent heat of vaporization:
970 Btu/lb. at 212 °F (100 °C)

Laws of thermodynamics:
The first law is one of conservation of mass and energy, whereby a balance exists between energy, work, and heat quantities. The second law relates to energy flow, whereby heat can only flow from a hotter body to a colder one.

Lime and lime soda softening:
The process of pre-treating hard water with lime and sometimes soda as well, based on standard precipitation methods, to reduce the hardness either to a minimum level or more usually to a preset level of, say, 85 ppm thereby lowering the total treatment costs. Usually carried out in specially designed tanks and followed by clarification and filtration. Calcium bicarbonate is always removed, requiring one equivalent of lime and precipitating as the carbonate. Calcium non-carbonate hardness is removed using one equivalent of soda ash. Magnesium bicarbonate, however, requires two equivalents of lime and precipitates as the hydroxide, while magnesium non-carbonate hardness removal requires one equivalent of soda ash and one of lime.

Lipophilic:
Property of substances having an affinity for oil, such as in certain surfactants.

Low solids treatment:
A boiler plant water treatment strategy designed to keep BW TDS levels as low as possible, minimizing BE requirements and limiting the potential for carryover. High quality, pre-boiler external treatment processes such as reverse osmosis or demineralization are supplemented by internal treatment programs that may consist of *all volatile treatments* (AVTs) or small amounts of inorganic and organic "*polishing*" treatments.

Macroporous resin:
Ion-exchange resin having large pores that reduce the potential for permanent fouling to take place.

Magnetic device:
One of many types of boiler and/or cooling water plant equipment variously claimed to control and prevent scaling or in addition, to prevent corrosion (or possibly even algae and sludge in open cooling water systems) in water circuits by nonchemical means. Usually employ external electrical circuits or permanent magnets to provide a magnetic induction (flux density) of perhaps 2,500 gauss. Usually clamped around or inserted into a pipe line.

Magnetite:
A form of rust. Magnetic, dark-gray-to-black form of iron oxide (Fe_3O_4) that forms a protective film on steel surfaces.

Makeup (MU) water:
Supplementary treated water required to compensate for losses due to steam consumption, blowdown, and leaks in boiler plant steam/water system.

Martensite:
A type of iron or steel exhibiting a needle-like microstructure of solid solution of supersaturated carbon.

Matrix:
The primary phase of a substance into which a secondary material is embedded.

Microstructure:
The structural appearance of a metal under a microscope.

Mild steel:
Carbon steel having a maximum carbon content of 0.25%.

Misting:
The development of an aerosol of *microdroplets* of BW into steam at the water/steam interface, caused by the sudden release of pressure *under* bubbles as the steam they contain is released. Typically, improved steam separation equipment is needed if misting persists in a boiler.

Moderator:
A substance employed to slow down the neutrons in a nuclear reactor in order that they can be captured by the nuclei. Boron, heavy water (D_2O) and graphite are commonly used moderators.

Molecular bridging:
The joining of particles by polymers as part of the process of flocculation. Usually higher MW polymers produce higher levels of molecular bridging.

Mud drum:
The bottom drum of a multiple drum WT boiler. Sludge and muds tend to collect in this drum.

Net positive suction head (NPSH):
The net head or pressure measured in ft. or m that causes a liquid to flow through the suction side of a pump, enter the pump chamber, and reach the impeller. When the source of liquid is *above* the pump, NPSH equals the barometric pressure *plus* the static head, *less* the entrance head, frictional losses in the suction piping and vapor pressure of the liquid. When the source of liquid is *below* the pump, NPSH equals the barometric pressure less the static head, entrance head, frictional losses in the suction piping and vapor pressure of the liquid. NPSH is specific for each pump design and application and must be supplied by the manufacturer.

Neutralizing amine:
A volatile, amine-based chemical treatment usually added to the boiler FW, designed to neutralize the corrosive effects of carbonic acid in steam/condensate and raise condensate pH.

NTA:
Nitrilotriacetic acid or its sodium salts.

Once-through boilers:
High pressure design of boiler with no BW recirculation.

Ordinary steel:
Plain carbon steel containing approximately 2% carbon together with traces of other elements.

Organic fouling:
Fouling of pores of ion-exchange resins by the presence of organic contaminants in the water being processed. The resin gradually loses its capacity and requires cleaning.

Orsat apparatus:
Portable flue-gas analyzer employing "wet chemical" techniques. Uses a liquid-filled leveling bottle to introduce a measured flue-gas sample into the glass apparatus. The flue-gas sample is then selectively passed into each of several chambers to permit selective absorption and other reactions to take place, resulting in measurable losses of original individual constituent gases. Orsat apparatus measures *carbon dioxide*, *carbon monoxide*, *oxygen* and *hydrogen*, or *water vapor*.

Osmotic pressure:
Pressure differential that exists between two solutions separated by a semipermeable membrane.

Overspeed trip:
Device that closes the throttle valve on a turbine should its speed exceed a predetermined value.

Oxidation:
Addition of oxygen, removal of hydrogen or loss of electrons.

Oxygenation Treatment:
Under some circumstances, corrosion can actually be controlled in high pressure boilers by adding oxygen to the boiler feedwater (FW) rather than by removing it. The process is called oxygenation treatment (OT) and is designed to ensure sufficient oxygen is present in the FW (> 5 ppb O_2), in order to ensure the economizer and feed line passivated magnetite film is not disrupted. OT also reduces the risk of erosion-corrosion problems, and limits iron transport to other parts of the boiler system.

Oxygen scavenger:
Any of a number of chemical treatments designed to remove traces of dissolved oxygen in boiler FW.

Package boiler:
Self-contained, shop-assembled boiler plant complete with FW pumps, fuel system, draft fans, and other auxiliaries.

Packing gland:
A device that effectively seals a pump against leakage around the shaft by means of various rubber/fiber packing materials.

Part per million:
A unit weight of solute dissolved in one million units of the same weight of solution. Approximately equivalent to mg/liter or g/m^3. 120 ppm = approx. 1 lb/1,000 U.S. gallon.

Passivation:
The conversion of a reactive metal surface into a lower energy state that does not readily further react or corrode. Usually carried out by *anodic inhibitors* producing a passive oxide film on a clean surface. A vital component of any program for long-term protection of a metal waterside surface.

Peaking boiler:
A steam generator designed to operate intermittently to meet peak demands for steam and electricity.

Pearlite:
An aggregate containing an alternate *ferrite* and *cementite* (Fe_3C) lamellae microstructure.

pH:
Logarithmic scale for expressing acidity or alkalinity of water (7.0 to 0 indicates increasing acidity; 7.0 to 14 indicates increasing alkalinity). Measured by means of a glass electrode/reference electrode pair immersed in the water sample under test. The potential difference depends upon the pH which is then displayed on a pH meter (high input impedance, millivoltmeter).

Phosphate conditioning:
A popular type of internal chemical conditioning, precipitation water treatment program. Relies on the careful management of permanent reserve of phosphate ions in the BW to prevent waterside scale formation.

Pit:
Visible sign of metal wastage in the form of a deep crevice resulting from various forms of localized corrosion.

pK:
Expression of the extent of dissociation of an electrolyte; the negative logarithm of a compounds ionization constant.

Plenum chamber:
A wind box or air chamber that receives and directs pressurized air to a furnace or other item of equipment.

Pneumatic system:
A control system that uses air as an operating medium.

Pollution:
In this context, pollution refers to the identification and measurement of polluting contaminants in a raw water source (such as organic debris, treated sewage, ammonia, fertilizer, oil, etc.,) that constitute a risk of fouling and can hinder the effectiveness of any chemical treatment program. Tests undertaken to determine the level of pollution include *permanganate value (PV)*, *biochemical oxygen demand (BOD_5)*, *chemical oxygen demand (COD)*, and *total organic carbon (TOC)*. The COD test, either by a laboratory dichromate reaction/titration or by automatic COD equipment, is probably the most useful for polluting contaminant assessment.

Polyamine BW programs:
Certain long-chain polyamines and amine derivatives have long been used as cationic coagulants for waste-water application and biostats for recirculating cooling systems and once-through condenser cooling, however they have also been promoted for use as single-formulation, multi-functional programs for BW and steam/condensate application, especially in France and other European countries (e.g. Polaris® from UCIO S.A.). These polyamines are claimed to provide a film-forming effect in boilers (thus negating the need for oxygen scavengers), yet are sufficiently volatile to provide protection to condensate lines and are suitable for up to 550 °C. Such claims seem greatly exaggerated and practical experience has shown that clogging of dosing pumps and fouling of boiler appurtenances is a problem.

Polymer:
General name for a wide range of (mainly organic) chemicals used in BW treatments and other formulation types and produced from linking individual chemical molecules (monomers) to form a chain.

Polyphosphate:
One of various molecularly dehydrated orthophosphates.

Potable water:
A water meeting drinking water standard quality.

Potential energy:
The inherent energy of a body or substance, potentially available in various forms including chemical or heat energy of a fuel.

Pour point:
The lowest temperature at which fuel oil will flow. *Residual oil* (No. 6 oil) will not usually flow at ambient temperature and requires heating to reduce the viscosity and raise the pour point.

Pressure-reducing station:
A control station employed to reduce high pressure steam to one or more lower pressures, thus rendering the steam suitable for a number of downstream processes.

Primary air:
Air mixed with fuel at or in the burner. Used to ensure instant combustion as the fuel enters the furnace.

Priming:
See **Surging**.

Process steam:
Steam required for a manufacturing or user process and often totally consumed so reducing the available CR.

Protective colloid:
A chemical treatment designed to prevent the coagulation of colloids by the provision of a surface coating onto the colloidal particles.

Pulverizing mill:
A mill that grinds or pulverizes fuel such as PF coal to a prescribed degree of fineness. Typically, 70% of PF will pass through a # 200 mesh (74 micron) screen.

Purge period:
The time period before fuel ignition and after boiler shutdown when explosive combustibles are removed from the furnace area by air purging.

Quick closing valve:
A valve that only requires one quarter turn to fully open or close.

Radiant heat:
Heat energy supplied by the emission of rays. Thermal radiation travels at the speed of light (186,000 miles per second).

Radiant superheater:
A type of tube bundle *superheater* located in the radiant section of a WT boiler.

Rank:
The grade of various types of coal based on size, calorific value, and ash content.

Rankine cycle:
A concept of the cycle of thermodynamic processes, introduced later than the *Carnot cycle*. Modifications of the Rankine cycle are of practical importance in boiler design, in relating the successive thermodynamic changes as water is converted to steam, expands and converted to mechanical energy in a turbine, then condenses and returns to the boiler.

Rapping:
A method used to dislodge ash particles collected by an electrostatic precipitator.

Raw water:
Water available on site not subjected to any in-house treatment process. City water, despite being treated at a primary city facility is described as "raw water" when being considered for suitability in industrial processes.

Reaction turbine:
A design of turbine in which a partial reduction in steam pressure takes place in fixed nozzles (vanes) and a further steam pressure reduction takes place in "nozzles" created by moving rotor blades. A reactive force is generated that results in the rotation of the turbine shaft.

Redox:
(See also **Oxidation, Reduction**). Some dissolved substances in water occur either in an oxidized or a reduced form, and their state can be changed by either the acquisition of electrons (reduction) or the loss of electrons (oxidation). This transfer system is an reduction-oxidation system, or redox. (Red. $\leftrightarrow$ Oxid. $n^+ = n^e-$, where n is number of electrons involved), and can be used to measure and

control such reactions, using an oxidation/ reduction millivolt potential meter (ORP meter), with a platinum and reference electrode. Example is the measurement of effectiveness of a chlorination/ dechlorination program.

Reduction:
The removal of oxygen, addition of hydrogen, or gain of electrons.

Refractory:
Heat tolerant brickwork used in boiler furnaces.

Regeneration:
As applied to ion exchange resins, regeneration refers to the process of restoring spent resin to a condition by which it can continue to exchange either cations or anions. Regeneration of softeners specifically refers to the addition of an 8 to 25% brine solution, typically applied at 2 to 7 BV/hr, at a salting rate of 6 to 25 lb NaCl/cu ft (100–400 g/l NaCl), depending on regional custom and practice. Regeneration has now typically come to mean the inclusion of a cycle of back-washing, brine injection and both slow and rapid rinsing.

Reheat:
The process of returning partially expanded steam from the HP stage of a turbine back to a reheat superheater before the steam passes to the turbine IP and LP stages.

Relief valve:
A valve designed to protect water system components from excess pressure.

Resin capacity:
The quantity of soluble material capable of being exchanged by an ion exchange resin. Expressed as grains $CaCO_3$/cu ft. or kg $CaCO_3/m^3$.

Retort:
The space below the grate of an underfeed stoker.

Reverse osmosis (RO):
The thoroughly practical implementation of reversing the natural phenomenon of osmosis, by applying a relatively high pressure to a high TDS content water in contact with one of various types of semi-permeable membrane. This typically results in a 30 to 70% recovery of permeate water, from an original, supply source, containing only 2 to 8% of the original level of TDS. The process requires close

attention to pre-treatment, to extend membrane life, but has become a major technology for world wide application. It is especially used in the treatment of MU water for high pressure boiler plant, usually in combination with ion-exchange demineralization processes.

Ringelmann chart:
A smoke density comparison chart.

Riser:
A pipe that permits the flow of BW up and towards the top drum. Usually receiving steam/water from a waterwall top header.

Rotameter (rotometer):
A variable-area, fluid or gas flow-rate meter. Usually a cone inside a glass measuring cylinder that is suspended by the upward flow of gas or liquid.

Ryznar Index or Stability Index; (SI):
A variant on the LSI. SI is generally believed to be more relevant than LSI due to being derived from operational studies of cooling systems. Although SI is scaleless, the industry generally accepts the following;

SI = 7.0 down to 4.0: increasing tendency for scaling
SI = 7.0 rising to 10.0: increasing tendency of corrosion
SI = 6.5 to 7.5: "uncertainty" zone

SAC Resin:
Strong acid, cation exchange resin.

Salt splitting:
The capability of conversion of a salt solution to caustic by an anion exchanger, or to an acid by a cation exchanger.

Saponification:
The hydrolysis of a fat to a soap by reaction with an alkali.

Saturated steam:
Steam that is fully saturated with heat and corresponding with a particular temperature and pressure.

SBA Resin:
Strong base, anion exchange resin.

Scale:
Layer, or layers, of *minerals* (especially *calcium carbonate*) deposited, by the throwing down, or precipitation, onto a heat transfer sur-

face, reducing its ***U*** value. Scales are often hard and dense and difficult to remove. The scale can be *crystalline* in nature (a solid body having a characteristic internal structure, with symmetrically arranged plane surfaces and definite angles), or *amorphous* (lacking any characteristic crystalline shape). Also, scale refers to thick layers of corrosion product on a metal surface that can occur at high temperature.

Secondary air:
Air brought in around the burner or wider furnace area, used to ensure complete combustion.

Sensible heat:
Heat which when supplied or removed from a substance causes a *sensible effect* on the substance, i.e. a rise or fall of temperature.

Silt density index:
A measurement of silt, colloids, bacteria, and other rapid foulants of RO membranes. The SDI test is used to determine the SDI of water and thus its suitability for an RO process. SDI of above 5.0 indicates the water is unacceptable. Ideally the water should have an SDI of below 1.0.

Sinuous header:
A design of WT boiler header that receives tubes in a serpentine (wavy) manner.

Slippage (leakage):
The resultant low level of particular salts remaining in a processed water after passing through an ion-exchange plant. Slippage occurs because of a less than totally efficient exchange capability processes.

Slag:
Commonly also known as cinder or clinker. Slag is the mass of fused ash that results after the incombustible residual material from combustion cools down from a molten state.

Sludge:
Any sedimentary deposit or foulant that fails to form a crystalline scale. Often the result of supersaturation or the binding of biological or other organic material with dust, sand, or other mineral deposits. Also, sludge is not always deposited at point of origin and can additionally bake onto heat transfer surfaces.

Sludge conditioner:
A chemical treatment designed to "condition" BW precipitants in order to prevent their coagulation and the subsequent likely accumulation of sludges that can cause fouling problems.

Slug treatment:
The intermittent addition of chemical treatments by hand rather than continuous addition by use of a feed pump.

Smoke:
Flue gases containing enough unburnt carbon and hydrocarbons so as to cause discoloration and usually measured by comparison with standard color charts.

Softening:
Any of a number of processes designed to remove alkaline earth elements (primarily calcium and magnesium) from MU water.

Soot:
Carbon deposits resulting from incomplete combustion.

Sootblowers:
Nozzles used to inject a medium, such as steam, into the boiler to dislodge deposits. Used to clean the fireside during operation of the boiler.

Spalling:
Hairline cracks, flakes, or splinters that can occur out of the surface of a refractory or steel as a result of changes in furnace temperature or *long-term overheating*.

Specific conductance:
A measure of ability of water to conduct an electric current and often related to TDS content of water. Typically, one μS/cm units of conductivity x 0.65 equals ppm TDS.

Specific gravity:
Ratio of the density of a substance to that of water.

Spheroidization:
The thermal transformation of laminar cementite in the pearlite phase of carbon steel to spherical grains.

Stainless steel (SS):
Any of a number of irons alloys containing more than 11.5% Cr and usually exhibiting passivity in water.

Types 304 and 316 and their low carbon equivalents (L) are commonly used as construction materials.

Types:

304 = < 0.08% C, 18–19% Cr, 9% Ni, < 0.01% Mo
304 L = < 0.03%, 18–19%, 9–10%, 0%
316 = < 0.08%, 17%, 11–12%, 0.2%
316 L = < 0.03%, 17%, 12–13%, > 2–5%.

Most types of SS used for water treatment have an *Austenitic* crystalline structure (centre-faced cubic). Others are *Ferritic* (centred cubic), *Marstenitic* (quadratic), or *Austeno-ferritic* types, which have superior mechanical strength and are resistant to *stress corrosion.*

Static suction lift:

Where a liquid is below the pump, relates to the vertical distance from the center line of a pump *down* to the free liquid source.

Static suction head:

Where the liquid is above the pump, relates to the vertical distance from the center line of a pump *up* to the free liquid source.

Steam:

Water vapor. Water that is at or near its saturation temperature and pressure where the liquid and the gas phases coexist.

Steam drum:

The top drum of a WT boiler that receives FW and chemical treatments, provides both a steam reservoir space and a point from which BD can take place.

Steam purity:

A measurement of the contamination of steam by various organic and inorganic materials. Some contamination is inadvertent (e.g. carryover) while some is intentional (e.g., neutralizing amines).

Steam trap:

An automatic device that removes condensate and *noncondensable gases* (such as air) from steam.

Steel or carbon steel:

Alloy of iron containing up to 2% carbon and other trace elements. It is a common construction material.

Strainer:

A metal screen designed to remove particles and sediments that would be detrimental to steam traps and other devices.

Stratified bed:
Bed containing resins of sufficient density differences so as to settle into layers within a tank or vessel.

Stress:
A measurement of force per unit area on, or within metals and other construction materials. Excess stress can lead to metal failure.

Stress corrosion cracking:
Any of a number of corrosion processes whereby in a corrosive environment localized stress accelerates the rate of corrosion and may result in metal failure.

Supercritical boiler:
A WT boiler that is designed to operate at a pressure above 3203.6 psia.

Superheat:
The increase in steam temperature over and above the *saturated steam temperature* for a specified pressure.

Surface condenser:
A type of shell and tube heat exchanger that condenses exhaust steam and creates a vacuum, improving the efficiency of a turbine.

Surface moisture:
External moisture that is not bonded to a particle of coal or other fuel. External moisture will ice in cold weather and lump fuel together in a solid mass. Where this occurs, thaw sheds may be used to heat the mass before further transport or use.

Surface tension:
Property of liquid, whereby molecular forces at the surface tend to minimize the contained volume, hence water droplets. Water has high surface tension which makes it poor at wetting thus requiring use of surfactant materials for certain processes.

Surfactant:
Surface active agent. Any of a wide range of detergents, emulsifiers, dispersants, defoamers, etc., that tend to reduce the surface tension of water and improve its wetting power.

Surging (priming):
The phenomenon of wildly fluctuating and spouting BW levels as a result of poor operational and/or water chemistry conditions.

Adverse conditions include too high a water level, uneven heat distribution, variable load swings, too high a steaming rate, too low a steam pressure, and excessive suspended or dissolved solids, alkalinity, chlorides, etc. The maintenance of any steam generating stability under surging conditions is impossible. Surging is closely associated to problems of *foaming* and *misting*, which can lead to the *carryover* of BW into the steam (*entrainment*).

Suspended solids:
Particles of matter suspended in water that can be removed by filtration or prevented from settling for periods of time by the use of dispersants.

Synergy:
Enhanced result from the action of two or more chemicals working together and greater than the sum of individual actions.

Tensile strength:
The ultimate strength of a metal under test, measured as the ratio of load to cross-sectional area.

Therm:
A unit of gas-fuel heat energy equivalent to 100,000 Btu.

Thermal fatigue:
A form of metal failure, whereby fracturing occurs under repeated cycles of thermally-induced stress.

Thermocouple:
A temperature measuring device that reports data back to a recorder.

Threshold effect:
The ability of small concentrations of chemicals such as certain phosphates and polymers to retard relatively large amounts of crystal growth and eventual deposition by incorporation of the chemical into the crystal lattice.

Titration:
A method of water analysis allowing the concentration of an unknown dissolved material to be determined. It requires the addition of a liquid titrant of known concentration into a water sample of known volume until an end-point is indicated by a color change.

Toxicity:
(TL_{50}). The concentration of a toxicant, such as a biocide, in which 50% of test animals (typically fish species) survive for 96 hours under prescribed conditions.

Tuberculation:
Very visible form of corrosion in which voluminous layers form of brittle, iron oxide corrosion debris, usually covering a pit or deep crevice.

Tube sheet:
Usually a circular perforated end sheet, into which heat exchanger tubes are welded, brazed, or rolled.

Turbine stage:
A section within a turbine where the steam transfers energy to the turbine blades. As steam pressure drops within a stage, the blade length become larger.

Ultrasonic testing:
A form of nondestructive testing in which an ultrasonic beam is applied to sound-conducting materials to locate any discontinuities.

Vacuum:
A degree of air pressure below atmospheric pressure.

Vapor:
A gas at or near saturation temperature and pressure and coexisting with a liquid phase.

Vapor phase inhibitor (VPI):
Or volatile corrosion inhibitor (VCI), are typically aminocarboxylates (the reaction products of an amine or amine derivatives, such as cyclohexylamine, dicyclohexylamine, guanidine or aminoalcohols, and an organic acid). VPIs are generally supplied in solid form for ease of handling and are effective in preventing general, pitting, galvanic and other forms of corrosion of both ferrous and non-ferrous metals. They are volatile materials designed to produce and disseminate vapors within enclosed spaces, that at equilibrium contact metal surfaces and form a protective, micro-crystal barrier film. In the presence of even minute traces of moisture, the crystals dissolve and are adsorbed at the metal surface as highly ionic species that provide corrosion inhibition without interfering with metal conductivity, dimensional tolerances, or other functional requirements.

VPIs can be employed to provide protection to boilers during layup periods, both for dry and wet layup.

Viscosity:
The property of a fluid that resists any force such as atmospheric or pump pressure, tending to produce flow. Viscosity is a function of the fluids cohesive forces and generally decreases with increase in temperature. Also, friction losses decrease with increase in temperature.

Water hammer:
Instantaneous surges of water under pressure caused by sudden interruptions in water flow in a pipe or water system, producing a hammering sound and leading to metal stress and possible eventual failure. Water hammer can develop where a steam main is incorrectly pitched, has un-drained pockets or where steam flows up and meets draining condensate flowing down causing a temporary interruption in both flows.

Waterwall:
Tubes in a WT boiler surrounding the furnace and convective pass sections that are welded together to form a continuous membrane. The waterwall prevents heat-path short-circuiting and provides a cooling mechanism for the boiler.

WAC resin:
Weak acid, cation exchange resin.

WBA resin:
Weak base, anion exchange resin.

Wire drawing (throttling):
The process by which steam forces its way through a narrow opening with a corresponding loss of pressure, as occurs to some extent during the admission of steam to a steam engine.

Zeolite:
A natural ion-exchange material used for softening water and other purposes. Typically minerals of hydrated aluminum or sodium silicates.

Zeta potential:
The potential between the Helmholtz double layer of a charged particle. Important for assessing the suitability of polyelectrolyte chemicals because it can be easily measured, unlike some other electrokinetic forces.

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