

Chapter Ten - Boiler Water Systems

The dissolved gases normally present in water cause many corrosion problems. For instance, oxygen in water produces pitting that is particularly severe because of its localized nature. Carbon dioxide corrosion is frequently encountered in condensate systems and less commonly in water distribution systems. Water containing ammonia, particularly in the presence of oxygen, readily attacks copper and copper-bearing alloys. The resulting corrosion leads to deposits on boiler heat transfer surfaces and reduces efficiency and reliability.

In order to meet industrial standards for both oxygen content and the allowable metal oxide levels in feedwater, nearly complete oxygen removal is required. This can be accomplished only by efficient mechanical deaeration supplemented by an effective and properly controlled chemical oxygen scavenger.

Several principles apply to the mechanical deaeration of feedwater:

- › The solubility of any gas in a liquid is directly proportional to the partial pressure of the gas at the liquid surface
- › The solubility of a gas in a liquid decreases with increasing liquid temperature (see Figure 10-2)
- › Efficiency of removal is increased when the liquid and gas are thoroughly mixed

The solubility of a gas in a liquid is expressed by Henry's Law:

$$C_{\text{total}} = kP$$

where:

C_{total} = total concentration of the gas in solution

P = partial pressure of the gas above solution

k = a proportionality constant known as Henry's Law Constant

For example, 8 ppm of oxygen can be dissolved in water when the partial pressure of oxygen is 0.2 atmosphere; only 4 ppm of oxygen can be dissolved in water if the partial pressure of oxygen is reduced to 0.1 atmosphere.

As is evident from Henry's Law, a dissolved gas can be removed from water by a reduction of the partial pressure of that gas in the atmosphere contacting the liquid. This can be accomplished in either of two ways:

1. a vacuum is applied to the system and the unwanted gas is vented
2. a new gas is introduced into the system while the unwanted gas is vented

Vacuum deaeration has been used successfully in water distribution systems. However, pressure deaeration (with steam as the purge gas) is normally used to prepare boiler feedwater. Steam is chosen as the purge gas for several reasons:

- › it is readily available
- › it heats the water and reduces the solubility of oxygen
- › it does not contaminate the water

- only a small quantity of steam must be vented, because most of the steam used to scrub the water is condensed and becomes a part of the deaerated water

In order to deaerate the boiler feedwater, water is sprayed into a steam atmosphere. This heats the water to within a few degrees of the temperature of the saturated steam. Because the solubility of oxygen in water is very low under these conditions, 97 to 98% of the oxygen in the incoming water is released to the steam and is purged from the system by venting. Although the remaining oxygen is not soluble under equilibrium conditions, it is not readily released to the steam. Therefore, water leaving the heating section of the deaerator must be scrubbed vigorously with steam to maximize removal.

Equipment

The purpose of a deaerator is to reduce dissolved gases, particularly oxygen, to a low level and improve a plant's thermal efficiency by raising the water temperature. In addition, deaerators provide feedwater storage and proper suction conditions for boiler feedwater pumps.

Pressure deaerators, or deaerating heaters, can be classified under two major categories: tray-type and [spray-type](#) (see Figure 10-3). Tray-type deaerators are also referred to as "spray-tray" type, because the water is initially introduced by spray valves or nozzles. The spray type is also referred to as the "spray-scrubber" type because a separate scrubbing section is used to provide additional steam-water contact after spraying.

The [tray-type deaerating heater](#), shown in Figures 10-4 and 10-5, consists of a shell, spray nozzles to distribute and spray the water, a direct-contact vent condenser, tray stacks, and protective interchamber walls. Although the shell is constructed of low carbon steel, more corrosion-resistant stainless steels are used for the spray nozzles, vent condenser, trays, and interchamber walls.

The [operation of this deaerator](#) is illustrated in Figure 10-5. Incoming water is sprayed into a steam atmosphere, where it is heated to within a few degrees of the saturation temperature of the steam. Most of the noncondensable gases (principally oxygen and free carbon dioxide) are released to the steam as the water is sprayed into the unit. Seals prevent the recontamination of tray stack water by gases from the spray section.

In the tray section, water cascades from tray to tray, breaking into fine droplets or films which intimately contact the incoming steam. The steam heats the water to the saturation temperature of the steam and removes all but the very last traces of oxygen. Deaerated water falls to the storage space below, where a steam blanket protects it from recontamination.

The steam, entering the deaerators through ports in the tray compartment, flows down through the tray stack parallel to the water flow. A very small amount of steam condenses in this section as the water temperature rises to the saturation temperature of the steam. The remainder of the steam scrubs the cascading water.

Upon leaving the tray compartment, the steam flows upward between the shell and the interchamber walls to the spray section. Most of the steam is condensed and becomes a part of the deaerated water. A small portion of the steam, which contains the noncondensable gases released from the water, is vented to the atmosphere. It is essential that sufficient venting is provided at all times or deaeration will be incomplete.

As mentioned, most tray and spray-type deaerators use [spring-loaded spray nozzles](#), which evenly distribute the inlet water (see Figure 10-6). Newer spray valves are designed to provide a uniform spray pattern under varying load conditions for efficient steam-water contact. The valve is designed to provide atomization of the inlet water into small droplets to improve heat transfer and to provide efficient scrubbing of the inlet water oxygen.

Steam flow through the tray stack may be cross-flow, counter-current, or co-current to the water. The deaerated water is usually stored in a separate tank, as illustrated in [Figure 10-4](#).

The spray-type deaerating heater consists of a shell, spring-loaded inlet spray valves, a direct-contact vent condenser, and a steam scrubber for final deaeration. The inlet spray valves and direct contact vent condenser section are stainless steel; the shell and steam scrubber may be low carbon steel.

The incoming water is sprayed into a steam atmosphere and heated to within a few degrees of the saturation temperature of the steam. Most of the noncondensable gases are released to the steam, and the heated water falls to a water seal and drains to the lowest section of the steam scrubber.

The water is scrubbed by a large volume of steam and heated to the saturation temperature prevailing at that point. The intimate steam-water contact achieved in the scrubber efficiently strips the water of dissolved gases. As the steam-water mixture rises in the scrubber, the deaerated water is a few degrees above the saturation temperature, due to a slight pressure loss. A small amount of flashing results, which aids in the release of dissolved gases. The deaerated water overflows from the steam scrubber to the storage section below.

Steam enters the deaerator through a chest on the side and flows to the steam scrubber. Because the volume of steam is large compared to the volume of water, thorough scrubbing is achieved. The steam, after flowing through the scrubber, passes up into the spray heater section to heat the incoming water. Most of the steam condenses in the spray section to become a part of the deaerated water. A small portion of the steam is vented to the atmosphere to remove the noncondensable gases.

In the jet-atomizing segment of spray-type deaerators, the incoming water is sprayed into a steam atmosphere. Here, the water is heated sufficiently to release the majority of the noncondensable gases. The water is then delivered into a high-velocity steam jet. It impinges on a baffle and is atomized into fine droplets. The high-velocity steam heats the water to its saturation temperature and scrubs all but the last traces of oxygen from the fine water droplets.

Other types of deaerating equipment, less common in industrial plants, include film-type and bubbling device type deaerators.

In film-type deaerators, the water flows along a surface, such as Raschig rings, in a thin film counter-current to steam flow. Oxygen is removed along the film surface. Water is collected at evenly spaced intervals.

In a bubbling device deaerator, oxygen is removed following preheating of the water, through intimate contact of steam and water moving over perforated plates.

Deaerating Condensers

In power generating stations, main turbine condensers have air ejectors to remove dissolved gases. Sometimes the pressure deaerator is omitted from the feedwater cycle. However, there is a danger of air leaking into the system, both during start-up/shutdown and while the condensers are operating at low loads. This may necessitate steam blanketing and increased chemical deaeration.

Vacuum Deaeration

Vacuum deaeration is used at temperatures below the atmospheric boiling point to reduce the corrosion rate in water distribution systems. A vacuum is applied to the system to bring the water to its saturation temperature. Spray nozzles break the water into small particles to facilitate gas removal and vent the exhaust gases.

Incoming water enters through spray nozzles and falls through a column packed with Raschig rings or other synthetic packings. In this way, water is reduced to thin films and droplets, which promote the release of dissolved gases. The released gases and water vapor are removed through the vacuum, which is maintained by steam jet eductors or vacuum pumps, depending on the size of the system. Vacuum deaerators remove oxygen less efficiently than pressure units. A typical [vacuum deaerator](#) is shown in Figure 10-7.

Important Considerations

Inlet water to the deaerators should be largely free from suspended solids, which can clog spray valves and ports of the inlet distributor and the deaerator trays. In addition, spray valves, ports, and deaerator trays may plug with scale which forms when the water being deaerated has high levels of hardness and alkalinity.

Pressure deaerators reduce oxygen to very low levels. Yet even trace amounts of oxygen may cause corrosion damage to a system. Therefore, good operating practice requires supplemental removal of oxygen by means of a chemical oxygen scavenger such as sodium sulfite or hydrazine, or other materials, such as organic, volatile oxygen scavengers.

Although deaeration removes free carbon dioxide, it removes only small amounts of combined carbon dioxide. The majority of the combined carbon dioxide is released with the steam in the boiler and subsequently dissolves in the condensate, frequently causing corrosion problems.

These problems can be controlled through the use of volatile neutralizing amines, filming amines, and metal oxide conditioners.

Monitoring Performance

Monitoring Performance Pressure deaerators, used to prepare boiler feedwater, produce deaerated water which is very low in dissolved oxygen and free carbon dioxide. Vendors usually guarantee less than $0.005 \text{ cm}^3/\text{L}$ (7 ppb) of oxygen.

Vacuum deaerators, used to protect water distribution lines, are not designed to deaerate as thoroughly as pressure deaerators. Usually, they reduce the oxygen content to about 0.25 to $0.50 \text{ cm}^3/\text{L}$ (330 to 650 ppb).

In order to ensure maximum oxygen removal, spot or continuous monitoring of dissolved oxygen in the effluent of the deaerator is essential. Continuous monitoring with an on-line oxygen meter is normally recommended (see Figure 10-8). For performance testing of the deaerator, the feed of the chemical oxygen scavenger is stopped for a brief period of time.

It is good practice to check the operation of the unit regularly. Care should be taken to ensure that the unit is not operated beyond its capacity. The system should also be checked for water hammer and thermal stress, which can be caused by the introduction of cold condensate. Thorough off-line inspection should be performed as often as possible and should include the following:

- > inlet water regulating valves and controls for storage tank level control
- > high and low alarms for storage tank levels
- > overflow valve and controller for prevention of high water level
- > steam pressure reducing valves to maintain required minimum deaerator pressure
- > safety relief valves
- > temperature and pressure gauges for proper monitoring of makeup water, deaerator, and storage tank
- > steam vent for removal of gases and vent condenser for integrity
- > steam inlet baffles for integrity
- > inlet spray valves for deposits and operation
- > trays for proper position
- > weld areas for damage (particularly cracking)

Chapter 11 - Preboiler And Boiler Corrosion

Corrosion is one of the main causes of reduced reliability in steam generating systems. It is estimated that problems due to boiler system corrosion cost industry billions of dollars per year.

Many corrosion problems occur in the hottest areas of the boiler-the water wall, screen, and superheater tubes. Other common problem areas include deaerators, feedwater heaters, and economizers.

Methods of corrosion control vary depending upon the type of corrosion encountered. The most common causes of corrosion are dissolved gases (primarily oxygen and carbon dioxide), under-deposit attack, low pH, and attack of areas weakened by mechanical stress, leading to stress and fatigue cracking.

These conditions may be controlled through the following procedures:

- maintenance of proper pH and alkalinity levels
- control of oxygen and boiler feedwater contamination
 - reduction of mechanical stresses
- operation within design specifications, especially for temperature and pressure
 - proper precautions during start-up and shutdown
 - effective monitoring and control

CORROSION TENDENCIES OF BOILER SYSTEM COMPONENTS

Most industrial boiler and feedwater systems are constructed of carbon steel. Many have copper alloy and/or stainless steel feedwater heaters and condensers. Some have stainless steel superheater elements.

Proper treatment of boiler feedwater effectively protects against corrosion of feedwater heaters, economizers, and deaerators. The ASME Consensus for Industrial Boilers (see Chapter 13) specifies maximum levels of contaminants for corrosion and deposition control in boiler systems.

The consensus is that feedwater oxygen, iron, and copper content should be very low (e.g., less than 7 ppb oxygen, 20 ppb iron, and 15 ppb copper for a 900 psig boiler) and that pH should be maintained between 8.5 and 9.5 for system corrosion protection.

In order to minimize boiler system corrosion, an understanding of the operational requirements for all critical system components is necessary.

Feedwater Heaters

Boiler feedwater heaters are designed to improve boiler efficiency by extracting heat from streams such as boiler water blowdown and turbine extraction or excess exhaust steam. Feedwater heaters are generally classified as low-pressure (ahead of the deaerator), high-pressure (after the deaerator), or deaerating heaters.

Regardless of feedwater heater design, the major problems are similar for all types. The primary problems are corrosion, due to oxygen and improper pH, and erosion from the tube side or the shell side. Due to the temperature increase across the heater, incoming metal oxides are deposited in the heater and then released during changes in steam load and chemical balances. Stress cracking of welded components can also be a problem. Erosion is common in the shell side, due to high-velocity steam impingement on tubes and baffles.

Corrosion can be minimized through proper design (to minimize erosion), periodic cleaning, control of oxygen, proper pH control, and the use of high-quality feedwater (to promote passivation of metal surfaces).

Deaerators

Deaerators are used to heat feedwater and reduce oxygen and other dissolved gases to acceptable levels. Corrosion fatigue at or near welds is a major problem in deaerators. Most corrosion fatigue cracking has been reported to be the result of mechanical factors, such as manufacturing procedures, poor welds, and lack of stress-relieved welds. Operational problems such as water/steam hammer can also be a factor.

Effective corrosion control requires the following practices:

- regular monitoring of operation
- minimization of stresses during start-up
- maintenance of stable temperature and pressure levels
- control of dissolved oxygen and pH in the feedwater
- regular out-of-service inspection using established nondestructive techniques

Other forms of corrosive attack in deaerators include stress corrosion cracking of the stainless steel tray chamber, inlet spray valve spring cracking, corrosion of vent condensers due to oxygen pitting, and erosion of the impingement baffles near the steam inlet connection.

Economizers

Economizer corrosion control involves procedures similar to those employed for protecting feedwater heaters.

Economizers help to improve boiler efficiency by extracting heat from flue gases discharged from the fireside of a boiler. Economizers can be classified as nonsteaming or steaming. In a steaming economizer, 5-20% of the incoming feedwater becomes steam. Steaming economizers are particularly sensitive to deposition from feedwater contaminants and resultant under-deposit corrosion. Erosion at tube bends is also a problem in steaming economizers.

Oxygen pitting, caused by the presence of oxygen and temperature increase, is a major problem in economizers; therefore, it is necessary to maintain essentially oxygen-free water in these units. The inlet is subject to severe pitting, because it is often the first area after the deaerator to be exposed to increased heat. Whenever possible, tubes in this area should be inspected closely for evidence of corrosion.

Economizer heat transfer surfaces are subject to corrosion product buildup and deposition of incoming metal oxides. These deposits can slough off during operational load and chemical changes.

Corrosion can also occur on the gas side of the economizer due to contaminants in the flue gas, forming low-pH compounds. Generally, economizers are arranged for downward flow of gas and upward flow of water. Tubes that form the heating surface may be smooth or provided with extended surfaces.

Superheaters

Superheater corrosion problems are caused by a number of mechanical and chemical conditions. One major problem is the oxidation of superheater metal due to high gas temperatures, usually occurring during transition periods, such as start-up and shutdown. Deposits due to carryover can contribute to the problem. Resulting failures usually occur in the bottom loops-the hottest areas of the superheater tubes.

Oxygen pitting, particularly in the pendant loop area, is another major corrosion problem in superheaters. It is caused when water is exposed to oxygen during downtime. Close temperature control helps to minimize this problem. In addition, a nitrogen blanket and chemical oxygen scavenger can be used to maintain oxygen-free conditions during downtime.

Low-Pressure Steam and Hot Water Heating Systems

Hot water boilers heat and circulate water at approximately 200°F. Steam heating boilers are used to generate steam at low pressures, such as 15 psig. Generally, these two basic heating systems are treated as closed systems, because makeup requirements are usually very low.

High-temperature hot water boilers operate at pressures of up to 500 psig, although the usual range is 35-350 psig. System pressure must be maintained above the saturation pressure of the heated water to maintain a liquid state. The most common way to do this is to pressurize the system with nitrogen. Normally, the makeup is of good quality (e.g., deionized or sodium zeolite softened water). Chemical treatment consists of sodium sulfite (to scavenge the oxygen), pH adjustment, and a synthetic polymer dispersant to control possible iron deposition.

The major problem in low-pressure heating systems is corrosion caused by dissolved oxygen and low pH. These systems are usually treated with an inhibitor (such as molybdate or nitrite) or with an oxygen scavenger (such as sodium sulfite), along with a synthetic polymer for deposit control. Sufficient treatment must be fed to water added to make up for system losses, which usually occur as a result of circulating pump leakage. Generally, 200-400 ppm P-alkalinity is maintained in the water for effective control of pH. Inhibitor requirements vary depending on the system.

Electric boilers are also used for heating. There are two basic types of electric boilers: resistance and electrode. Resistance boilers generate heat by means of a coiled heating element. High-quality makeup water is necessary, and sodium sulfite is usually added to

remove all traces of dissolved oxygen. Synthetic polymers have been used for deposit control. Due to the high heat transfer rate at the resistance coil, a treatment that precipitates hardness should not be used.

Electrode boilers operate at high or low voltage and may employ submerged or water-jet electrodes. High-purity makeup water is required. Depending on the type of system, sodium sulfite is normally used for oxygen control and pH adjustment. Some systems are designed with copper alloys, so chemical addition must be of the correct type, and pH control must be in the range suitable for copper protection.

TYPES OF CORROSION

Corrosion control techniques vary according to the type of corrosion encountered. Major methods of corrosion control include maintenance of the proper pH, control of oxygen, control of deposits, and reduction of stresses through design and operational practices.

Galvanic Corrosion

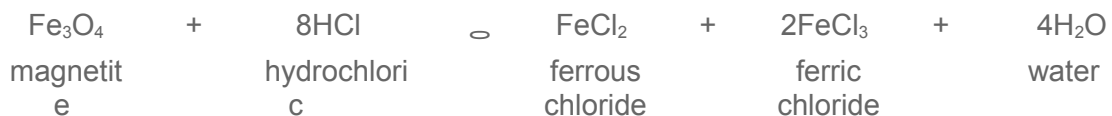
Galvanic corrosion occurs when a metal or alloy is electrically coupled to a different metal or alloy.

The most common type of galvanic corrosion in a boiler system is caused by the contact of dissimilar metals, such as iron and copper. These differential cells can also be formed when deposits are present. Galvanic corrosion can occur at welds due to stresses in heat-affected zones or the use of different alloys in the welds. Anything that results in a difference in electrical potential at discrete surface locations can cause a galvanic reaction. Causes include:

- scratches in a metal surface
- differential stresses in a metal
- differences in temperature
- conductive deposits

A general illustration of a [corrosion cell for iron in the presence of oxygen](#) is shown in Figure 11-1. Pitting of boiler tube banks has been encountered due to metallic copper deposits. Such deposits may form during acid cleaning procedures if the procedures do not completely compensate for the amount of copper oxides in the deposits or if a copper removal step is not included. Dissolved copper may be plated out on freshly cleaned surfaces, establishing anodic corrosion areas and forming pits, which are very similar to oxygen pits in form and appearance. This process is illustrated by the following reactions involving hydrochloric acid as the cleaning solvent.

Magnetite is dissolved and yields an acid solution containing both ferrous (Fe^{2+}) and ferric (Fe^{3+}) chlorides (ferric chlorides are very corrosive to steel and copper)



acid

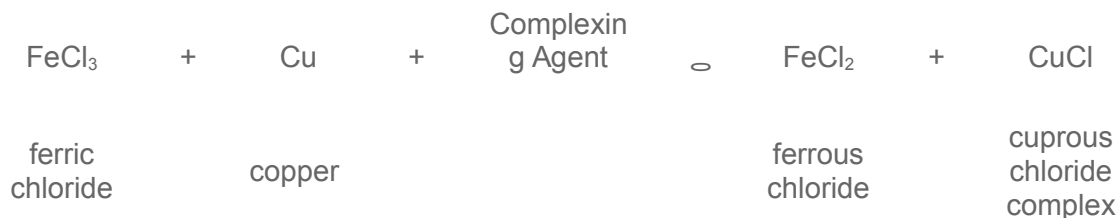
Metallic or elemental copper in boiler deposits is dissolved in the hydrochloric acid solution by the following reaction:



Once cuprous chloride is in solution, it is immediately redeposited as metallic copper on the steel surface according to the following reaction:



Thus, hydrochloric acid cleaning can cause galvanic corrosion unless the copper is prevented from plating on the steel surface. A complexing agent is added to prevent the copper from redepositing. The following chemical reaction results:



This can take place as a separate step or during acid cleaning. Both iron and the copper are removed from the boiler, and the boiler surfaces can then be passivated.

In most cases, the copper is localized in certain tube banks and causes random pitting. When deposits contain large quantities of copper oxide or metallic copper, special precautions are required to prevent the plating out of copper during cleaning operations.

Caustic Corrosion

Concentration of caustic (NaOH) can occur either as a result of steam blanketing (which allows salts to concentrate on boiler metal surfaces) or by localized boiling beneath porous deposits on tube surfaces.

Caustic corrosion (gouging) occurs when caustic is concentrated and dissolves the protective magnetite (Fe_3O_4) layer. Iron, in contact with the boiler water, forms magnetite and the protective layer is continuously restored. However, as long as a high caustic concentration exists, the magnetite is constantly dissolved, causing a loss of base metal and eventual failure (see Figure 11-2).

Steam blanketing is a condition that occurs when a steam layer forms between the boiler water and the tube wall. Under this condition, insufficient water reaches the tube surface for efficient heat transfer. The water that does reach the overheated boiler wall is rapidly vaporized, leaving behind a concentrated caustic solution, which is corrosive.

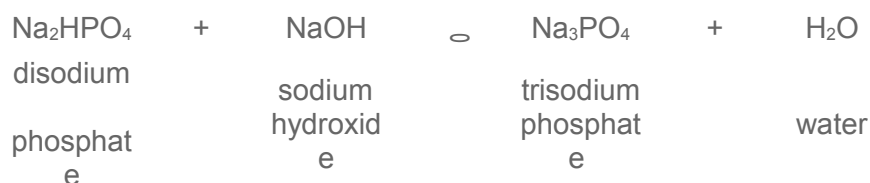
Porous metal oxide deposits also permit the development of high boiler water concentrations.

Water flows into the deposit and heat applied to the tube causes the water to evaporate, leaving a very concentrated solution. Again, corrosion may occur.

Caustic attack creates irregular patterns, often referred to as gouges. Deposition may or may not be found in the affected area.

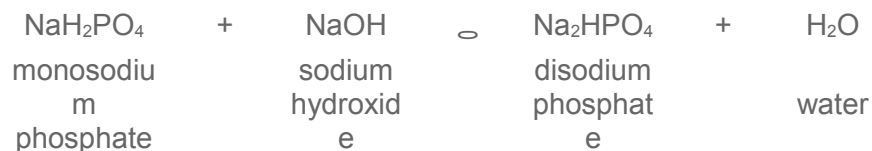
Boiler feedwater systems using demineralized or evaporated makeup or pure condensate may be protected from caustic attack through coordinated phosphate/pH control. Phosphate buffers the boiler water, reducing the chance of large pH changes due to the development of high caustic concentrations. Excess caustic combines with disodium phosphate and forms trisodium phosphate. Sufficient disodium phosphate must be available to combine with all of the free caustic in order to form trisodium phosphate.

Disodium phosphate neutralizes caustic by the following reaction:

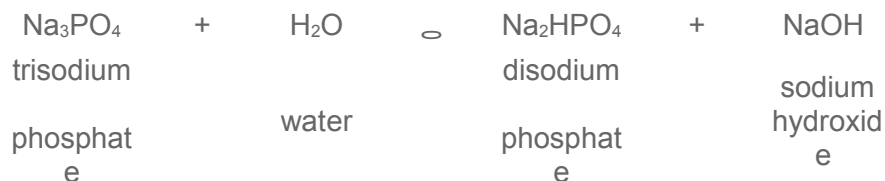


This results in the prevention of [caustic buildup beneath deposits or within a crevice where leakage is occurring](#). Caustic corrosion (and caustic embrittlement, discussed later) does not occur, because high caustic concentrations do not develop (see Figure 11-3).

Figure 11-4 shows the [phosphate/pH relationship](#) recommended to control boiler corrosion. Different forms of phosphate consume or add caustic as the phosphate shifts to the proper form. For example, addition of monosodium phosphate consumes caustic as it reacts with caustic to form disodium phosphate in the boiler water according to the following reaction:



Conversely, addition of trisodium phosphate adds caustic, increasing boiler water pH:



Control is achieved through feed of the proper type of phosphate to either raise or lower the pH while maintaining the proper phosphate level. Increasing blowdown lowers both phosphate and pH. Therefore, various combinations and feed rates of phosphate, blowdown adjustment, and caustic addition are used to maintain proper phosphate/pH levels.

Elevated temperatures at the boiler tube wall or deposits can result in some precipitation of phosphate. This effect, termed "phosphate hideout," usually occurs when loads increase. When the load is reduced, phosphate reappears.

Clean boiler water surfaces reduce potential concentration sites for caustic. Deposit control treatment programs, such as those based on chelants and synthetic polymers, can help provide clean surfaces.

Where steam blanketing is occurring, corrosion can take place even without the presence of caustic, due to the steam/magnetite reaction and the dissolution of magnetite. In such cases, operational changes or design modifications may be necessary to eliminate the cause of the problem.

Acidic Corrosion

Low makeup or feedwater pH can cause serious acid attack on metal surfaces in the preboiler and boiler system. Even if the original makeup or feedwater pH is not low, feedwater can become acidic from contamination of the system. Common causes include the following:

- improper operation or control of demineralizer cation units
- process contamination of condensate (e.g., sugar contamination in food processing plants)
- cooling water contamination from condensers

Acid corrosion can also be caused by chemical cleaning operations. Overheating of the cleaning solution can cause breakdown of the inhibitor used, excessive exposure of metal to cleaning agent, and high cleaning agent concentration. Failure to neutralize acid solvents completely before start-up has also caused problems.

In a boiler and feedwater system, acidic attack can take the form of general thinning, or it can be localized at areas of high stress such as drum baffles, "U" bolts, acorn nuts, and tube ends.

Hydrogen Embrittlement

Hydrogen embrittlement is rarely encountered in industrial plants. The problem usually occurs only in units operating at or above 1,500 psi.

Hydrogen embrittlement of mild steel boiler tubing occurs in high-pressure boilers when atomic hydrogen forms at the boiler tube surface as a result of corrosion. Hydrogen permeates the tube metal, where it can react with iron carbides to form methane gas, or with other hydrogen atoms to form hydrogen gas. These gases evolve predominantly along grain boundaries of the metal. The resulting increase in pressure leads to metal failure.

The initial surface corrosion that produces hydrogen usually occurs beneath a hard, dense scale. Acidic contamination or localized low-pH excursions are normally required to generate atomic hydrogen. In high-purity systems, raw water in-leakage (e.g., condenser leakage) lowers boiler water pH when magnesium hydroxide precipitates, resulting in corrosion, formation of atomic hydrogen, and initiation of hydrogen attack.

Coordinated phosphate/pH control can be used to minimize the decrease in boiler water pH that results from condenser leakage. Maintenance of clean surfaces and the use of proper procedures for acid cleaning also reduce the potential for hydrogen attack.

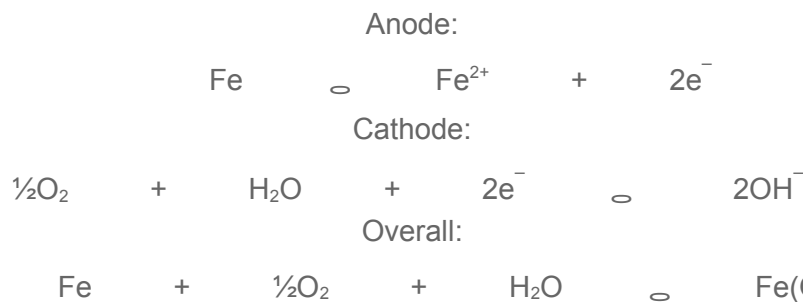
Oxygen Attack

Without proper mechanical and chemical deaeration, oxygen in the feedwater will enter the boiler. Much is flashed off with the steam; the remainder can attack boiler metal. The point of attack varies with boiler design and feedwater distribution. Pitting is frequently visible in the feedwater distribution holes, at the steam drum waterline, and in downcomer tubes.

Oxygen is highly corrosive when present in hot water. Even small concentrations can cause serious problems. Because pits can penetrate deep into the metal, oxygen corrosion can result in rapid failure of feedwater lines, economizers, boiler tubes, and condensate lines. Additionally, iron oxide generated by the corrosion can produce iron deposits in the boiler.

Oxygen corrosion may be highly localized or may cover an extensive area. It is identified by well defined pits or a very pockmarked surface. The pits vary in shape, but are characterized by sharp edges at the surface. Active oxygen pits are distinguished by a reddish brown oxide cap (tubercle). [Removal of this cap exposes black iron oxide within the pit](#) (see Figure 11-5).

Oxygen attack is an electrochemical process that can be described by the following reactions:



The influence of temperature is particularly important in feedwater heaters and economizers. A temperature rise provides enough additional energy to accelerate reactions at the metal surfaces, resulting in rapid and severe corrosion.

At 60°F and atmospheric pressure, the solubility of oxygen in water is approximately 8 ppm. Efficient mechanical deaeration reduces dissolved oxygen to 7 ppb or less. For complete protection from oxygen corrosion, a chemical scavenger is required following mechanical deaeration.

Major sources of oxygen in an operating system include poor deaerator operation, in-leakage of air on the suction side of pumps, the breathing action of receiving tanks, and leakage of undeaerated water used for pump seals.

The acceptable dissolved oxygen level for any system depends on many factors, such as feedwater temperature, pH, flow rate, dissolved solids content, and the metallurgy and physical condition of the system. Based on experience in thousands of systems, 3-10 ppb of feedwater oxygen is not significantly damaging to economizers. This is reflected in industry guidelines.

the ASME consensus is less than 7 ppb (ASME recommends chemical scavenging to "essentially zero" ppb)

TAPPI engineering guidelines are less than 7 ppb

EPRI fossil plant guidelines are less than 5 ppb dissolved oxygen

MECHANICAL CONDITIONS AFFECTING CORROSION

Many corrosion problems are the result of mechanical and operational problems. The following practices help to minimize these corrosion problems:

- election of corrosion-resistant metals
- reduction of mechanical stress where possible (e.g., use of proper welding procedures and stress-relieving welds)
- minimization of thermal and mechanical stresses during operation
- operation within design load specifications, without over-firing, along with proper start-up and shutdown procedures
- maintenance of clean systems, including the use of high-purity feedwater, effective and closely controlled chemical treatment, and acid cleaning when required

Where boiler tubes fail as a result of caustic embrittlement, circumferential cracking can be seen. In other components, cracks follow the lines of greatest stress. A microscopic examination of a properly prepared section of embrittled metal shows a characteristic pattern, with cracking progressing along defined paths or grain boundaries in the crystal structure of the metal (see Figure 11-6). The cracks do not penetrate the crystals themselves, but travel between them; therefore, the term "intercrystalline cracking" is used.

Good engineering practice dictates that the boiler water be evaluated for embrittling characteristics. An embrittlement detector (described in Chapter 14) is used for this purpose.

If a boiler water possesses embrittling characteristics, steps must be taken to prevent attack of the boiler metal. Sodium nitrate is a standard treatment for inhibiting embrittlement in lower-pressure boiler systems. The inhibition of embrittlement requires a definite ratio of nitrate to the caustic alkalinity present in the boiler water. In higher-pressure boiler systems, where demineralized makeup water is used, embrittling characteristics in boiler water can be prevented by the use of coordinated phosphate/pH treatment control, described previously under "Caustic Corrosion." This method prevents high concentrations of free sodium hydroxide from forming in the boiler, eliminating embrittling tendencies.

Caustic Embrittlement

Caustic embrittlement (caustic stress corrosion cracking), or intercrystalline cracking, has long been recognized as a serious form of boiler metal failure. Because chemical attack of the metal is normally undetectable, failure occurs suddenly-often with catastrophic results.

For caustic embrittlement to occur, three conditions must exist:

- the boiler metal must have a high level of stress

- a mechanism for the concentration of boiler water must be present
- the boiler water must have embrittlement-producing characteristics

Where boiler tubes fail as a result of caustic embrittlement, circumferential cracking can be seen. In other components, cracks follow the lines of greatest stress. A microscopic examination of a properly prepared section of embrittled metal shows a characteristic pattern, with cracking progressing along defined paths or grain boundaries in the crystal structure of the metal (see Figure 11-6). The cracks do not penetrate the crystals themselves, but travel between them; therefore, the term "intercrystalline cracking" is used.

Good engineering practice dictates that the boiler water be evaluated for embrittling characteristics. An embrittlement detector (described in Chapter 14) is used for this purpose.

If a boiler water possesses embrittling characteristics, steps must be taken to prevent attack of the boiler metal. Sodium nitrate is a standard treatment for inhibiting embrittlement in lower-pressure boiler systems. The inhibition of embrittlement requires a definite ratio of nitrate to the caustic alkalinity present in the boiler water. In higher-pressure boiler systems, where demineralized makeup water is used, embrittling characteristics in boiler water can be prevented by the use of coordinated phosphate/pH treatment control, described previously under "Caustic Corrosion." This method prevents high concentrations of free sodium hydroxide from forming in the boiler, eliminating embrittling tendencies.

Fatigue Cracking

Fatigue cracking (due to repeated cyclic stress) can lead to metal failure. The metal failure occurs at the point of the highest concentration of cyclic stress. Examples of this type of failure include cracks in boiler components at support brackets or rolled in tubes when a boiler undergoes thermal fatigue due to repeated start-ups and shutdowns.

Thermal fatigue occurs in horizontal tube runs as a result of steam blanketing and in water wall tubes due to frequent, prolonged lower header blowdown.

Corrosion fatigue failure results from cyclic stressing of a metal in a corrosive environment. This condition causes more rapid failure than that caused by either cyclic stressing or corrosion alone. In boilers, corrosion fatigue cracking can result from continued breakdown of the protective magnetite film due to cyclic stress.

Corrosion fatigue cracking occurs in deaerators near the welds and heat-affected zones. Proper operation, close monitoring, and detailed out-of-service inspections (in accordance with published recommendations) minimize problems in deaerators.

Steam Side Burning

Steam side burning is a chemical reaction between steam and the tube metal. It is caused by excessive heat input or poor circulation, resulting in insufficient flow to cool the tubes. Under such conditions, an insulating superheated steam film develops. Once the tube metal temperature has reached 750°F in boiler tubes or 950-1000°F in superheater tubes (assuming low alloy steel construction), the rate of oxidation increases dramatically; this oxidation occurs repeatedly and consumes the base metal. The problem is most frequently encountered in superheaters and in horizontal generating tubes heated from the top.

Erosion

Erosion usually occurs due to excessive velocities. Where two-phase flow (steam and water) exists, failures due to erosion are caused by the impact of the fluid against a surface. Equipment vulnerable to erosion includes turbine blades, low-pressure steam piping, and heat exchangers that are subjected to wet steam. Feedwater and condensate piping subjected to high-velocity water flow are also susceptible to this type of attack. Damage normally occurs where flow changes direction.

METALLIC OXIDES IN BOILER SYSTEMS

Iron and copper surfaces are subject to corrosion, resulting in the formation of metal oxides. This condition can be controlled through careful selection of metals and maintenance of proper operating conditions.

Iron Oxide Formation

Iron oxides present in operating boilers can be classified into two major types. The first and most important is the 0.0002-0.0007 in. (0.2-0.7 mil) thick magnetite formed by the reaction of iron and water in an oxygen-free environment. This magnetite forms a protective barrier against further corrosion.

Magnetite forms on boiler system metal surfaces from the following overall reaction:



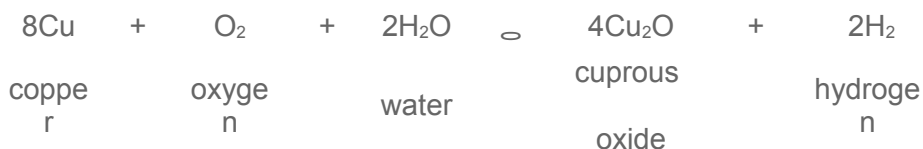
The magnetite, which provides a protective barrier against further corrosion, consists of two layers. The inner layer is relatively thick, compact, and continuous. The outer layer is thinner, porous, and loose in structure. Both of these layers continue to grow due to water diffusion (through the porous outer layer) and lattice diffusion (through the inner layer). As long as the magnetite layers are left undisturbed, their growth rate rapidly diminishes.

The second type of iron oxide in a boiler is the corrosion products, which may enter the boiler system with the feedwater. These are frequently termed "migratory" oxides, because they are not usually generated in the boiler. The oxides form an outer layer over the metal surface. This layer is very porous and easily penetrated by water and ionic species.

Iron can enter the boiler as soluble ferrous ions and insoluble ferrous and ferric hydroxides or oxides. Oxygen-free, alkaline boiler water converts iron to magnetite, Fe_3O_4 . Migratory magnetite deposits on the protective layer and is normally gray to black in color.

Copper Oxide Formation

A truly passive oxide film does not form on copper or its alloys. In water, the predominant copper corrosion product is cuprous oxide (Cu_2O). A typical corrosion reaction follows:



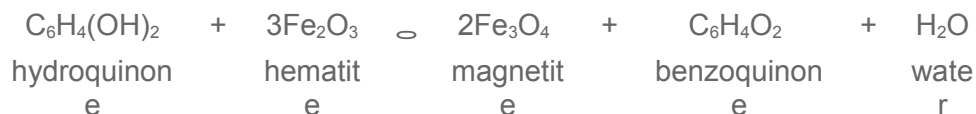
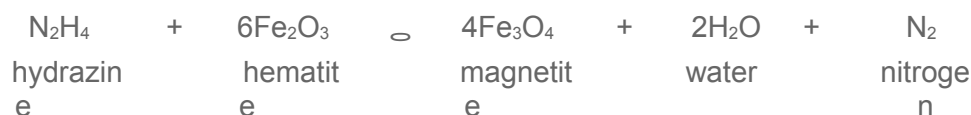
As shown in Figure 11-7, the oxide that develops on the copper surfaces is comprised of two layers. The inner layer is very thin, adherent, nonporous, and comprised mostly of cupric oxide (CuO). The outer layer is thick, adherent, porous and comprised mainly of cuprous oxide (Cu₂O). The outer layer is formed by breakup of the inner layer. At a certain thickness of the outer layer, an equilibrium exists at which the oxide continually forms and is released into the water.

Maintenance of the proper pH, elimination of oxygen, and application of metal-conditioning agents can minimize the amount of copper alloy corrosion.

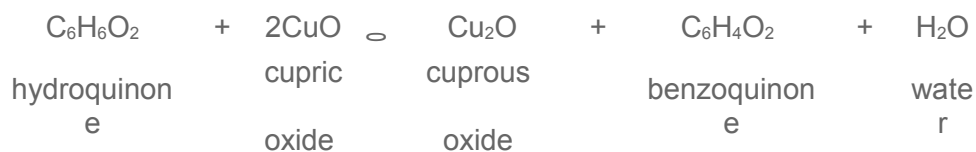
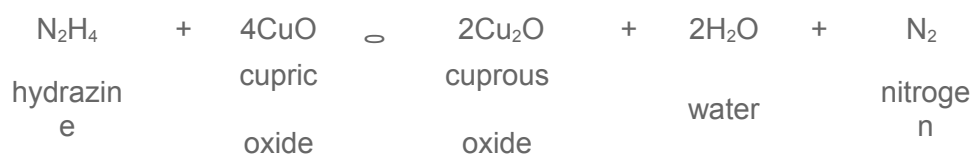
Metal Passivation

The establishment of protective metal oxide layers through the use of reducing agents (such as hydrazine, hydroquinone, and other oxygen scavengers) is known as metal passivation or metal conditioning. Although "metal passivation" refers to the direct reaction of the compound with the metal oxide and "metal conditioning" more broadly refers to the promotion of a protective surface, the two terms are frequently used interchangeably.

The reaction of hydrazine and hydroquinone, which leads to the passivation of iron-based metals, proceeds according to the following reactions:



Similar reactions occur with copper-based metals:



Magnetite and cuprous oxide form protective films on the metal surface. Because these oxides are formed under reducing conditions, removal of the dissolved oxygen from boiler feedwater and condensate promotes their formation. The effective application of oxygen scavengers indirectly leads to passivated metal surfaces and less metal oxide transport to the boiler whether or not the scavenger reacts directly with the metal surface.

A significant reduction in feedwater oxygen and metal oxides can occur with proper application of oxygen scavengers (see Figure 11-8).

CORROSION CONTROL FACTORS

Steel and Steel Alloys

Protection of steel in a boiler system depends on temperature, pH, and oxygen content. Generally, higher temperatures, high or low pH levels, and higher oxygen concentrations increase steel corrosion rates.

Mechanical and operational factors, such as velocities, metal stresses, and severity of service can strongly influence corrosion rates. Systems vary in corrosion tendencies and should be evaluated individually.

Copper and Copper Alloys

Many factors influence the corrosion rate of copper alloys:

- temperature
 - pH
- oxygen concentration
- amine concentration
- ammonia concentration
 - flow rate

The impact of each of these factors varies depending on characteristics of each system. Temperature dependence results from faster reaction times and greater solubility of copper oxides at elevated temperatures. Maximum temperatures specified for various alloys range from 200 to 300°F.

Methods of minimizing copper and copper alloy corrosion include:

- replacement with a more resistant metal
 - elimination of oxygen
- maintenance of high-purity water conditions
 - operation at the proper pH level
 - reduction of water velocities
- application of materials which passivate the metal surfaces

pH Control

Maintenance of proper pH throughout the boiler feedwater, boiler, and condensate systems is essential for corrosion control. Most low-pressure boiler system operators monitor boiler water alkalinity because it correlates very closely with pH, while most feedwater, condensate, and high-pressure boiler water requires direct monitoring of pH. Control of pH is important for the following reasons:

- corrosion rates of metals used in boiler systems are sensitive to variations in pH
 - low pH or insufficient alkalinity can result in corrosive acidic attack
- high pH or excess alkalinity can result in caustic gouging/cracking and foaming, with resultant carryover
- speed of oxygen scavenging reactions is highly dependent on pH levels

The pH or alkalinity level maintained in a boiler system depends on many factors, such as system pressure, system metals, feedwater quality, and type of chemical treatment applied.

The corrosion rate of carbon steel at feedwater temperatures approaches a minimum value in the pH range of 9.2-9.6 (see Figure 11-9). It is important to monitor the feedwater system for corrosion by means of iron and copper testing. For systems with sodium zeolite or hot lime softened makeup, pH adjustment may not be necessary. In systems that use deionized water makeup, small amounts of caustic soda or neutralizing amines, such as morpholine and cyclohexylamine, can be used.

In the boiler, either high or low pH increases the corrosion rates of mild steel (see Figure 11-10). The pH or alkalinity that is maintained depends on the pressure, makeup water characteristics, chemical treatment, and other factors specific to the system.

The best pH for protection of copper alloys is somewhat lower than the optimum level for carbon steel. For systems that contain both metals, the condensate and feedwater pH is often maintained between 8.8 and 9.2 for corrosion protection of both metals. The optimum pH varies from system to system and depends on many factors, including the alloy used (see Figure 11-11).

To elevate pH, neutralizing amines should be used instead of ammonia, which (especially in the presence of oxygen) accelerates copper alloy corrosion rates. Also, amines form protective films on copper oxide surfaces that inhibit corrosion.

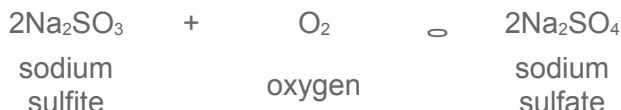
Oxygen Control

Chemical Oxygen Scavengers. The oxygen scavengers most commonly used in boiler systems are sodium sulfite, sodium bisulfite, hydrazine, catalyzed versions of the sulfites and hydrazine, and organic oxygen scavengers, such as hydroquinone and ascorbate.

It is of critical importance to select and properly use the best chemical oxygen scavenger for a given system. Major factors that determine the best oxygen scavenger for a particular application include reaction speed, residence time in the system, operating temperature and pressure, and feedwater pH. Interferences with the scavenger/oxygen reaction, decomposition

products, and reactions with metals in the system are also important factors. Other contributing factors include the use of feedwater for attemperation, the presence of economizers in the system, and the end use of the steam. Chemical oxygen scavengers should be fed to allow ample time for the scavenger/oxygen reaction to occur. The deaerator storage system and the feedwater storage tank are commonly used feed points.

In boilers operating below 1,000 psig, sodium sulfite and a concentrated liquid solution of catalyzed sodium bisulfite are the most commonly used materials for chemical deaeration due to low cost and ease of handling and testing. The oxygen scavenging property of sodium sulfite is illustrated by the following reaction:



Theoretically, 7.88 ppm of chemically pure sodium sulfite is required to remove 1.0 ppm of dissolved oxygen. However, due to the use of technical grades of sodium sulfite, combined with handling and blowdown losses during normal plant operation, approximately 10 lb of sodium sulfite per pound of oxygen is usually required. The concentration of excess sulfite maintained in the feedwater or boiler water also affects the sulfite requirement.

Sodium sulfite must be fed continuously for maximum oxygen removal. Usually, the most suitable point of application is the drop leg between the deaerator and the storage compartment. Where hot process softeners are followed by hot zeolite units, an additional feed is recommended at the filter effluent of the hot process units (prior to the zeolite softeners) to protect the ion exchange resin and softener shells.

As with any oxygen scavenging reaction, many factors affect the speed of the sulfite-oxygen reaction. These factors include temperature, pH, initial concentration of oxygen scavenger, initial concentration of dissolved oxygen, and catalytic or inhibiting effects. The most important factor is temperature. As temperature increases, reaction time decreases; in general, every 18°F increase in temperature doubles reaction speed. At temperatures of 212°F and above, the reaction is rapid. Overfeed of sodium sulfite also increases reaction rate. The reaction proceeds most rapidly at pH values in the range of 8.5-10.0.

Certain materials catalyze the oxygen-sulfite reaction. The most effective catalysts are the heavy metal cations with valences of two or more. Iron, copper, cobalt, nickel, and manganese are among the more effective catalysts.

Figure 11-12 compares the removal of oxygen using commercial sodium sulfite and a catalyzed sodium sulfite. After 25 seconds of contact, catalyzed sodium sulfite removed the oxygen completely. Uncatalyzed sodium sulfite removed less than 50% of the oxygen in this same time period. In a boiler feedwater system, this could result in severe corrosive attack.

The following operational conditions necessitate the use of catalyzed sodium sulfite:

- low feedwater temperature
- incomplete mechanical deaeration

- rapid reaction required to prevent pitting in the system
- short residence time
- use of economizers

High feedwater sulfite residuals and pH values above 8.5 should be maintained in the feedwater to help protect the economizer from oxygen attack.

Some natural waters contain materials that can inhibit the oxygen/sulfite reaction. For example, trace organic materials in a surface supply used for makeup water can reduce speed of scavenger/oxygen reaction time. The same problem can occur where contaminated condensate is used as a portion of the boiler feedwater. The organic materials complex metals (natural or formulated catalysts) and prevent them from increasing the rate of reaction.

Sodium sulfite must be fed where it will not contaminate feedwater to be used for attemporation or desuperheating. This prevents the addition of solids to the steam.

At operating pressures of 1,000 psig and higher, hydrazine or organic oxygen scavengers are normally used in place of sulfite. In these applications, the increased dissolved solids contributed by sodium sulfate (the product of the sodium sulfite-oxygen reaction) can become a significant problem. Also, sulfite decomposes in high-pressure boilers to form sulfur dioxide (SO₂) and hydrogen sulfide (H₂S). Both of these gases can cause corrosion in the return condensate system and have been reported to contribute to stress corrosion cracking in turbines. Hydrazine has been used for years as an oxygen scavenger in high-pressure systems and other systems in which sulfite materials cannot be used. Hydrazine is a reducing agent that removes dissolved oxygen by the following reaction:



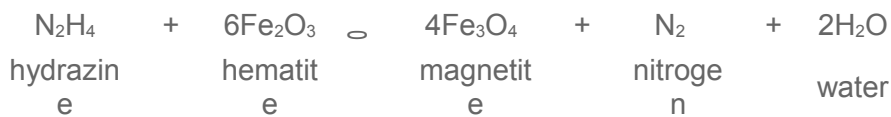
Because the products of this reaction are water and nitrogen, the reaction adds no solids to the boiler water. The decomposition products of hydrazine are ammonia and nitrogen.

Decomposition begins at approximately 400°F and is rapid at 600°F. The alkaline ammonia does not attack steel. However, if enough ammonia and oxygen are present together, copper alloy corrosion increases. Close control of the hydrazine feed rate can limit the concentration of ammonia in the steam and minimize the danger of attack on copper-bearing alloys. The ammonia also neutralizes carbon dioxide and reduces the return line corrosion caused by carbon dioxide.

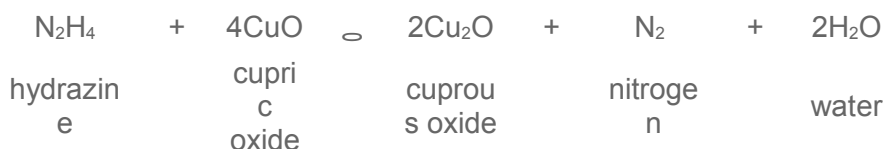
Hydrazine is a toxic material and must be handled with extreme care. Because the material is a suspected carcinogen, federally published guidelines must be followed for handling and reporting. Because pure hydrazine has a low flash point, a 35% solution with a flash point of greater than 200°F is usually used. Theoretically, 1.0 ppm of hydrazine is required to react with 1.0 ppm of dissolved oxygen. However, in practice 1.5-2.0 parts of hydrazine are required per part of oxygen.

The factors that influence the reaction time of sodium sulfite also apply to other oxygen scavengers. Figure 11-13 shows rate of reaction as a function of temperature and hydrazine concentration. The reaction is also dependent upon pH (the optimum pH range is 9.0-10.0).

In addition to its reaction with oxygen, hydrazine can also aid in the formation of magnetite and cuprous oxide (a more protective form of copper oxide), as shown in the following reactions:



and



Because hydrazine and organic scavengers add no solids to the steam, feedwater containing these materials is generally satisfactory for use as attemperating or desuperheating water.

The major limiting factors of hydrazine use are its slow reaction time (particularly at low temperatures), ammonia formation, effects on copper-bearing alloys, and handling problems.

Organic Oxygen Scavengers. Several organic compounds are used to remove dissolved oxygen from boiler feedwater and condensate. Among the most commonly used compounds are hydroquinone and ascorbate. These materials are less toxic than hydrazine and can be handled more safely. As with other oxygen scavengers, temperature, pH, initial dissolved oxygen concentration, catalytic effects, and scavenger concentration affect the rate of reaction with dissolved oxygen. When fed to the feedwater in excess of oxygen demand or when fed directly to the condensate, some organic oxygen scavengers carry forward to protect steam and condensate systems.

Hydroquinone is unique in its ability to react quickly with dissolved oxygen, even at ambient temperature. As a result of this property, in addition to its effectiveness in operating systems, hydroquinone is particularly effective for use in boiler storage and during system start-ups and shutdowns. It is also used widely in condensate systems.

Hydroquinone reacts with dissolved oxygen as shown in the following reactions:



Benzoquinone reacts further with oxygen to form polyquinones:



benzoquinon
e

oxygen

These reactions are not reversible under the alkaline conditions found in boiler feedwater and condensate systems. In fact, further oxidation and thermal degradation (in higher-pressure systems) leads to the final product of carbon dioxide. Intermediate products are low molecular weight organic compounds, such as acetates.

Oxygen Level Monitoring. Oxygen monitoring provides the most effective means of controlling oxygen scavenger feed rates. Usually, a slight excess of scavenger is fed. Feedwater and boiler water residuals provide an indication of excess scavenger feed and verify chemical treatment feed rates. It is also necessary to test for iron and copper oxides in order to assess the effectiveness of the treatment program. Proper precautions must be taken in sampling for metal oxides to ensure representative samples.

Due to volatility and decomposition, measurement of boiler residuals is not a reliable means of control. The amount of chemical fed should be recorded and compared with oxygen levels in the feedwater to provide a check on the control of dissolved oxygen in the system. With sodium sulfite, a drop in the chemical residual in the boiler water or a need to increase chemical feed may indicate a problem. Measures must be taken to determine the cause so that the problem can be corrected.

Sulfite residual limits are a function of boiler operating pressure. For most low- and medium-pressure systems, sulfite residuals should be in excess of 20 ppm. Hydrazine control is usually based on a feedwater excess of 0.05-0.1 ppm. For different organic scavengers, residuals and tests vary.

MONITORING AND TESTING

Effective corrosion control monitoring is essential to ensure boiler reliability. A well planned monitoring program should include the following:

- proper sampling and monitoring at critical points in the system
 - completely representative sampling
 - use of correct test procedures
- checking of test results against established limits
- a plan of action to be carried out promptly when test results are not within established limits
- a contingency plan for major upset conditions
- a quality improvement system and assessment of results based on testing and inspections

Monitoring Techniques

Appropriate monitoring techniques vary with different systems. Testing should be performed at least once per shift. Testing frequency may have to be increased for some systems where control is difficult, or during periods of more variable operating conditions. All monitoring data, whether spot sampling or continuous, should be recorded.

Boiler feedwater hardness, iron, copper, oxygen, and pH should be measured. Both iron and copper, as well as oxygen, can be measured on a daily basis. It is recommended that, when possible, a continuous oxygen meter be installed in the feedwater system to detect oxygen intrusions. Iron and copper, in particular, should be measured with care due to possible problems of sample contamination.

If a continuous oxygen meter is not installed, periodic testing with spot sampling ampoules should be used to evaluate deaerator performance and potential for oxygen contamination from pump seal water and other sources.

For the boiler water, the following tests should be performed:

- phosphate (if used)
- P-alkalinity or pH
- sulfite (if used)
- conductivity

Sampling

It is critical to obtain representative samples in order to monitor conditions in the boiler feedwater system properly. Sample lines, continuously flowing at the proper velocity and volume, are required. Generally, a velocity of 5-6 ft/sec and a flow of 800-1000 mL/min are satisfactory. The use of long sample lines should be avoided. Iron and copper sampling should be approached with extreme care because of the difficulty of obtaining representative samples and properly interpreting results. Trends, rather than individual samples, should be used to assess results. Copper sampling requires special precautions, such as acidification of the stream. Composite sampling, rather than spot sampling, can also be a valuable tool to determine average concentrations in a system.

Oxygen sampling should be performed as close to the line as possible, because long residence time in sampling lines can allow the oxygen scavenger to further react and reduce oxygen readings. Also, if in-leakage occurs, falsely high data may be obtained. Sampling for oxygen should also be done at both the effluent of the deaerator and effluent of the boiler feedwater pump, to verify that oxygen ingress is not occurring.

Results and Action Required

All inspections of equipment should be thorough and well documented.

Conditions noted must be compared to data from previous inspections. Analytical results and procedures must be evaluated to ensure that quality standards are maintained and that steps are taken for continual improvement. [Cause-and-effect diagrams](#) (see Figure 11-14) can be

used either to verify that all potential causes of problems are reviewed, or to troubleshoot a particular corrosion-related problem.

CORROSION PROTECTION DURING DOWNTIME AND STORAGE

Oxygen corrosion in boiler feedwater systems can occur during start-up and shutdown and while the boiler system is on standby or in storage, if proper procedures are not followed. Systems must be stored properly to prevent corrosion damage, which can occur in a matter of hours in the absence of proper lay-up procedures. Both the water/steam side and the fireside are subject to downtime corrosion and must be protected.

Off-line boiler corrosion is usually caused by oxygen in-leakage. Low pH causes further corrosion. Low pH can result when oxygen reacts with iron to form hydroferric acid. This corrosion product, an acidic form of iron, forms at water-air interfaces.

Corrosion also occurs in boiler feedwater and condensate systems. Corrosion products generated both in the preboiler section and the boiler may deposit on critical heat transfer surfaces of the boiler during operation and increase the potential for localized corrosion or overheating.

The degree and speed of surface corrosion depend on the condition of the metal. If a boiler contains a light surface coating of boiler sludge, surfaces are less likely to be attacked because they are not fully exposed to oxygen-laden water. Experience has indicated that with the improved cleanliness of internal boiler surfaces, more attention must be given to protection from oxygen attack during storage. Boilers that are idle even for short time periods (e.g., weekends) are susceptible to attack.

Boilers that use undeaerated water during start-up and during their removal from service can be severely damaged. The damage takes the form of oxygen pitting scattered at random over the metal surfaces. Damage due to these practices may not be noticed for many years after installation of the unit.

The choice of storage methods depends on the length of downtime expected and the boiler complexity. If the boiler is to be out of service for a month or more, dry storage may be preferable. Wet storage is usually suitable for shorter down-time periods or if the unit may be required to go on-line quickly. Large boilers with complex circuits are difficult to dry, so they should be stored by one of the wet storage methods.

Dry Storage

For dry storage, the boiler is drained, cleaned, and dried completely. All horizontal and non-drainable boiler and superheater tubes must be blown dry with compressed gas. Particular care should be taken to purge water from long horizontal tubes, especially if they have bowed slightly.

Heat is applied to optimize drying. After drying, the unit is closed to minimize air circulation. Heaters should be installed as needed to maintain the temperature of all surfaces above the dew point.

Immediately after surfaces are dried, one of the three following desiccants is spread on water-tight wood or corrosion-resistant trays:

- quicklime-used at a rate of 6 lb/100 ft³ of boiler volume
- silica gel-used at a rate of 17 lb/100 ft³ of boiler volume
- activated alumina-used at a rate of 27 lb/100 ft³ of boiler volume

The trays are placed in each drum of a water tube boiler, or on the top flues of a fire-tube unit. All manholes, handholes, vents, and connections are blanked and tightly closed. The boiler should be opened every month for inspection of the desiccant. If necessary, the desiccant should be renewed.

Wet Storage

For wet storage, the unit is inspected, cleaned if necessary, and filled to the normal water level with deaerated feedwater.

Sodium sulfite, hydrazine, hydroquinone, or another scavenger is added to control dissolved oxygen, according to the following requirements:

- Sodium sulfite. 3 lb of sodium sulfite and 3 lb of caustic soda should be added per 1000 gal of water contained in the boiler (minimum 400 ppm P-alkalinity as CaCO₃ and 200 ppm sulfite as SO₃).
- Hydrazine. 5 lb of a 35% solution of hydrazine and 0.1 lb of ammonia or 2-3 lb of a 40% solution of neutralizing amine can be added per 1000 gal (minimum 200 ppm hydrazine and 10.0 pH). Due to the handling problems of hydrazine, organic oxygen scavengers are normally recommended.
- Hydroquinone. Hydroquinone-based materials are added to achieve approximately 200 ppm as hydroquinone in previously passivated on-line systems. In new systems, or those considered to have a poorly formed magnetite film, the minimum feed rate is 400 ppm as hydroquinone. pH should be maintained at 10.0.

No matter which treatment is used, pH or alkalinity adjustment to minimum levels is required.

After chemical addition, with vents open, heat is applied to boil the water for approximately 1 hr. The boiler must be checked for proper concentration of chemicals, and adjustments made as soon as possible.

If the boiler is equipped with a nondrainable superheater, the superheater is filled with high-quality condensate or demineralized water and treated with a volatile oxygen scavenger and pH control agent. The normal method of filling nondrainable superheaters is by back-filling and discharging into the boiler. After the superheater is filled, the boiler should be filled completely with deaerated feedwater. Morpholine, cyclohexylamine, or similar amines are used to maintain the proper pH.

If the superheater is drainable or if the boiler does not have a superheater, the boiler is allowed to cool slightly after firing. Then, before a vacuum is created, the unit is filled completely with deaerated feedwater.

A surge tank (such as a 55-gal drum) containing a solution of treatment chemicals or a nitrogen tank at 5 psig pressure is connected to the steam drum vent to compensate for volumetric changes due to temperature variations.

The drain between the nonreturn valve and main steam stop valve is left open wide. All other drains and vents are closed tightly.

The boiler water should be tested weekly with treatment added as necessary to maintain treatment levels. When chemicals are added, they should be mixed by one of the following methods:

- circulate the boiler water with an external pump
- reduce the water level to the normal operating level and steam the boiler for a short time

If the steaming method is used, the boiler should subsequently be filled completely, in keeping with the above recommendations.

Although no other treatment is required, standard levels of the chemical treatment used when the boiler is operating can be present.

Boilers can be protected with nitrogen or another inert gas. A slightly positive nitrogen (or other inert gas) pressure should be maintained after the boiler has been filled to the operating level with deaerated feedwater.

Storage of Feedwater Heaters and Deaerators

The tube side of a feedwater heater is treated in the same way the boiler is treated during storage. The shell side can be steam blanketed or flooded with treated condensate.

All steel systems can use the same chemical concentrations recommended for wet storage. Copper alloy systems can be treated with half the amount of oxygen scavenger, with pH controlled to 9.5.

Deaerators are usually steam or nitrogen blanketed; however, they can be flooded with a lay-up solution as recommended for wet lay-up of boilers. If the wet method is used, the deaerator should be pressurized with 5 psig of nitrogen to prevent oxygen ingress.

Cascading Blowdown

For effective yet simple boiler storage, clean, warm, continuous blowdown can be distributed into a convenient bottom connection on an idle boiler. Excess water is allowed to overflow to an appropriate disposal site through open vents. This method decreases the potential for oxygen ingress and ensures that properly treated water enters the boiler. This method should not be used for boilers equipped with nondrainable superheaters.

Cold Weather Storage

In cold weather, precautions must be taken to prevent freezing. Auxiliary heat, light firing of the boiler, cascade lay-up, or dry storage may be employed to prevent freezing problems. Sometimes, a 50/50 water and ethylene glycol mixture is used for freeze protection. However, this method requires that the boiler be drained, flushed, and filled with fresh feedwater prior to start-up.

Disposal of Lay-up Solutions

The disposal of lay-up chemicals must be in compliance with applicable federal, state, and local regulations.

Fireside Storage

When boilers are removed from the line for extended periods of time, fireside areas must also be protected against corrosion.

Fireside deposits, particularly in the convection, economizer, and air heater sections, are hygroscopic in nature. When metal surface temperatures drop below the dew point, condensation occurs, and if acidic hygroscopic deposits are present, corrosion can result.

The fireside areas (particularly the convection, economizer, and air heater sections) should be cleaned prior to storage.

High-pressure alkaline water is an effective means of cleaning the fireside areas. Before alkaline water is used for this purpose, a rinse should be made with fresh water of neutral pH to prevent the formation of hydroxide gels in the deposits (these deposits can be very difficult to remove).

Following chemical cleaning with a water solution, the fireside should be dried by warm air or a small fire. If the boiler is to be completely closed up, silica gel or lime can be used to absorb any water of condensation. As an alternative, metal surfaces can be sprayed or wiped with a light oil.

If the fireside is to be left open, the metal surfaces must be maintained above the dew point by circulation of warm air.

Chapter 12 - Boiler Deposits: Occurrence And Controls

Deposition is a major problem in the operation of steam generating equipment. The accumulation of material on boiler surfaces can cause overheating and/or corrosion. Both of these conditions frequently result in unscheduled downtime.

Boiler feedwater pretreatment systems have advanced to such an extent that it is now possible to provide boilers with ultrapure water. However, this degree of purification requires the use of elaborate pretreatment systems. The capital expenditures for such pretreatment equipment trains can be considerable and are often not justified when balanced against the capability of internal treatment.

The need to provide boilers with high-quality feedwater is a natural result of the advances made in boiler performance. The ratio of heating surface to evaporation has decreased. Consequently, heat transfer rates through radiant water wall tubes have increased-occasionally in excess of 200,000 Btu/ft²/hr. The tolerance for deposition is very low in these systems.

The quality of feedwater required is dependent on boiler operating pressure, design, heat transfer rates, and steam use. Most boiler systems have sodium zeolite softened or demineralized makeup water. Feedwater hardness usually ranges from 0.01 to 2.0 ppm, but even water of this purity does not provide deposit-free operation. Therefore, good internal boiler water treatment programs are necessary.

DEPOSITS

Common feedwater contaminants that can form boiler deposits include calcium, magnesium, iron, copper, aluminum, silica, and (to a lesser extent) silt and oil. Most deposits can be classified as one of two types (Figure 12-1):

- scale that crystallized directly onto tube surfaces
- sludge deposits that precipitated elsewhere and were transported to the metal surface by the flowing water

Scale is formed by salts that have limited solubility but are not totally insoluble in boiler water. These salts reach the deposit site in a soluble form and precipitate when concentrated by evaporation. The precipitates formed usually have a fairly homogeneous composition and crystal structure.

High heat transfer rates cause high evaporation rates, which concentrate the remaining water in the area of evaporation. A number of different scale-forming compounds can precipitate from the concentrated water. The nature of the scale formed depends on the chemical composition of the concentrated water. Normal deposit constituents are calcium, magnesium, silica, aluminum, iron, and (in some cases) sodium.

The exact combinations in which they exist vary from boiler to boiler, and from location to location within a boiler (Table 12-1). Scale may form as calcium silicate in one boiler and as sodium iron silicate in another.

Compared to some other precipitation reactions, such as the formation of calcium phosphate, the crystallization of scale is a slow process. As a result, the crystals formed are well defined, and a hard, dense, and highly insulating material is formed on the tube metal. Some forms of scale are so tenacious that they resist any type of removal-mechanical or chemical.

Sludge is the accumulation of solids that precipitate in the bulk boiler water or enter the boiler as suspended solids. Sludge deposits can be hard, dense, and tenacious. When exposed to high heat levels (e.g., when a boiler is drained hot), sludge deposits are often baked in place. Sludge deposits hardened in this way can be as troublesome as scale.

Once deposition starts, particles present in the circulating water can become bound to the deposit. Intraparticle binding does not need to occur between every particle in a deposit mass. Some nonbound particles can be captured in a network of bound particles.

Table 12-1. Crystalline scale constituents identified by X-ray diffraction.

Name	Formula
Acmite	$\text{Na}_2\text{OFe}_2\text{O}_34\text{SiO}_2$
Analcite	$\text{Na}_2\text{OAl}_2\text{O}_34\text{SiO}_22\text{H}_2\text{O}$
Anhydrite	CaSO_4
Aragonite	CaCO_3
Brucite	$\text{Mg}(\text{OH})_2$

Calcite	CaCO_3
Cancrinite	$4\text{Na}_2\text{OCaO}4\text{Al}_2\text{O}_32\text{CO}_29\text{SiO}_23\text{H}_2\text{O}$
Hematite	Fe_2O_3
Hydroxyapatite	$\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$
Magnetite	Fe_3O_4
Noselite	$4\text{Na}_2\text{O}3\text{Al}_2\text{O}_36\text{SiO}_2\text{SO}_4$
Pectolite	$\text{Na}_2\text{O}4\text{CaO}6\text{SiO}_2\text{H}_2\text{O}$
Quartz	SiO_2
Serpentine	$3\text{MgO}2\text{SiO}_22\text{H}_2\text{O}$
Thenardite	Na_2SO_4
Wallastonite	CaSiO_3
Xonotlite	$5\text{CaO}5\text{SiO}_2\text{H}_2\text{O}$

Binding is often a function of surface charge and loss of water of hydration. Iron oxide, which exists in many hydrated and oxide forms, is particularly prone to bonding. Some silicates will do the same, and many oil contaminants are notorious deposit binders, due to polymerization and degradation reactions.

In addition to causing material damage by insulating the heat transfer path from the boiler flame to the water (Figure 12-2), [deposits restrict boiler water circulation](#). They roughen the tube surface and increase the drag coefficient in the boiler circuit. Reduced circulation in a generating tube contributes to accelerated deposition, overheating, and premature steam-water separation.

BOILER CIRCULATION

Figures 12-3 and 12-4 illustrate the [process of boiler circulation](#). The left legs of the U-tubes represent downcomers and are filled with relatively cool water. The right legs represent generating tubes and are heated. The heat generates steam bubbles, and convection currents create circulation. As more heat is applied, more steam is generated and the circulation rate increases.

If deposits form ([Figure 12-4](#)), the roughened surface and partially restricted opening resist flow, reducing circulation. At a constant heat input the same amount of steam is generated, so the steam-water ratio in the generating tube is increased. The water in the tube becomes more concentrated, increasing the potential for deposition of boiler water salts.

In extreme cases, deposition becomes heavy enough to reduce circulation to a point at which premature steam-water separation occurs. When this happens in a furnace tube, failure due to overheating is rapid. When deposits are light they may not cause tube failures, but they reduce any safety margin in the boiler design.

Up to the point of premature steam-water separation, the circulation rate of a boiler is increased with increased heat input. [Often, as illustrated in Figure 12-5, the inflection point \(A\) is above](#)

the nominal boiler rating. When the circuit is dirty, the inflection point of the circulation-to-heat input curve moves to the left, and the overall water circulation is reduced. This is represented by the lower broken line.

Circulation and deposition are closely related. The deposition of particles is a function of water sweep as well as surface charge (Figure 12-6). If the surface charge on a particle is relatively neutral in its tendency to cause the particle either to adhere to the tube wall or to remain suspended, an adequate water sweep will keep it off the tube. If the circulation through a circuit is not adequate to provide sufficient water sweep, the neutral particle may adhere to the tube. In cases of extremely low circulation, total evaporation can occur and normally soluble sodium salts deposit.

CHEMICAL TREATMENT

Sodium carbonate treatment was the original method of controlling calcium sulfate scale.

Today's methods are based on the use of phosphates and chelants. The former is a precipitating program, the latter a solubilizing program.

Carbonate Control

Before the acceptance of phosphate treatment in the 1930's, calcium sulfate scaling was a major boiler problem. Sodium carbonate treatment was used to precipitate calcium as calcium carbonate to prevent the formation of calcium sulfate. The driving force for the formation of calcium carbonate was the maintenance of a high concentration of carbonate ion in the boiler water. Even where this was accomplished, major scaling by calcium carbonate was common. As boiler pressures and heat transfer rates slowly rose, the calcium carbonate scale became unacceptable, as it led to tube overheating and failure.

Phosphate Control

Calcium phosphate is virtually insoluble in boiler water. Even small levels of phosphate can be maintained to ensure the precipitation of calcium phosphate in the bulk boiler water-away from heating surfaces. Therefore, the introduction of phosphate treatment eliminated the problem of calcium carbonate scale. When calcium phosphate is formed in boiler water of sufficient alkalinity (pH 11.0-12.0), a particle with a relatively nonadherent surface charge is produced. This does not prevent the development of deposit accumulations over time, but the deposits can be controlled reasonably well by blowdown.

In a phosphate precipitation treatment program, the magnesium portion of the hardness contamination is precipitated preferentially as magnesium silicate. If silica is not present, the magnesium will precipitate as magnesium hydroxide. If insufficient boiler water alkalinity is being maintained, magnesium can combine with phosphate. Magnesium phosphate has a surface charge that can cause it to adhere to tube surfaces and then collect other solids. For this reason, alkalinity is an important part of a phosphate precipitation program.

The magnesium silicate formed in a precipitating program is not particularly adherent. However, it contributes to deposit buildup on a par with other contaminants. Analyses of typical boiler deposits show that magnesium silicate is present in roughly the same ratio to calcium phosphate as magnesium is to calcium in boiler feedwater.

Phosphate/Polymer Control

Phosphate treatment results are improved by organic supplements. Naturally occurring organics such as lignins, tannins, and starches were the first supplements used. The organics were added to promote the formation of a fluid sludge that would settle in the mud drum.

Bottom blowdown from the mud drum removed the sludge.

There have been many advances in organic treatments (Figure 12-7). Synthetic polymers are now used widely, and the emphasis is on dispersion of particles rather than fluid sludge formation. Although this mechanism is quite complex, polymers alter the surface area and the surface charge to mass ratio of typical boiler solids. With proper polymer selection and application, the surface charge on the particle can be favorably altered (Figure 12-8).

Many synthetic polymers are used in phosphate precipitation programs. Most are effective in dispersing magnesium silicate and magnesium hydroxide as well as calcium phosphate. The polymers are usually low in molecular weight and have numerous active sites. Some polymers are used specifically for hardness salts or for iron; some are effective for a broad spectrum of ions. Figure 12-9 shows the relative performance of different polymers used for boiler water treatment.

Table 12-2. Phosphate/polymer performance can be maintained at high heat transfer rates through selection of the appropriate polymer.

Chelant Control

Chelants are the prime additives in a solubilizing boiler water treatment program. Chelants have the ability to complex many cations (hardness and heavy metals under boiler water conditions). They accomplish this by locking metals into a soluble organic ring structure. The chelated cations do not deposit in the boiler. When applied with a dispersant, chelants produce clean waterside surfaces.

Suppliers and users of chelants have learned a great deal about their successful application since their introduction as a boiler feedwater treatment method in the early 1960's. Chelants were heralded as "miracle treatment" additives. However, as with any material, the greatest challenge was to understand the proper application.

Chelants are weak organic acids that are injected into boiler feedwater in the neutralized sodium salt form. The water hydrolyzes the chelant, producing an organic anion. The degree of hydrolysis is a function of pH; full hydrolysis requires a relatively high pH.

The anionic chelant has reactive sites that attract coordination sites on cations (hardness and heavy metal contaminants). Coordination sites are areas on the ion that are receptive to chemical bonding. For example, iron has six coordination sites, as does EDTA (ethylenediaminetetraacetic acid). Iron ions entering the boiler (e.g., as contamination from the condensate system) combine with EDTA. All coordination sites on the iron ion are used by the EDTA, and a stable metal chelate is formed (Figure 12-10).

NTA (nitrilotriacetic acid), another chelant applied to boiler feedwater, has four coordination sites and does not form as stable a complex as EDTA. With NTA, the unused coordination sites on the cation are susceptible to reactions with competing anions.

Chelants combine with cations that form deposits, such as calcium, magnesium, iron, and copper. The metal chelate formed is water-soluble. When the chelate is stable, precipitation

does not occur. Although there are many substances having chelating properties, EDTA and NTA are, to date, the most suitable chelants for boiler feedwater treatment.

The logarithm of the equilibrium constant for the chelant-metal ion reaction, frequently called the Stability Constant (K_s), can be used to assess the chemical stability of the complex formed. For the calcium-EDTA reaction:

$$K_s = \log \frac{(\text{Ca-EDTA})^2}{(\text{Ca})^{2+} (\text{EDTA})^4} = 10.59$$

Table 12-3 lists stability constants for EDTA and NTA with common feedwater contaminants.

Table 12-3. Stability constants provide a measure of chemical stability of the chelant-metal ion complexes.

Metal Ion	EDTA	NTA
Ca+2	10.59	6.41
Mg+2	8.69	5.41
Fe+2	14.33	8.82
Fe+3	25.1	15.9

The effectiveness of a chelant program is limited by the concentration of the competing anions. With the exception of phosphate, the competing anion limitations on EDTA chelation are not usually severe. Alkalinity and silica, in addition to phosphate, are restricting considerations in the use of NTA.

Chelant/Polymer Control

Iron oxide is of particular concern in today's boiler water treatment programs. Deposition from low (less than 1.0 ppm) hardness boiler feedwater is eliminated with chelant programs and can be reduced by up to 95% by a good polymer/phosphate treatment program. Iron oxide is an increasingly significant contributor to boiler deposits because of the virtual elimination of hardness deposits in many systems and because the high heat transfer rates of many boilers encourage iron deposition.

Chelants with high stability values, such as EDTA, can complex iron deposits. However, this ability is limited by competition with hydrate ions. Experience has shown that relying on EDTA or other chelants alone is not the most satisfactory method for iron control.

At normal chelant feed rates, limited chelation of incoming particulate iron occurs. This is usually enough to solubilize some condensate iron contamination. The chelation of magnetite (the oxide formed under boiler conditions—a mix of Fe_2O_3 and FeO) is possible because the chelant combines with the ferrous (FeO) portion of the magnetite.

Overfeed (high levels) of chelant can remove large quantities of iron oxide. However, this is undesirable because high excess chelant cannot distinguish between the iron oxide that forms the protective magnetite coating and iron oxide that forms deposits.

A chelant/polymer combination is an effective approach to controlling iron oxide. Adequate chelant is fed to complex hardness and soluble iron, with a slight excess to solubilize iron contamination. **Polymers are then added to condition and disperse any remaining iron oxide contamination (Figure 12-11).**

A chelant/polymer program can produce clean waterside surfaces, contributing to much more reliable boiler operation (Figure 12-12). Out-of-service boiler cleaning schedules can be extended and, in some cases, eliminated. This depends on operational control and feedwater quality. Chelants with high complexing stabilities are "forgiving" treatments—they can remove deposits that form when feedwater quality or treatment control periodically deviates from standard.

Boilers with moderate deposition in the forms of calcium carbonate and calcium phosphate can be cleaned effectively through an in-service chelant cleanup program. In-service chelant cleanup programs should be controlled and not attempted on a heavily deposited boiler or applied at too fast a pace. Chelants can cause large accumulations of deposit to slough off in a short period of time. These accumulations can plug headers or redeposit in critical circulation areas, such as furnace wall tubes.

In a chelant cleanup program, sufficient chelant is added to solubilize incoming feedwater hardness and iron. This is followed by a recommended excess chelant feed. Regular inspections (usually every 90 days) are highly recommended so that the progress of the treatment may be monitored.

The polymer level in the boiler should also be increased above the normal concentration. This confines particles to the bulk water as much as possible until they settle in the mud drum. An increased number of mud drum "blows" should be performed to remove the particles from the boiler.

In-service chelant cleanup programs are not advisable when deposit analyses reveal that major constituents are composed of silicates, iron oxide, or any scale that appears to be hard, tightly bound, or lacking in porosity. Because such scales are not successfully removed in most instances, an in-service chelant cleanup cannot be justified in these situations.

Phosphate/Chelant/Polymer Combinations

Combinations of polymer, phosphate, and chelant are commonly used to produce results comparable to chelant/polymer treatment in low- to medium-pressure boilers. Boiler cleanliness is improved over phosphate treatment, and the presence of phosphate provides an easy means of testing to confirm the presence of treatment in the boiler water.

Polymer-Only Treatment

Polymer-only treatment programs are also used with a degree of success. In this treatment, the polymer is usually used as a weak chelant to complex the feedwater hardness. These treatments are most successful when feedwater hardness is consistently very low.

High-Pressure Boiler Water Treatment

High-pressure boilers usually have areas of high heat flux and feedwater, composed of demineralized makeup water and a high percentage of condensate returns. Because of these

conditions, high-pressure boilers are prone to caustic attack. Low-pressure boilers that use demineralized water and condensate as feedwater are also susceptible to caustic attack.

There are several means by which boiler water can become highly concentrated. One of the most common is iron oxide deposition on radiant wall tubes. Iron oxide deposits are often quite porous and act as miniature boilers. Water is drawn into the iron oxide deposit. Heat applied to the deposit from the tube wall generates steam, which passes out through the deposit. More water enters the deposit, taking the place of the steam. This cycle is repeated and the water beneath the deposit is concentrated to extremely high levels. [It is possible to have 100,000 ppm of caustic beneath the deposit while the bulk water contains only about 5-10 ppm of caustic \(Figure 12-13\).](#)

Steam generating units supplied with demineralized or evaporated makeup water or pure condensate may be protected from caustic corrosion by a treatment known by the general term "coordinated phosphate/pH control." Phosphate is a pH buffer in this program and limits the localized concentration of caustic. A detailed discussion of this treatment is included in Chapter 11.

If deposits are minimized, the areas where caustic can be concentrated is reduced. To minimize the iron deposition in high-pressure (1000-1750 psig) boilers, specific polymers have been designed to disperse the iron and keep it in the bulk water.

As with phosphate precipitation and chelant control programs, the use of these polymers with coordinated phosphate/pH treatment improves deposit control. [Figure 12-14 illustrates the effectiveness of dispersants in controlling iron oxide deposition.](#) Test conditions were 1500 psig (590°F), 240,000 Btu/ft²/hr heat flux, and coordinated phosphate/pH program water chemistry. A comparison of the untreated heat transfer surface (shown at left) with the polymer dispersant treated conditions (shown at right) provides a graphic illustration of the value of dispersants in preventing steam generator deposition. The ability to reduce iron oxide accumulations is an important requirement in the treatment of boiler systems operating at high pressures and with high-purity feedwater.

Supercritical boilers use all-volatile treatments, generally consisting of ammonia and hydrazine. Because of the extreme potential for deposit formation and steam contamination, no solids can be tolerated in supercritical once-through boiler water, including treatment solids.

Chapter 13 - Boiler Blowdown Control

Boiler blowdown is the removal of water from a boiler. Its purpose is to control boiler water parameters within prescribed limits to minimize scale, corrosion, carryover, and other specific problems. Blowdown is also used to remove suspended solids present in the system. These solids are caused by feedwater contamination, by internal chemical treatment precipitates, or by exceeding the solubility limits of otherwise soluble salts.

In effect, some of the boiler water is removed (blowdown) and replaced with feedwater. The percentage of boiler blowdown is as follows:

$$\frac{\text{quantity blowdown water}}{\text{quantity feedwater}} \times 100 = \% \text{ blowdown}$$

The blowdown can range from less than 1% when an extremely high-quality feedwater is available to greater than 20% in a critical system with poor-quality feedwater. In plants with sodium zeolite softened makeup water, the percentage is commonly determined by means of a chloride test. In higher-pressure boilers, a soluble, inert material may be added to the boiler water as a tracer to determine the percentage of blowdown. The formula for calculating blowdown percentage using chloride and its derivation are shown in Table 13-1.

Table 13-1. Algebraic proof of blowdown formula.

Let
x = Quantity feedwater
y = quantity blowdown water
a = chloride concentration in feedwater
b = chloride concentration in boiler water
k = percent blowdown
By definition of percent blowdown
$k = \frac{100y}{x}$
Because the total chlorides entering the boiler must equal total chlorides leaving boiler,
$xa = xb$
Multiplying both sides by $\frac{100}{xb}$ gives:
gives:

$$\frac{100a}{b} = \frac{100y}{x}$$

Because by definition $\frac{100y}{x} = k$, then $k = \frac{100a}{b}$ or

$$\frac{\text{Cl in feedwater}}{\text{Cl in boiler water}} \times 100 = \% \text{ blowdown}$$

LIMITING FACTORS AFFECTING BLOWDOWN

The primary purpose of blowdown is to maintain the solids content of boiler water within certain limits. This may be required for specific reasons, such as contamination of the boiler water. In this case, a high blowdown rate is required to eliminate the contaminants as rapidly as possible.

The blowdown rate required for a particular boiler depends on the boiler design, the operating conditions, and the feedwater contaminant levels. In many systems, the blowdown rate is determined according to total dissolved solids. In other systems, alkalinity, silica, or suspended solids levels determine the required blowdown rate.

For many years, boiler blowdown rates were established to limit boiler water contaminants to levels set by the American Boiler Manufacturers' Association (ABMA) in its Standard Guarantee of Steam Purity. These standards were used even though they were of a general nature and not applicable to each individual case. Today, the ASME "[Consensus on Operating Practices for the Control of Feedwater and Boiler Water Quality in Modern Industrial Boilers](#)," shown in Table 13-2, is frequently used for establishing blowdown rates.

This consensus applies to deposition control as well as steam quality. Good engineering judgment must be used in all cases. Because each specific boiler system is different, control limits may be different as well. There are many mechanical factors that can affect the blowdown control limits, including boiler design, rating, water level, load characteristics, and type of fuel.

In some cases, the blowdown control limits for a particular system may be determined by operating experience, equipment inspections, or steam purity testing rather than ASME or ABMA water quality criteria. In certain cases, it is possible to exceed standard total solids (or conductivity), silica, or alkalinity limits. [Antifoam agents have been applied successfully to allow higher-than-normal solids limits, as shown in Figure 13-1](#). Chelating and effective dispersant programs also may allow certain water criteria to be exceeded.

The maximum levels possible for each specific system can be determined only from experience. The effect of water characteristics on steam quality can be verified with steam purity testing. However, the effects on internal conditions must be determined from the results observed during the turnaround for the specific unit.

Certain boilers may require lower than normal blowdown levels due to unusual boiler design or operating criteria or an exceptionally pure feedwater requirement. In some plants, boiler blowdown limits are lower than necessary due to a conservative operating philosophy.

MANUAL BLOWDOWN

Intermittent manual blowdown is designed to remove suspended solids, including any sludge formed in the boiler water. The manual blowdown take-off is usually located in the bottom of the lowest boiler drum, where any sludge formed would tend to settle.

Properly controlled intermittent manual blowdown removes suspended solids, allowing satisfactory boiler operation. Most industrial boiler systems contain both a manual intermittent blowdown and a continuous blowdown system. In practice, the manual blowdown valves are opened periodically in accordance with an operating schedule. To optimize suspended solids removal and operating economy, frequent short blows are preferred to infrequent lengthy blows. Very little sludge is formed in systems using boiler feedwater of exceptionally high quality. The manual blowdown can be less frequent in these systems than in those using feedwater that is contaminated with hardness or iron. The water treatment consultant can recommend an appropriate manual blowdown schedule.

Blowdown valves on the water wall headers of a boiler should be operated in strict accordance with the manufacturer's recommendations. Usually, due to possible circulation problems, water wall headers are not blown down while the unit is steaming. Blowdown normally takes place when the unit is taken out of service or banked. The water level should be watched closely during periods of manual blowdown.

CONTINUOUS BLOWDOWN

Continuous blowdown, as the term implies, is the continuous removal of water from the boiler. It offers many advantages not provided by the use of bottom blowdown alone. For instance, water may be removed from the location of the highest dissolved solids in the boiler water. As a result, proper boiler water quality can be maintained at all times. Also, a maximum of dissolved solids may be removed with minimal loss of water and heat from the boiler.

Another major benefit of continuous blowdown is the recovery of a large amount of its heat content through the use of blowdown flash tanks and heat exchangers. Control valve settings must be adjusted regularly to increase or decrease the blowdown according to control test results and to maintain close control of boiler water concentrations at all times.

When continuous blowdown is used, manual blowdown is usually limited to approximately one short blow per shift to remove suspended solids which may have settled out near the manual blowdown connection.

ENERGY CONSERVATION

Several factors can contribute to reduced energy consumption on the water side of steam generation equipment.

Scale Reduction

Heat transfer is inhibited by scale formation on internal surfaces. Scale reduction through proper pretreatment and internal chemical treatment results in cleaner internal surfaces for more efficient heat transfer and resultant energy savings.

Boiler Water Blowdown Reduction

A reduction in boiler water blowdown can result in significant fuel and water savings.

In some installations, boiler water solids are lower than the maximum level permissible. Through improved control methods, including automatic boiler blowdown equipment, boiler water blowdown can be reduced to maintain the solids close to but not above the maximum level permissible.

The rate of blowdown required depends on feedwater characteristics, load on the boiler, and mechanical limitations. Variations in these factors will change the amount of blowdown required, causing a need for frequent adjustments to the manually operated continuous blowdown system. Even frequent manual adjustment may be inadequate to meet the changes in operating conditions. [Table 13-3 illustrates the savings possible with automatic boiler blowdown control.](#)

Blowdown rate is often the most poorly controlled variable of an internal treatment program.

Conductivity limits for manually controlled boiler blowdown are usually quite wide, with the lower limits below 70% of the maximum safe value. This is often necessary with manual control because a narrow range cannot be maintained safely.

In plants with sodium zeolite softened makeup water, automatic control systems can maintain boiler water conductivity within 5% of the set-point. Plant operating records have verified that with manual adjustment, continuous blowdown is within this 5% range no more than 20% of the time. In general, the average plant saves approximately 20% of boiler blowdown when changing from manually adjusted continuous blowdown to automatically controlled continuous blowdown. This reduction is gained without risk of scale or carryover due to high boiler water solids.

In some instances, an increase in feedwater quality permits a significant reduction in the blowdown rate at the existing maximum allowable solids level. This can be accomplished through reuse of additional condensate as feedwater, or through improvement of external treatment methods for higher makeup water quality.

[Any reduction in blowdown contributes to water and fuel savings, as illustrated in Table 13-4.](#)

When uniform concentrations are maintained at or near maximum permissible levels in the boiler water, savings result in several areas, including makeup water demand, cost of processing water, cost of blowdown water waste treatment, fuel consumption, and chemical treatment requirements. These savings are noticeably greater where makeup water quality is poor, where heat recovery equipment is nonexistent or inefficient, and where operating conditions are frequently changed.

Heat Recovery

Heat recovery is used frequently to reduce energy losses that result from boiler water blowdown. [Figure 13-2 illustrates a typical boiler blowdown heat recovery system using a flash tank and heat exchanger.](#)

Installation of heat recovery equipment is valuable only when energy from the flash tank or the blowdown water can be recovered and utilized. When an excess supply of exhaust or low-pressure steam is already available, there is little justification for installing heat recovery equipment.

If economically justified, boiler water blowdown can be used to heat process streams. In most cases, boiler water blowdown heat recovery systems use flash steam from the flash tank for deaeration. The blowdown from the flash tank is passed through an exchanger and used to preheat boiler makeup water. With the use of an efficient heat exchange unit, the only heat loss is the terminal temperature difference between the incoming makeup water and the blowdown water to the sewer. This difference usually amounts to 10-20°F (5-10°C).

Table 13-5 provides a typical calculation for determining the fuel savings achieved in a heat recovery system using a low-pressure flash tank and heat exchanger. [Figure 13-3 can be used to determine the quantity of flash steam recoverable from a flash tank.](#)

Table 13-5. Example of fuel savings possible through use of heat recovery on continuous blowdown.

Evaporation (steam)	5,000,000	lb
Blowdown:	+263,000	lb/day (5.0%)
Feedwater (steam + blowdown)	5,263,000	lb
Boiler Pressure:	600	psig
Feedwater Temperature (live steam used):	240	°F
Makeup water temperature:	60	°F
Fuel (oil) volume	145,000	Btu/gal
(@ 75% boiler efficiency)	X 0.75	
Available fuel heat:	108,750	Btu/gal

Employing a flash tank at 5 psig, the quantity of steam available may be calculated from the formula:

$$\% \text{ flashed steam} = \frac{H_b - H_f}{V_t} \times 100$$

where

H_b : heat of liquid at boiler pressure 475 Btu/lb

H_f : heat of liquid at flash pressure -196 Btu/lb

V_t : latent heat of vaporization at flash pressure 960 X 100 Btu/lb

% flashed steam =	29.1	
(blowdown)	263,000	lb
(@29.1% flashed steam)	X.291	
Flashed steam available at 5 psig:	76,500	lb
Total heat of flashed steam at 5 psig:	1,156	Btu/lb
(Heat of makeup water at 60° F)	-28	Btu/lb
Heat available in flashed steam	1,128	Btu/lb
(flashed steam available)	X 76,500	lb
Heat savings in flashed steam	86,292,000	Btu
Heat of liquid at psig	196	Btu/lb
Heat of liquid at 80° F	- 48	Btu/lb
Heat recovery (blowdown)	148	Btu/lb
(blowdown not flashed)	263,000	lb
(heat recovery)	X 0.709	
Heat savings from heat exchanger:	X 148	Btu/lb
(heat savings in flashed steam)	27,597,000	Btu
Total heat savings: (available fuel heat)	86,292,000	Btu
Fuel savings: (@ \$0.80/gal)	113,889,000	Btu
Daily savings	108,750	Btu/gal
	1.047	gal
	X .80	
	\$837.60	
	X 365	days/yr

Annual savings

\$305,724

EQUIPMENT EMPLOYED

Manual Blowdown

Equipment for manual blowdown, considered a part of the boiler and installed with the unit, usually consists of a take-off line, a quick-opening valve, and a shut-off valve. The take-off line is always located in the lowest part of the lowest boiler drum, where the greatest concentration of suspended solids should form.

Several types of water-tube boilers have more than one blowdown connection. They permit blowdown from both ends of the mud drum. Blowdown connections are installed on headers for draining and for removal of suspended solids which may accumulate and restrict circulation.

The boiler manufacturer usually specifies certain restrictions on the blowdown of water wall headers. These restrictions should be followed closely.

Continuous Blowdown

Usually, continuous blowdown equipment is installed by the boiler manufacturer. The exact location of the continuous blowdown take-off line depends primarily on the water circulation pattern. Its position must ensure the removal of the most concentrated water. The line must also be located so that boiler feedwater or chemical feed solution does not flow directly into it.

The size of the lines and control valves depends on the quantity of blowdown required.

[Figure 13-4 illustrates a typical location in a steam drum for a continuous blowdown connection.](#) In most units, the take-off line is several inches below the low water level. In other designs, the take-off is close to the bottom of the steam drum.

Automatic Blowdown

An automatic blowdown control system continuously monitors the boiler water, adjusts the rate of blowdown, and maintains the specific conductance of the boiler water at the desired level.

The basic components of an automatic blowdown control system include a measurement assembly, a control center, and a modulating blowdown control valve. [A typical modulating automatic boiler blowdown control system is shown in Figure 13-5.](#)

BLOWDOWN CONTROL

If an economical blowdown rate is to be maintained, suitable boiler water tests must be run frequently to check concentrations in the boiler water. When sodium zeolite softened makeup is used, the need for boiler blowdown is usually determined by measurement of the boiler water conductivity, which provides an indirect measure of the boiler water dissolved solids.

Other boiler water constituents such as chlorides, sodium, and silica are also used as a means of controlling blowdown. The alkalinity test has been used as a supplementary blowdown control for systems in which boiler water alkalinity can be particularly high.

Total Solids

From a technical standpoint, gravimetric measurement provides a satisfactory way to determine boiler water total solids; however, this method is rarely used because the analysis is time-consuming and is too difficult for routine control. Also, a comparison of the total solids

content of boiler water with the total solids content of feedwater does not necessarily provide an accurate measure of the feedwater concentration within the boiler, because of the following:

- the boiler water samples may not show a representative suspended solids content due to settling or deposit formation
- internal treatment can add various solids to the boiler water
- breakdown of bicarbonates and carbonates can liberate carbon dioxide gas and lower the total solids in the boiler water

Dissolved Solids

The specific conductance of boiler water provides an indirect measure of dissolved solids and can usually be used for blowdown control. However, establishing the rate of blowdown on the basis of the relative specific conductance of feedwater and boiler water does not give a direct measure of the feedwater concentrations within the boiler. Specific conductance is affected by the loss of carbon dioxide with steam and by the introduction of solids as internal chemical treatment. Moreover, the specific conductance of feedwater (a dilute solution) and boiler water (a concentrated solution) cannot be compared directly.

The specific conductance of a sample is caused by ionization of the various salts present. In dilute solutions, the dissolved salts are almost completely ionized, so the specific conductance increases proportionally to the dissolved salt concentration. In concentrated solutions, ionization is repressed and the ratio of specific conductance to dissolved salts decreases. The relationship between specific conductance and dissolved solids is determined most accurately through measurement of both parameters and the establishment of a correlation factor for each system. However, the factor may be estimated. The solids content of very dilute solutions such as condensate may be calculated with a factor of 0.5-0.6 ppm of dissolved solids per microsiemens (micromho) of specific conductance. For a more concentrated solution such as boiler water, the factor can vary between 0.55 and 0.90 ppm of dissolved solids per microsiemens of specific conductance. The hydroxide ion present in many boiler waters is highly conductive compared to the other ions. Therefore, it is common practice to neutralize the caustic with an organic acid prior to measuring conductivity. Although gallic acid is conventionally used to neutralize the phenolphthalein alkalinity in samples with high specific conductance, boric acid may be used in samples of low and high specific conductance with minimal impact on the correlation factor between dissolved solids and specific conductance.

Silica, Alkalinity, Sodium, Lithium, and Molybdate

Under certain circumstances, measurement of the silica and alkalinity content of boiler water can be used to control blowdown. Sodium, lithium, and molybdate have been used for accurate calculation of blowdown rates in high-pressure units where demineralized water is used as feedwater.

Chloride

If the chloride concentration in the feedwater is high enough to measure accurately, it can be used to control blowdown and to calculate the rate of blowdown. Because chlorides do not

precipitate in the boiler water, the relative chloride concentrations in feedwater and boiler water provide an accurate basis for calculating the rate of blowdown.

The chloride test is unsuitable for this calculation when the feedwater chloride is too low for accurate determination. A slight analytical error in determining feedwater chloride content will cause an appreciable error in calculating blowdown rate.

Specific Gravity

The specific gravity of a boiler water is proportional to the dissolved solids. However, determination of dissolved solids by hydrometer measurement of specific gravity is so inaccurate that it cannot be recommended for proper blowdown control.

Chapter 14 - Boiler System Failures

Successful, reliable operation of steam generation equipment requires the application of the best available methods to prevent scale and corrosion. When equipment failures do occur, it is important that the cause of the problem be correctly identified so that proper corrective steps can be taken to prevent a recurrence. An incorrect diagnosis of a failure can lead to improper corrective measures; thus, problems continue.

There are times when the reasons for failures are obscure. In these instances, considerable investigation may be required to uncover the causes. However, in most cases the problem area displays certain specific, telltale signs. When these characteristics are properly interpreted, the cause of a problem and the remedy become quite evident.

DEAERATOR CRACKING

In numerous deaerators, cracks have developed at welds and heat-affected zones near the welds. The cracking most commonly occurs at the head-to-shell weld below the water level in the storage compartment. However, it may also occur above the water level and at longitudinal welds. Because cracks can develop to the point of equipment failure, they represent a potential safety hazard requiring periodic equipment inspection and, when warranted, repair or replacement. Wet fluorescent magnetic particle testing is recommended for identification of cracks.

The mechanism of most deaerator cracking has been identified as environmentally assisted fatigue cracking. Although the exact causes are not known, steps can be taken to minimize the potential for cracking (e.g., stress-relieving of welds and minimization of thermal and mechanical stress during operation). In addition, water chemistry should be designed to minimize corrosion.

FEEDWATER LINE EROSION

High-velocity water and especially water/steam mixtures cause erosion in feedwater systems. The most commonly encountered erosion problems occur at the hairpin bends in steaming economizers. Here, the mixture of steam and water thins the elbows, leaving a characteristic reverse horseshoe imprint.

Similar problems can be encountered in feedwater lines where high velocities create the familiar thinning pattern. These problems can occur even at moderate average flow velocities when a sequence of bends causes a significant increase in local velocity.

In order to mitigate erosion problems, it is helpful to maintain water chemistry conditions that form the most tenacious oxide layer. However, the problems cannot be completely resolved without design or operational changes.

ECONOMIZER TUBES

Water tube economizers are often subject to the serious damage of oxygen pitting (see Figure 14-1). The most severe damage occurs at the economizer inlet and, when present, at the tube weld seams. Where economizers are installed, effective deaerating heater operation is absolutely essential. The application of a fast-acting oxygen scavenger, such as catalyzed sodium sulfite, also helps protect this vital part of the boiler.

While oxygen pitting is the most common form of waterside corrosion that causes economizer tube failures, caustic soda has occasionally accumulated under deposits and caused caustic gouging. Usually, this type of attack develops in an area of an economizer where steam generation is taking place beneath a deposit and free caustic soda is present in the feedwater. The best solution to this problem is improved treatment that will eliminate the deposition.

Other common causes of economizer failure include fatigue cracking at the rolled tube ends and fireside corrosion caused by the condensation of acid from the boiler flue gas.

FAILURES DUE TO OVERHEATING

When tube failures occur due to overheating and plastic flow (conditions commonly associated with deposits), the cause is usually identified by the deposits which remain, as shown in Figure 14-2. An accurate analysis of the deposits indicates the source of the problem and the steps needed for correction. Metallographic analyses are useful, at times, in confirming whether a short- or long-term exposure to overheating conditions existed prior to failure. Such analyses are helpful also when metal quality or manufacturing defects are suspected, although these factors are significant only in isolated instances.

When tube failures occur due to overheating, a careful examination of the failed tube section reveals whether the failure is due to rapid escalation in tube wall temperature or a long-term, gradual buildup of deposit. When conditions cause a rapid elevation in metal temperature to 1600°F or above, plastic flow conditions are reached and a violent rupture occurs. Ruptures characterized by thin, sharp edges are identified as "thin-lipped" bursts (see Figure 14-3).

Violent bursts of the thin-lipped variety occur when water circulation in the tube is interrupted by blockage or by circulation failure caused by low water levels. In some steam drum designs, water level is extremely critical because the baffling may isolate a generating section of the boiler when the steam drum water level falls below a certain point.

Thin-lipped bursts also occur in superheater tubes when steam flow is insufficient, when deposits restrict flow, or when tubes are blocked by water due to a rapid firing rate during boiler start-up.

Interruptions in flow do not always result in rapid failure. Depending on the metal temperature reached, the tube can be damaged by corrosive or thinning mechanisms over a long period of time before bulges or blisters or outright failures develop. In such instances, a metallurgical examination in addition to an examination of the contributing mechanical factors can be helpful in identifying the source of the problem.

A long-term scaling condition which will lead to a tube leak is usually indicated by a wrinkled, bulged external surface and a final thick-lipped fissure or opening. This appearance is indicative of long-term creep failure created by repetitive scale formation, causing overheating and swelling of the tube surface in the form of a bulge or blister. The scale, in such instances, tends to crack off; water contacts the metal and cools it until further scaling repeats the process. The iron oxide coating on the external surface cracks during the process, giving rise to the characteristic longitudinal creep cracks.

FAILURES DUE TO CORROSION

Stress Corrosion Cracking

Various corrosion mechanisms contribute to boiler tube failure. Stress corrosion may result in either intercrystalline or transgranular cracking of carbon steel. It is caused by a combination of metal stress and the presence of a corrosive. A metallurgical examination of the failed area is required to confirm the specific type of cracking. Once this is determined, proper corrective action can be taken.

Caustic Embrittlement

Caustic embrittlement, a specific form of stress corrosion, results in the intercrystalline cracking of steel. Intercrystalline cracking results only when all of the following are present: specific conditions of stress, a mechanism for concentration such as leakage, and free NaOH in the boiler water. Therefore, boiler tubes usually fail from caustic embrittlement at points where tubes are rolled into sheets, drums, or headers.

The possibility of embrittlement may not be ignored even when the boiler is of an all-welded design. Cracked welds or tube-end leakage can provide the mechanism by which drum metal may be adversely affected. When free caustic is present, embrittlement is possible.

An embrittlement detector may be used to determine whether or not a boiler water has embrittling tendencies. The device, illustrated in Figure 14-4, was developed by the United States Bureau of Mines. If boiler water possesses embrittling characteristics, steps must be taken to protect the boiler from embrittlement-related failure.

Sodium nitrate is the standard treatment for inhibiting embrittlement in boilers operating at low pressures. The ratios of sodium nitrate to sodium hydroxide in the boiler water recommended by the Bureau of Mines depend on the boiler operating pressure. These ratios are as follows:

Pressure,psi	NaNO ₃ /NaOH Ratio
Up to 250	0.20
Up to 400	0.25
Up to 1000	0.40-0.50

The formula for calculating the sodium nitrate/sodium hydroxide ratio in the boiler water is:

$$\frac{\text{NaNO}_3}{\text{NaOH}} = \frac{\text{ppm nitrate (as NO}_3^-)}{\text{ppm M alkalinity (as CaCO}_3) - \text{ppm phosphate (as PO}_4^{3-})}$$

At pressures above 900 psig, coordinated phosphate/pH control is the usual internal treatment. When properly administered, this treatment method precludes the development of high concentrations of caustic, eliminating the potential for caustic embrittlement.

Fatigue and Corrosion Fatigue

Transgranular cracking primarily due to cyclic stress is the most common form of cracking encountered in industrial boilers. In order to determine the cause of a transgranular failure, it is necessary to study both the design and the operating conditions of the boiler. Straight tube, shell-and-tube waste heat boilers frequently develop tube and tube sheet failures due to the imposition of unequal stresses. A primary cause of this is the uneven distribution of hot gases across the face of the tube sheet. The tubes involved tend to come loose, creating leakage problems. Even when the tubes are securely welded, imposed stresses can cause transverse cracking of the tubes.

Any design feature that allows steam pockets to form within a unit can cause cyclic overheating and quenching. This can lead to transverse cracking of tubes and, occasionally, shells. Such cracking always appears in the area of greatest stress and results in cracks that are primarily transgranular.

Some intercrystalline cracking may develop in this type of failure whether or not free NaOH is present. However, the predominant type of cracking is across the grain structure of the metal. Because it is mechanically induced, the cracking occurs irrespective of boiler water chemical concentrations. The cracks are often accompanied by a number of pits adjacent to or in line with the cracking- another specific indicator of the mechanical stresses imposed. Any corrosives present contribute to the formation of the pits. The normal reaction between iron and water is sufficient to cause pitting at breaks in the thin oxide film formed on freshly exposed surfaces under stress.

Stress-Induced Corrosion

Certain portions of the boiler can be very susceptible to corrosion as a result of stress from mechanical forces applied during the manufacturing and fabrication processes. Damage is commonly visible in stressed components, such as rolled tube ends, threaded bolts, and cyclone separators. However, [corrosion can also occur at weld attachments throughout the boiler \(see Figure 14-5\) and can remain undetected until failure occurs](#). Regular inspection for evidence of corrosion, particularly in the windbox area of Kraft recovery boilers, is recommended because of the potential for an explosion caused by a tube leak.

The potential for stress-induced corrosion can be reduced if the following factors are minimized: stresses developed in the boiler components, the number of thermal cycles, and the number of boiler chemical cleanings. In addition, it is necessary to maintain proper water chemistry control during operation and to provide protection from corrosion during shutdowns.

Dissolved Oxygen

Dissolved oxygen corrosion is a constant threat to feedwater heater, economizer, and boiler tube integrity. As deposit control treatment methods have improved, the need for effective control of oxygen has become increasingly important.

The first serious emphasis on oxygen control began when phosphate-based treatments were introduced to replace the soda ash treatments common before that time. The dense, hard

calcium carbonate scale which developed with the soda ash treatments protected tubes and drums from serious oxygen corrosion. With the application of phosphate treatment, the tube and drum surfaces were cleaner. Therefore, more of the surface area was exposed to corrosives in the water. This spurred the use of improved open feedwater heaters to remove most of the oxygen prior to the entrance of water into the boiler. Today, most plants are equipped with efficiently operated deaerating heaters. The use of oxygen scavengers, such as catalyzed sodium sulfite, hydrazine, and organic scavengers, is also standard practice.

The use of chelant treatments and demineralized water has improved the cleanliness of boiler heat transfer surfaces to such an extent that essentially bare-metal conditions are common.

Only a thin, protective, magnetic oxide film remains in such instances. As a result, oxygen control has become even more essential today. The use of catalyzed sulfite, where applicable, is a standard recommendation in chelant applications.

The control of downtime corrosion has become increasingly important in recent years to prevent or inhibit pitting failures. Often, cold water that has not been deaerated is used for rapid cooling or start-up of a boiler. This is a risky operating practice, usually chosen for economical reasons. Severe pitting can occur in such instances, especially in boilers that have been maintained in a deposit-free condition. Therefore, it is usually more economical to maintain clean heat transfer surfaces and eliminate the use of cold water containing dissolved oxygen during cool-down and start-up periods. This practice can result in fuel savings and improved boiler reliability.

Chelant Corrosion

During the early years of chelant use, nearly all internal boiler corrosion problems were labeled "chelant corrosion." However, other corrosives such as oxygen, carbon dioxide, caustic, acid, copper plating, and water are still common causes of boiler corrosion. In addition, mechanical conditions leading to caustic embrittlement, film boiling, and steam blanketing are even more prevalent today than ever, as a result of increasing heat transfer rates and the more compact design of steam generators. Chelant corrosion, or chelant attack, has some specific characteristics, and develops only under certain conditions.

Chelant corrosion of boiler metal occurs only when excess concentration of the sodium salt is maintained over a period of time. The attack is of a dissolving or thinning type-not pitting-and is concentrated in areas of stress within the boiler. It causes thinning of rolled tube ends, threaded members, baffle edges, and similar parts of stressed, unrelieved areas. Normally, annealed tubes and drum surfaces are not attacked. When tube thinning occurs in a chelant-treated boiler, evidence of steam blanketing and/or film boiling is sometimes present. In such instances, failure occurs regardless of the type of internal treatment used.

Pitting is often thought to be a result of chelant attack. However, pitting of carbon steel boiler tubes is almost always due to the presence of uncontrolled oxygen or acid. Infrequently, copper plating (usually the result of an improper acid cleaning operation) may lead to pitting problems.

Caustic Attack

Caustic attack (or caustic corrosion), as differentiated from caustic embrittlement, is encountered in boilers with demineralized water and most often occurs in phosphate-treated boilers where tube deposits form, particularly at high heat input or poor circulation areas.

Deposits of a porous nature allow boiler water to permeate the deposits, causing a continuous buildup of boiler water solids between the metal and the deposits.

Because caustic soda does not crystallize under such circumstances, caustic concentration in the trapped liquid can reach 10,000 ppm or more. Complex caustic-ferritic compounds are formed when the caustic dissolves the protective film of magnetic oxide. Water in contact with iron attempts to restore the protective film of magnetite (Fe_3O_4). As long as the high caustic concentrations remain, this destructive process causes a continuous loss of metal.

The thinning caused by caustic attack assumes irregular patterns and is often referred to as **caustic gouging** (see Figure 14-6). When deposits are removed from the tube surface during examination, the characteristic gouges are very evident, along with the white salts deposit which usually outlines the edges of the original deposition area. The whitish deposit is sodium carbonate, the residue of caustic soda reacting with carbon dioxide in the air.

Inspections of boilers with caustic attack often show excessive accumulations of magnetic oxide in low flow areas of drums and headers. This is caused by the flaking off, during operation, of deposits under which the complex caustic-ferritic material has formed. When contacted and diluted by boiler water, this unstable complex immediately reverts to free caustic and magnetic oxide. The suspended and released magnetic oxide moves to and accumulates in low flow or high heat flux areas of the boiler.

While caustic attack is sometimes referred to as caustic pitting, the attack physically appears as irregular gouging or thinning and should not be confused with the concentrated, localized pit penetration representative of oxygen or acid attack.

Steam Blanketing

A number of conditions permit stratified flow of steam and water in a given tube, which usually occurs in a low heat input zone of the boiler. This problem is influenced by the angle of the affected tubes, along with the actual load maintained on the boiler. Stratification occurs when, for any reason, velocity is not sufficient to maintain turbulence or thorough mixing of water and steam during passage through the tubes. **Stratification most commonly occurs in sloped tubes (Figure 14-7)** located away from the radiant heat zone of the boiler, where heat input is low and positive circulation in the tubes may be lacking.

Examination of the affected tubes usually reveals a prominent water line with general thinning in the top area of the tube or crown. In rare instances, the bottom of the tube is thinned. When the boiler water contains caustic, high concentrations accumulate and lead to caustic corrosion and gouging under the deposits that accumulate at the water line.

In certain instances, stratification may occur together with input of heat to the top or crown of the tube. This creates a high degree of superheat in the steam blanket. Direct reaction of steam with the hot steel develops if the metal temperature reaches 750°F or higher. Corrosion of the steel will proceed under such circumstances whether or not caustic is present. When there is doubt about the exact cause, a metallographic analysis will show if abnormal temperature excursions contributed to the problem. Deposits usually found under such circumstances are composed primarily of magnetic iron oxide (Fe_3O_4). Hydrogen is also formed as a result of the reaction and is released with the steam.

A somewhat unusual problem related to circulation and heat input problems has been encountered in roof tubes. These tubes are usually designed to pick up heat on the bottom side

only. Problems generally develop when the tubes sag or break away from the roof, causing exposure of the entire surface of the tube to the hot gases. The overheating that usually develops, along with the internal pressure, causes a gradual enlargement of the tube, sometimes quite uniformly. Failure occurs when the expanded tube can no longer withstand the combined effects of the thermal stress and internal pressure.

Superheater tubes often show the same swelling or enlargement effect. In such instances, steam flow has been restricted for some reason, leading to overheating and eventually to failure.

Acidic Attack

[Acid attack of boiler tubes and drums is usually in the form of general thinning of all surfaces.](#)

This results in a visually irregular surface appearance, as shown in Figure 14-8. Smooth surfaces appear at areas of flow where the attack has been intensified. In severe occurrences, other components, such as baffling, nuts and bolts, and other stressed areas, may be badly damaged or destroyed, leaving no doubt as to the source of the problem.

Severe instances of acid attack can usually be traced to either an unsatisfactory acid cleaning operation or process contamination. Some industrial plants encounter periodic returned condensate contamination, which eliminates boiler water alkalinity. Occasionally, regeneration acid from an ion exchange process is discharged accidentally into the boiler feedwater system. Cooling water contamination of condensate can depress boiler water pH and cause severe deposition and pitting in areas of high heat flux. Damage can be quite severe if immediate steps are not taken to neutralize the acid.

In the case of industrial process contamination, it is possible for organic contaminants to decompose under boiler temperature and pressure to form organic acids. Sugar is an excellent example of an organic which, when returned in a large quantity, can cause rapid loss of boiler water alkalinity and reduce pH of the boiler water to 4.3 and lower. Most sugar refining plants maintain standby pumping systems, to add caustic soda to neutralize these acids as quickly as possible.

Corrosion Due to Copper

Pitting of boiler drums and tube banks has been encountered due to metallic copper deposits, formed during acid cleaning procedures which do not completely compensate for the amount of copper oxides in the original deposits. Dissolved copper may be plated out on freshly cleaned steel surfaces, eventually establishing anodic corrosion areas and forming pits very similar in form and appearance to those caused by oxygen.

In such instances, metallic copper plating is quite evident. In most cases, it is localized in certain tube banks, giving rise to random pitting in those particular areas. Whenever deposits are found containing large quantities of copper or its oxide, special precautions are required to prevent the plating out of copper during cleaning operations.

[Copper deposits and temperatures over 1600°F can cause liquid metal embrittlement.](#) Weld repair of a tube containing copper deposits leads to the failure shown in Figure 14-9.

Hydrogen Attack or Embrittlement

Since around 1960, hydrogen attack, or embrittlement, has been encountered with increasing frequency in high-pressure, high-purity systems. It is not encountered in the average industrial plant because the problem usually occurs only in units operating at pressures of 1500 psig or higher.

In systems of this type, the alkalinity of the boiler water is maintained at values that are quite low compared to usual standards for lower-pressure operation. At the operating pressures indicated and water conditions imposed, either coordinated pH/phosphate or total volatile programs are used. Because the boiler water is relatively unbuffered, total volatile programs are more affected by contaminants that may lower boiler water alkalinity or pH.

When contaminants lower the boiler water pH sufficiently, the acid attack of the steel generates hydrogen. If this occurs under hard, adherent, nonporous tube deposits, the hydrogen pressure within the deposit can build up to the point at which the hydrogen penetrates the steel tubing.

When atomic hydrogen permeates the metal structure, it reacts with the carbon content to form methane. Because the methane molecule is too large to diffuse through the steel, excessive pressure develops within the metal structure, causing the metal to rupture along the crystalline boundaries where methane has formed. The cracking that develops is primarily intercrystalline or intergranular in nature, the metallic area affected becoming decarburized in the process.

Failure occurs when the ruptured section can no longer withstand the internal pressure.

Ruptures are violent and sudden, and can be disastrous (see Figure 14-10). Failed sections of tubing are cracked in the intergranular mode and decarburized, but usually retain the original dimensions or thickness of the tubing material.

Although there are many causes of low boiler water pH, it most frequently occurs when brackish water is used for condenser cooling. Small quantities of magnesium chloride, in particular, have caused extremely low pH excursions, requiring very close supervision and detection of very low levels of contamination in the condensate.

To summarize, hydrogen embrittlement occurs only when a hard, dense scale is present on the tube surfaces, permitting hydrogen to concentrate under the deposit and permeate the metal. Acidic contamination or low pH excursions commonly produce the conditions for generation of hydrogen. This type of attack may develop very quickly; therefore, constant surveillance of condensate purity is required.

As indicated, hydrogen embrittlement usually occurs in high-purity systems that operate at 1500 psig or higher. Although it is sometimes confused with intergranular creep cracking, this type of failure can be positively identified by the distinctive intergranular nature of the cracking and decarburized condition of the metal.

Surveys of units operating at these pressures and under these conditions have generally indicated that the application of a coordinated pH/phosphate control will lessen the possibility of hydrogen embrittlement. This is due primarily to the improved buffering of the boiler water with phosphate present.

Superheater Tubes

Superheater tube failures are caused by a number of conditions, both mechanical and chemical. In any instance of superheater tube failure, analysis of the deposits found is an important factor in solving the problem. **Magnetic oxide deposits at the point of failure are a direct indication of oxidation of the tube metal (see Figure 14-11).** This oxidation occurs during

overheating where metal temperatures exceed the design temperature and the steel enters into a direct reaction with the steam to form magnetic iron oxide with hydrogen release. When the deposits found in the area of failure are primarily iron oxide, it may be necessary to explore a number of operating conditions in order to determine the initial cause.

Oxidation may occur if the flow of steam through the tubes is restricted or if the heat input is excessive, permitting overheating. In the case of insufficient steam flow, the restriction may be due to conditions prevalent during the transition periods of boiler start-up or shutdown. This occurs if adequate precautions have not been taken to protect the superheater during the transition periods. At no time should gas temperatures exceed 900°F in the area of the superheater until the boiler is up to operating pressure and all superheater tubes are clear of any water which may have accumulated during the downtime. Overheating conditions may develop during times of low-load operation when adequate distribution of saturated steam across the tube bank at the inlet header has not been achieved.

Soluble-salt deposits may form at a superheater tube inlet as a result of excessive entrainment of boiler water solids with the steam. This can result in restricted flow. However, overheating and direct oxidation failures may occur in areas distinctly removed from the blockage, such as the bottom loops or the hottest areas of the superheater tubes.

In some cases, there is a very clear delineation between oxidation products in the hot area and soluble-salts deposits at the inlet. However, in most occurrences, a high percentage of sodium salt deposits is found in the hot areas along with the oxidation products. There is little doubt in such instances that boiler water carryover has contributed to the problem.

Periodic overheating of superheaters, caused by insufficient control of firebox temperatures during start-up and shutdown periods, usually results in thick-lipped fissures and blistering with all the evidence of creep failure. As in the case of water tubes, a superheater tube will fail rapidly (often violently) when flow is blocked for a short period of time and tube temperature escalates rapidly to plastic flow temperatures. Determination of whether a failure is due to a long- or short-term situation depends essentially on the same general characteristics that apply to water tube examination.

Oxygen pitting of superheater tubes, particularly in the pendant loop area, is rather common and occurs during downtime. It is caused by the exposure of water in these areas to oxygen in the air.

It is essential that the manufacturer's instructions be followed rigidly to prevent overheating problems during start-up or shutdown and to prevent oxygen corrosion during downtime.

When soluble-salts deposits are found in superheater tubes, steam purity is of paramount concern. It has been the experience of Betz Laboratories, after conducting thousands of steam purity studies over many years, that soluble-salts deposits in superheaters can be expected, with attendant problems, whenever steam solids exceed 300 ppb. Therefore, when soluble-salts deposits are found, a thorough investigation of steam purity (and reasons for poor purity) is necessary.

Boiler Design Problems

Certain basic design flaws can contribute to tube failures. Problems which occur as a result of a design flaw may be intensified by the boiler water chemistry. The boiler water often contains

elements that become corrosive when concentrated far beyond normal values as a result of design problems.

Many industrial boilers, for example, are treated in such a manner that low concentrations of caustic soda are present in the boiler water. The caustic can become corrosive to steel when the boiler water is allowed to concentrate to abnormally high values as a result of poor design. Even in the absence of caustic, conditions which permit stratification or steam blanketing and localized elevation of metal temperatures in excess of 750°F allow direct oxidation or corrosion of the steel in contact with water or steam. This causes loss of metal and eventual rupture of the tube.

Roof tubes, nose arch tubes, and convection pass tubes with slopes of less than 30 degrees from the horizontal are more subject to deposition and stratification problems and tube failures than vertical tubes. Whenever chelant is present in boiler water, the sodium salts of ethylenediaminetetraacetic acid (EDTA), in particular, are destroyed at high temperature, leaving a residue of caustic soda. The caustic soda residue from the chelant is usually an insignificant additive to whatever caustic may be present normally.

A frequent contributor to waste heat boiler problems is the uneven distribution of gases across the inlet tubes at the hot end. This causes unequal stresses and distortion and leads to mechanical stress and fatigue problems.

The use of horizontal hairpin tube configurations with inadequate forced circulation of water through the tubes often permits stratification of steam and water. This often leads to steam blanketing or caustic corrosion problems.

Procedures for Boiler Tube Failure Analysis

At times, the cause of a failure cannot be readily determined, making it difficult to determine the appropriate corrective action. A detailed examination of the failure and associated operating data is usually helpful in identifying the mechanism of failure so that corrective action may be taken.

Proper investigative procedures are needed for accurate metallurgical analyses of boiler tubes. Depending on the specific case, macroscopic examination combined with chemical analysis and microscopic analysis of the metal may be needed to assess the primary failure mechanism(s). When a failed tube section is removed from a boiler, care must be taken to prevent contamination of deposits and damage to the failed zones. Also, the tube should be properly labeled with its location and orientation.

The first step in the lab investigation is a thorough visual examination. Both the fireside and the waterside surfaces should be inspected for failure or indications of imminent failure.

Photographic documentation of the as-received condition of tubing can be used in the correlation and interpretation of data obtained during the investigation. Particular attention should be paid to color and texture of deposits, fracture surface location and morphology, and metal surface contour. A stereo microscope allows detailed examination under low-power magnification.

Dimensional analysis of a failed tube is important. Calipers and point micrometers are valuable tools that allow quantitative assessment of failure characteristics such as bulging, wall thinning at a rupture lip, and corrosion damage. The extent of ductile expansion and/or oxide formation can provide clues toward determining the primary failure mechanism. External wall thinning

from fireside erosion or corrosion mechanisms can result in tube ruptures which often mimic the appearance of overheating damage. In those cases, dimensional analysis of adjacent areas can help to determine whether or not significant external wall thinning occurred prior to failure. A photograph of a tube cross section taken immediately adjacent to a failure site can assist in dimensional analysis and provide clear-cut documentation.

The extent, orientation, and frequency of tube surface cracking can be helpful in pinpointing a failure mechanism. While overheating damage typically causes longitudinal cracks, fatigue damage commonly results in cracks that run transverse to the tube axis. In particular, zones adjacent to welded supports should be examined closely for cracks. Nondestructive testing (e.g., magnetic particle or dye penetrant inspection) may be necessary to identify and assess the extent of cracking.

When proper water chemistry guidelines are maintained, the waterside surfaces of boiler tubes are coated with a thin protective layer of black magnetite. Excessive waterside deposition can lead to higher-than-design metal temperatures and eventual tube failure. Quantitative analysis of the internal tube surface commonly involves determination of the deposit-weight density (DWD) value and deposit thickness. Interpretation of these values can define the role of internal deposits in a failure mechanism. DWD values are also used to determine whether or not chemical cleaning of boiler tubing is required. In addition, the tube surface may be thoroughly cleaned by means of glass bead blasting during DWD testing. This facilitates accurate assessment of waterside or fireside corrosion damage (e.g., pitting, gouging) that may be hidden by deposits.

The presence of unusual deposition patterns on a waterside surface can be an indication that nonoptimal circulation patterns exist in a boiler tube. For example, longitudinal tracking of deposits in a horizontal roof tube may indicate steam blanketing conditions. Steam blanketing, which results when conditions permit stratified flow of steam and water in a given tube, can lead to accelerated corrosion damage (e.g., wall thinning and/or gouging) and tube failure.

When excessive internal deposits are present in a tube, accurate chemical analyses can be used to determine the source of the problem and the steps necessary for correction. Whenever possible, it is advisable to collect a "bulk" composition, by scraping and crimping the tube and collecting a cross section of the deposit for chemical analysis. Typically, a loss-on-ignition (LOI) value is also determined for the waterside deposit. The LOI value, which represents the weight loss obtained after the deposit is heated in a furnace, can be used to diagnose contamination of the waterside deposit by organic material.

In many cases, chemical analysis of a deposit from a specific area is desired. Scanning electron microscope-energy dispersive spectroscopy (SEM-EDS) is a versatile technique that allows inorganic chemical analysis on a microscopic scale. [SEM-EDS analyses are shown in Figures 14-12 and 14-13](#). For example, SEM-EDS can be useful in the following determinations:

- differences in deposit composition between corroded and noncorroded areas on a tube surface
- the extent to which under-deposit concentration of boiler salts on heat transfer surfaces is promoting corrosion damage

- elemental differences between visually different tube surface deposits

Inorganic analyses through SEM-EDS can also be performed on ground and polished cross sections of a tube covered with thick layers of waterside deposit. This testing is called elemental mapping and is particularly valuable when the deposits are multilayered. Similar to the examination of rings on a tree, cross-sectional analysis of boiler deposits can identify periods when there have been upsets in water chemistry, and thereby provides data to help determine exactly how and when deposits formed. With elemental mapping, the spatial distribution of elements in a deposit cross section is represented by color-coded dot maps. Separate elements of interest can be represented by individual maps, or selected combinations of elements can be represented on composite maps.

A scanning electron microscope (SEM) can also be utilized to analyze the topography of surface deposits and/or morphology of fracture surfaces. Fractography is particularly helpful in classifying a failure mode. For example, microscopic features of a fracture surface can reveal whether the steel failed in a brittle or ductile manner, whether cracks propagated through grains or along grain boundaries, and whether or not fatigue (cyclic stress) was the primary cause of failure. In addition, SEM-EDS testing can be used to identify the involvement of a specific ion or compound in a failure mechanism, through a combination of fracture surface analysis and chemical analysis.

Most water-bearing tubes used in boiler construction are fabricated from low-carbon steel. However, steam-bearing (superheater and reheater) tubes are commonly fabricated from low-alloy steel containing differing levels of chromium and molybdenum. Chromium and molybdenum increase the oxidation and creep resistance of the steel. For accurate assessment of metal overheating, it is important to have a portion of the tube analyzed for alloy chemistry. Alloy analysis can also confirm that the tubing is within specifications. In isolated instances, initial installation of the wrong alloy type or tube repairs using the wrong grade of steel can occur. In these cases, chemical analysis of the steel can be used to determine the cause of premature failure.

At times, it is necessary to estimate the mechanical properties of boiler components. Most often, this involves hardness measurement, which can be used to estimate the tensile strength of the steel. This is particularly useful in documenting the deterioration of mechanical properties that occurs during metal overheating. Usually, a Rockwell hardness tester is used; however, it is sometimes advantageous to use a microhardness tester. For example, microhardness measurements can be used to obtain a hardness profile across a welded zone to assess the potential for brittle cracking in the heat-affected zone of a weld.

Microstructural analysis of a metal component is probably the most important tool in conducting a failure analysis investigation. This testing, called metallography, is useful in determining the following:

- whether a tube failed from short-term or long-term overheating damage
 - whether cracks initiated on a waterside or fireside surface
- whether cracks were caused by creep damage, corrosion fatigue, or stress-corrosion cracking (SCC)

- whether tube failure resulted from hydrogen damage or internal corrosion gouging

Proper sample orientation and preparation are critical aspects of microstructural analysis. The orientation of the sectioning is determined by the specific failure characteristics of the case.

After careful selection, metal specimens are cut with a power hacksaw or an abrasive cut-off wheel and mounted in a mold with resin or plastic. After mounting, the samples are subjected to a series of grinding and polishing steps. The goal is to obtain a flat, scratch-free surface of metal in the zone of interest. After processing, a suitable etchant is applied to the polished metal surface to reveal microstructural constituents (grain boundaries, distribution and morphology of iron carbides, etc.)

Metallographic analysis of the mounted, polished, and etched sections of metal is performed with a reflective optical microscope (Figure 14-14). This is followed by a comparison of microstructures observed in various areas of a tube section-for example, the heated side versus the unheated side of a waterwall tube. Because the microstructure on the unheated side often reflects the as-manufactured condition of the steel, comparison with the microstructure in a failed region can provide valuable insight into the degree and extent of localized deterioration (Figure 14-15).

Chapter 15 - Chemical Cleaning Of Steam Generator Systems s

Internal surfaces of steam generator systems are cleaned to remove contaminants that impair heat transfer and may ultimately cause tube failure. In the decision to clean chemically and the selection of the cleaning method, the following factors should be considered:

- the type of design, amount of flow, operating temperature, and pressure of the steam generator
 - the characteristics and quantity of deposit
- the compatibility of the cleaning solvent with system metallurgy
 - the method of spent solvent disposal
- the availability of demineralized water or condensate
 - safety
 - cost

PREOPERATIONAL CLEANING

Traditionally, preoperational cleaning has not been a major consideration in plant design and construction. This area has recently received more attention because of costs, environmental restrictions on plant discharges, smaller boiler design margins, higher boiler operating pressures and temperatures, and noise abatement requirements.

The purpose of preoperational cleaning is to remove construction contaminants which could cause operating problems or even failure during initial operation. Preoperational contaminants include mill scale, weld slag, corrosion products, oil, grease, debris and dirt, temporary protective coatings, and other contaminants remaining after fabrication and erection of the unit.

Mill scale, a dense magnetite layer produced on steel surfaces during fabrication, is subject to fracture and erosion during system operation. Because the exposed metal is anodic to the mill scale, these surface cracks are potential corrosion sites. In addition, mill scale and weld scale can become deposit accumulation sites and may cause damage if they break loose. Removal of metallic scale and corrosion products generally requires chemical cleaning.

Frequently, sand and dirt (which add scale-forming contaminants such as silica and calcium to the boiler water) can be removed by flushing.

Oils and grease are also used in boiler fabrication. The insulating effect of even thin films of these substances can lead to overheating failure. Oil and grease, including temporary protective coatings, are generally removed by hot alkaline chemical cleaning.

Two areas merit consideration in the planning of preoperational cleaning. First, plant design should include provisions that allow field cleaning with a minimum of temporary piping, time, and cost. Second, fabrication and erection cleanliness should be maintained at the highest

practical level so that only a minimum of field cleaning is necessary. Increased attention is being given to cleanliness during fabrication due to several factors:

- the trend toward more shop fabrication and less field fabrication allows better cleanliness control
 - system start-up is quicker when complex cleaning methods are not required
 - environmental regulations complicate the disposal of chemical cleaning solutions
 - noise abatement limits the use of steam blows in some locations

The preoperational cleaning method chosen depends largely on the cleanliness maintained during fabrication and erection. If a high degree of construction cleanliness is maintained, a water flush of condensate and feedwater systems may be used, along with an alkaline boil-out followed by a steam blow of the steam generator. This can provide sufficient cleaning in most boilers that operate at less than 900 psig.

A hot alkaline flush of the condensate and feedwater systems and an alkaline boil-out of the boiler and economizer are required if certain contaminants are present. In addition to removing oil, grease, and temporary protective coatings, the alkaline conditions and the flushing action may cause dislodging of some flaky surface oxide and mill scale. If no other cleaning is required, the alkaline cleaning should be followed by steam blowing.

Contaminated boiler and steam systems, as well as systems that operate at over 900 psig, may require a more thorough chemical cleaning. This should be preceded by an alkaline cleaning to prevent oil or grease from interfering with the cleaning process unless a single-stage alkaline/chelant cleaning solution is used.

Preoperational acid or chelant cleaning procedures vary greatly depending on individual circumstances. The equipment to be cleaned may include any combination of the following:

- boiler/economizer
- condensate/feedwater systems
- superheater/reheater
- main steam lines

The other variable, when to clean, also depends on the individual application. Typical sequences include the following:

1. alkaline clean before initial operation
2. alkaline clean and acid/chelant clean before initial operation

3. alkaline clean before initial operation followed by an acid/chelant cleaning after several weeks to 1 year of operation

Subcritical boilers operated at pressures greater than 900 psig are generally given a hot alkaline cleaning and an acid or chelant cleaning of the boiler and economizer. Supercritical boilers and systems are usually given a hot alkaline cleaning along with an acid or chelant cleaning of the condensate/feedwater systems, boiler, and economizer. Often the superheater and reheater are cleaned as well.

Acid or chelant cleaning of the boiler and economizer is generally performed before initial operation to prevent contaminant damage or water chemistry upsets. Sometimes, this cleaning is delayed until after initial operation (i.e., until after most condensate and feedwater system contaminants have been carried to the boiler). However, this presents the risk of contamination in the economizer and high heat zones of the boiler.

Acid or chelant cleaning can be beneficial in condensate/feedwater systems because of the equipment's large surface area. However, the necessity for additional chemical cleaning is reduced when these systems are made primarily of copper alloys and stainless steel. Acid or chelant cleaning removes contaminants in these systems, and there is no reason to delay boiler and economizer cleaning until after initial operation.

Acid or chelant cleaning of the superheater and reheater increases cleaning costs and complexity but minimizes possible turbine problems by removing contaminants which could cause solid particle erosion. Although it was not common in the past, chemical cleaning of superheaters or reheaters is becoming more frequent.

POSTOPERATIONAL CLEANING

Unless a proper inspection program is in place, a blown tube may be the first indication of a need for chemical cleaning of a boiler. The type and frequency of inspection required vary with the boiler design, its operating requirements, and the history of operation and water treatment. Visual inspection of the fireside may reveal blistered tubes, while waterside inspection of the drums, tube internals, and headers may reveal deposit accumulations that indicate a need for boiler cleaning.

Boroscopes and [miniature video cameras \(Figure 15-1\)](#) can be used to monitor conditions in tubes and headers not otherwise visible. Tube samples are often cut from the highest heat flux area of the boiler to permit visual examination of conditions at this critical location, along with quantitative measurement of the deposit accumulation. [Chordal thermocouples \(Figure 15-2\)](#) may be used to measure the effect of any boiler deposition on the resistance to heat transfer in certain critical tubes and thereby identify the need for cleaning.

After a boiler has been in operation for some time, its cleaning schedule may be based on number of years in operation or amount of steam generated.

Deposits may include corrosion products, mineral scale, sludge, or process contaminants, in any combination. Deposits form from low levels of accumulation for long periods of operation, due to improperly controlled water treatment or process contamination. Deposit characteristics are influenced by raw water characteristics, type of external treatment, feedwater treatment methods and control, and the nature and degree of external contaminants which have entered

the feedwater during operation. Power and water plant operators play a big part in the deposit control of a unit.

Corrosion product deposits are the major contaminant in high-pressure boilers using demineralized makeup water. Condensate and feedwater system corrosion products can be carried into the boiler, where they can deposit on the metal surfaces. Boiler tube metal corrosion can add to this deposit, but with good boiler operation and proper water treatment practices, tube metal corrosion is not usually significant. The insulating effect of a corrosion product deposit can cause tube metal overheating and subsequent failure. Because they are usually porous, corrosion product deposits can also provide sites for boiler water concentration and, consequently, the potential for caustic attack.

In boilers that receive some hardness in the makeup water, typical deposits are calcium, magnesium, and phosphate compounds. These mineral scales, along with sludge and process contaminants such as oils, can also cause an insulating effect which leads to overheating. The principal cause of mineral scale formation in boilers is the fact that scale-forming salt solubility decreases with increasing temperature. Thus, as boiler water is heated, the solubility of scale-forming salts is exceeded and crystallization takes place on the boiler heating surfaces.

Removal of deposits has advantages other than minimization of failures. Cleaning reveals the true boiler metal condition, allowing more complete inspection. Previously unnoticed pits or gouges may become clearly visible. Cracks resulting from fatigue, embrittlement, or corrosion may be revealed. Also, a clean unit may be operated more efficiently.

Most internal deposits can be removed with mineral acid, organic acid, or chelant. The most widely used solvent is a 5% hydrochloric acid solution with inhibitor and complexors. Phosphoric, sulfuric, and sulfamic acids are also used in boilers that operate at less than 2000 psig. Inhibited ammonium citrate and a combination of hydroxyacetic and formic acids are commonly used organics. Salts of EDTA (ethylenediaminetetraacetic acid) have been used for both off-line and on-line cleaning.

Environmental regulations must be considered in solvent selection. Plants with no waste treatment facilities must have spent cleaning solution trucked away, or they must use a process in which the spent solution can be evaporated.

A new boiler or an operating boiler that is subject to oil contamination should be given an alkaline boil-out before chemical cleaning. Otherwise, oil-based contaminants will interfere with cleaning. Brass or bronze parts should be replaced temporarily with steel or steel alloy parts before a chemical cleaning. Proper provisions should be made for venting of chemical vapors. Connections to steam headers or other equipment should be valved shut with provisions for backfilling and draining.

There are two basic methods of acid or chelant cleaning: the circulation method and the static (sometimes called fill-and-soak) method.

In the circulation method, the cleaning solution is intermittently circulated through the unit until the chemical content and the iron and copper content of the cleaning solution reach a constant value, indicating the end of the reaction between the solvent and deposits. This method is suitable for units with positive liquid flow paths, and it allows monitoring of the cleaning operation at multiple sample points.

In the static method, the cleaning solution soaks in the unit for a prescribed length of time. This method is used when positive circulation of the cleaning solution is impractical.

In addition to inhibited solvent, intensifier chemicals are required in some instances to help remove particular scale constituents. The addition of certain wetting agents with the inhibitor can reduce corrosion rates during cleaning.

WATER FLUSHING AND STEAM BLOWING

Alkaline water flushes are usually performed with potable-quality tempered water. Flush velocity should be greater than system design velocity. After the flush, the condenser hot well, deaerator, and deaerator storage tank are usually cleaned by hand, because these units do not drain completely.

Steam blowing normally follows the last boiler and economizer chemical cleaning operation.

When reheaters are present, this step is usually done in two stages. First, the main steam piping and superheater are blown. Then, the main steam piping, superheater, and reheater are blown. The most effective cleaning is accomplished when the blowing steam force exceeds maximum operating steam force. A 1.6:1 force ratio has been found to provide satisfactory cleaning of particles from the piping. Continuous blowing is used, but intermittent blow periods of several minutes each are more common.

In order to assess blowing effectiveness, blow steam may be directed onto a target plate in the main steam line. This practice is most common in high-pressure boilers generating superheated steam for a turbine drive. Successive blows are made until solid particle erosion is no longer visible on the target plate. The required blow time varies, but in general is approximately 24 hr unless chemical cleaning has preceded the blow. Chemical cleaning can significantly reduce required blow times.

ALKALINE CLEANING

Alkaline cleaning (flush/boil-out) solutions are basically trisodium phosphate and surfactant.

Trisodium phosphate concentrations typically range from 0.1 to 1%. Disodium phosphate and/or sodium hydroxide may be added. Sodium nitrate is often added when caustic is used, as a precaution against caustic embrittlement. Sodium sulfite is occasionally used to prevent oxygen corrosion.

Although mill scale removal is not one of the purposes of alkaline cleaning, the addition of chelating agents may remove enough mill scale to eliminate the need for further chemical cleaning. However, where mill scale removal is specifically desired, acid or chelant cleaning should follow alkaline cleaning. Commercial alkaline cleaning products may include chelants and other compounds specifically formulated to provide effective cleaning.

Alkaline cleaning should follow procedures that boiler manufacturers furnish for their specific boilers. During cleaning, boilers are fired at a low rate, but not enough to establish positive circulation. Boil-out pressure is usually about half the operating pressure. Several times during the alkaline boil-out, half of the boiler water should be blown down as shown on the gauge glass through the bottom blowdown valves. Alternate valves are used where there is more than one blowdown connection. The boiler is refilled close to the top of the glass after each blow. Superheaters and reheaters are protected by backfilling with a properly treated condensate. Each chemical cleaning stage lasts for approximately 6 to 24 hr.

When alkaline cleaning is completed, the unit is slowly cooled, the alkaline solution is drained to the disposal area, and the unit is flushed with good-quality condensate. Flushing, with intermediate blowdown, should be continued until flush water conductivity is less than 50 mhos and phosphate is less than 1 ppm. Alkaline cleaning should be repeated if organic or residual oil-based contaminants are found upon inspection of the unit.

SOLVENT CLEANING

The choice of solvent should be based on laboratory studies of the deposit sample found inside the tube. This will help ensure that the expected results of the chemical cleaning are achieved at minimum expense and risk to the system.

Inhibited hydrochloric acid is the most commonly used solvent. It is effective for removing most calcium and iron deposits. Hydrofluoric acid or ammonium bifluoride is often added to the hydrochloric acid to aid in the removal of silicate-containing scales. This mixture is also used to accelerate the removal of certain complex scales.

When copper oxide is present in the deposit, it may dissolve and then plate out as metallic copper, causing pitting of the system metal. For this reason, a copper complexing agent such as thiourea is often added to the hydrochloric acid to keep the copper in solution.

Chelating agents, such as EDTA and citric acid, are used to dissolve iron oxide deposits. They can also be used to dissolve deposits containing copper oxides by the injection of an oxidizing agent through the boiler circuits.

In superheaters and the water-steam circuits of once-through supercritical boilers, magnetite and complex scales may be removed by inhibited hydroxyacetic and formic acid, inhibited EDTA, or inhibited ammoniated citrate. Because these materials are highly volatile, they are useful in units that are difficult to fill, circulate, and drain.

After the cleaning, the unit must be drained under a nitrogen blanket and flushed with pure water until it is free of solvent and soluble iron. If a mineral acid solvent is used, a boil-out should follow to repassivate the metal surface. If a chelant is used, oxygen injection into the cleaning solution provides passivation.

Following cleaning, the boiler should be inspected to verify that the expected results have been achieved. Visual inspection of the drums and headers may reveal the accumulation of loose particulate matter, which signifies a need for additional flushing. Video or boroscope inspection of the tubes or cutting of tube samples may reveal the need for further cleaning.

Because of possible harm to personnel and equipment, only qualified personnel should be involved in solvent selection, planning, and supervision of the cleaning.

Chapter 16 - Steam Purity

Precise system control is required for the operation of modern superheated steam turbines. Solids in the steam leaving a boiler can deposit in the superheater and turbines, causing costly damage. For this reason, close control of steam purity is critical.

Steam purity refers to the amount of solid, liquid, or vaporous contamination in the steam. High-purity steam contains very little contamination. Normally, steam purity is reported as the solids content.

Steam purity should not be confused with steam quality. Steam quality is a measure of the amount of moisture in the steam. It is expressed as the weight of dry steam in a mixture of steam and water droplets. For example, steam of 99% quality contains 1% liquid water.

Carryover is any solid, liquid, or vaporous contaminant that leaves a boiler steam drum with the steam. In boilers operating at pressures of less than 2000 psig, entrained boiler water is the most common cause of steam contamination. The entrained boiler water contains dissolved solids and can also contain suspended solids.

There are many causes of boiler water entrainment in steam. A few of the more common mechanisms have been given specific names, such as "spray carryover," "priming," "foaming," and "leakage carryover."

EFFECTS OF CARRYOVER

Boiler water solids carried over with steam form deposits in nonreturn valves, superheaters, and turbine stop and control valves. Carryover can contaminate process streams and affect product quality. [Deposition in superheaters can lead to failure due to overheating and corrosion, as shown in Figure 16-1.](#)

Superheated steam turbines are particularly prone to damage by carryover. Sticking of governor and stop valves due to deposits can cause turbine overspeed and catastrophic damage. Solid particles in steam can erode turbine parts, while deposition on turbine blades can reduce efficiency and capacity. Losses of 5% in turbine efficiency and 20% in turbine capacity have occurred due to deposition. When large slugs of boiler water carry over with steam, the resulting thermal and mechanical shock can cause severe damage.

Loss of production may result from reduced capacity or equipment failure caused by carryover. In some instances, the effect of carryover on production overshadows all other considerations.

Steam can be contaminated with solids even where carryover is not occurring. Contaminated spray attemperating water, used to control superheated steam temperature at the turbine inlet, can introduce solids into steam. [A heat exchanger coil may be placed in the boiler mud drum \(Figure 16-2\) to provide attemperation of the superheated steam.](#) Because the mud drum is at a higher pressure than superheated steam, contamination will occur if leaks develop in the coil. Failure to check for these possible sources of contamination may necessitate time-consuming steam purity studies.

CAUSES OF CARRYOVER

Carryover results from incomplete separation of steam from the steam-water mixture in a boiler. Many factors, both mechanical and chemical, contribute to incomplete separation. Mechanical

factors include boiler design, inadequate or leaking separating equipment, high water levels, method of firing, and load characteristics.

Among the chemical causes are high total solids concentrations (dissolved and/or suspended solids), excessive alkalinity, and the presence of oily materials and other organic contaminants.

Methods of external and internal treatment can also affect steam purity. In certain instances, vaporization of solids may occur-another form of chemical carryover.

Mechanical Causes

In the modern water-tube boiler, separation of the steam-water mixture entering a relatively small steam drum is a complex process. For every pound of steam generated, as many as 15-20 lb of water may circulate through a drum. As a result, 99.97% or more of the circulating water must be removed from steam to ensure the desired steam purity.

Boiler Design. Certain types of boilers are known for their ability to produce clean steam constantly; other types are traditionally recognized as troublesome. Factors that affect carryover include design pressure, steam drum size, design generating rate, circulation rate, arrangement of downcomers and risers, and the type of mechanical separating equipment used.

In some older boiler designs, the steam-carrying or riser tubes discharge below the water level, causing severe turbulence within the steam drum. This condition is minimal for units in which the steam generating tubes discharge above the working water level or beneath a baffle that separates them from the drum water.

The use of suitable steam separation equipment also effectively prevents severe steam contamination. However, these devices impose a small pressure drop. Therefore, if any leaks occur in this equipment, leakage carryover occurs.

Operating Conditions. Operation at loads in excess of design rating can increase carryover. Sudden increases in load (e.g., when a safety valve blows or when soot blowing begins) also promote carryover.

Sudden increases in process steam demand may lower the steam header pressure and, in turn, the boiler drum pressure, causing rapid expansion of steam-water mixture in the boiler. This can significantly raise the drum water level and cause carryover. Sudden changes in boiler operation should be avoided as much as possible. In a plant with more than one boiler in operation, the boiler most susceptible to carryover should be operated at a safe, constant load while others are used to accommodate load swings.

High water levels in the steam drum reduce deentrainment space, increasing carryover.

Chemical Causes

Foaming. Foaming and selective vaporous carryover are the two basic mechanisms of chemical carryover. Foaming is the formation of stable bubbles in boiler water. Because bubbles have a density approaching that of steam, they are not readily removed by steam purifying equipment. Foaming has caused a variety of carryover problems and can cause erroneous water level readings that produce swings in feedwater flow.

Foaming tendencies of boiler water are increased with increases in alkalinity and solids content. Boiler water solids have a dual effect on carryover. First, for a given boiler and static

operating conditions, high solids in the boiler water result in high solids in each drop of boiler water carried over. Second, foaming potential increases with increasing boiler water solids. If boiler water solids are allowed to double (without any foaming), carryover will be doubled. If the higher solids cause foaming, the carryover may be increased even more.

Organic and Synthetic Contamination. Oil and other organic contaminants in boiler water can cause severe carryover conditions. The alkalinity of the boiler water saponifies fatty acids, producing a crude soap that causes foaming.

Conventional mineral analysis of water does not reveal the foaming tendencies originating from organic contamination. Even determination of the organic content of the water does not necessarily provide this information, because many surface supplies from heavily wooded areas contain a relatively high concentration of harmless or beneficial lignin-type organics.

Wastes discharged into many surface water supplies contain synthetic detergents and wetting agents. Contamination of surface supplies by these agents has caused difficulty with boiler foaming.

Selective Vaporous Carryover. Selective vaporous carryover occurs as a result of variances in the solvent properties of steam for different water phase impurities. Boiler water salts, such as sodium sulfate, sodium chloride, sodium hydroxide, and sodium phosphate, are soluble in water and (to varying degrees) in steam. However, the solubility of these salts in steam is low and is usually not a problem when boiler pressure is less than 2400 psig.

Selective vaporous carryover of silica can occur at pressures as low as 400 psig. However, silica vaporization is not usually a problem below 900 psig.

PREVENTION OF CARRYOVER

Carryover can never be eliminated completely. Even the best boiler designs operating with well controlled water chemistry produce trace amounts (0.001-0.01 ppm total solids) of carryover. However, the primary consideration in the selection of a boiler and its operating conditions is the amount of carryover that can be tolerated.

Whenever superheated steam is required for process use or turbines, steam purity as low as 10-30 ppb total solids may be necessary to prevent deposits. These limits apply to most industrial applications within a pressure range of 300-1500 psig, to ensure uninterrupted service of superheaters and turbines.

Although boiler manufacturers do not ordinarily guarantee less than 0.03% carryover, purity levels well below this level are routinely achieved in many systems. To obtain the desired steam purity, both the boiler designer and the operator must carefully select system equipment and operating conditions. The methods used to achieve the required steam purity can be divided into mechanical and chemical means of carryover prevention.

Mechanical Separation

Low-capacity, low-pressure boilers (usually fire-tube boilers) rely principally on simple gravity separation of steam and water. At 200 psig and saturation conditions, the density of water is 115 times greater than that of steam. Because the steam is typically used for heating, steam purity requirements are not very stringent. [The installation of a dry pipe near the top of the drum \(Figure 16-3\) to enhance steam-water separation is normally satisfactory.](#)

To meet the needs of superheated steam turbines, steam purity requirements become more stringent at higher boiler pressure. In these applications, the density difference between water and steam decreases rapidly. At 1000 psig, water density is only 20 times that of steam. In comparison with low-pressure boilers, the separating force is reduced by 83%, making entrainment possible at relatively low steam velocities. The cost of a drum adequately sized to separate steam and water at this higher pressure by gravity alone is prohibitive.

Internal mechanical separating devices may be installed to allow the use of economical drum sizes at higher pressures. These devices are classified into two categories: primary separators and secondary separators.

Primary Separation. Primary separation of steam and boiler water is secured by changes in direction of flow. In this method, the difference in density between water and steam is used as the means of separation. [The major separation is effected by primary devices \(such as baffle plates\), which also reduce turbulence and the steam content of recirculating boiler water \(Figure 16-4\).](#) Any appreciable amount of steam in a downcomer circuit (carryunder) reduces the head available for circulation, thereby lowering the boiler circulation rate. In addition, errors in water level indication caused by the presence of steam in the drum water are reduced.

[Figure 16-5 shows an installation of centrifugal primary separators in a boiler drum.](#) Steam and water from the risers enter the separator tangentially. Water moves downward in a long helical path on the inside wall of the cylinder, and steam spirals upward. Centrifugal force on the mixture whirling around the cylinder helps to separate steam from water.

Secondary Separation. Also termed "steam scrubbing" or "steam drying," secondary separation is used to separate small amounts of moisture from large amounts of steam. Steam flow is directed in a frequently reversing pattern through a large contact surface. A mist of boiler water collects on the surface and is drained from the separating unit.

Closely fitted screens or corrugated plates are normally used. Steam velocity is kept to a low level to prevent reentrainment of separated boiler water and to ensure maximum surface contact. [Figure 16-6 depicts a typical arrangement of primary separators and steam scrubbers in a boiler steam drum. Figure 16-7 shows a steam drum with typical steam purity equipment.](#)

Although steam separation is usually performed in a steam drum, external separating devices are also available. They are usually centrifugal separators, similar to those used for primary separation in many boilers. They are particularly useful where only a portion of the steam production must be purified for a single application. In some instances, the cost of external purification may be lower than that of modifying boiler drum internals to improve steam purity.

Chemical Control

The principal chemical factors that cause carryover are the concentrations of total dissolved solids, alkalinity, silica, and organic contaminants in the boiler water.

[The American Boiler Manufacturers Association \(ABMA\) recommendations for boiler water limits are provided in Table 16-1.](#) These guidelines should not be considered absolute. Some systems cannot tolerate operation at these concentrations; others operate continuously at significantly higher concentrations.

Operating conditions also have an effect. It is difficult to predict the maximum boiler water solids that can be tolerated without significant carryover under most operating conditions. The

maximum specific limits for a set of operating conditions can be established only after a steam purity study has been conducted for those conditions.

Whenever carryover is being caused by excessive boiler water concentrations, an increase in boiler blowdown rate is normally the simplest and most expedient solution. When high concentrations are caused by high levels of feedwater impurities, adjustment or upgrading of the external treatment may provide the most economical solution.

Because various suspended solids and organic matter in boiler feedwater have different effects on carryover, no generalization of their permissible concentration can be made. Concentrations should be kept as close to zero as possible. No method of internal treatment can be relied on to overcome carryover problems caused by oil and other organics. In order to prevent the carryover difficulties caused by these contaminants, they must be removed from the boiler feedwater.

The organic compounds and blends used as boiler water and condensate treatment chemicals are selected on the basis of two factors:

- the ability to prevent deposition, corrosion, and carryover, as well as condensate system corrosion
- low tendency to cause foaming in the boiler water

Steam Purity Studies. The design of modern steam turbines is such that the tolerance for steam impurities is very low. There is an ever-increasing demand not only for higher steam purity, but also for techniques to measure impurities at very low levels. The sodium tracer and cation conductivity techniques are commonly used to detect impurities in the parts per billion range.

Carryover can be a serious steam plant problem, and frequently the cause of steam contamination can be determined only through extensive studies employing sensitive sampling and testing techniques. A water treatment engineer, through proper use of these tools, is able to help plant operators obtain maximum steam purity with minimum blowdown while maintaining clean boiler waterside surfaces.

Antifoam Agents. Frequently, the cause of a carryover problem cannot be economically corrected through adjustment of boiler water balances or installation of additional external treatment facilities. [In many of these instances, the use of an effective antifoam agent can reduce carryover tendencies significantly \(see Figure 16-8\).](#)

The primary purpose of antifoam application is the generation of high-purity steam. However, antifoam agents also contribute to reduced blowdown requirements. Antifoam feed allows boiler water concentrations to be carried at much higher values without compromising steam purity.

Chapter 17 - Measurement Of Steam Purity

Accurate measurement of steam purity is essential to identifying the cause of potential or existing steam purity problems in modern boiler plants. One reason for this is that superheated steam turbines have an extremely low tolerance for solids contamination in the steam. Fortunately, techniques are available to determine steam contamination in the parts per billion range to satisfy the demands of most systems. The test results make it possible to determine the effect of changing boiler operation on steam purity.

IMPURITIES

Impurities present in steam can be solid, liquid, or gaseous. Solids are usually dissolved in water droplets or are present as dust. Because water treatment practices are such that most soluble chemical constituents of boiler feedwater are converted to sodium salts, most solids present in steam are sodium salts, with minor amounts of calcium, magnesium, iron, and copper also present.

Gaseous constituents commonly found in low-pressure steam (less than 2000 psig) are ammonia, carbon dioxide, nitrogen, amines, and silica. Of these, only silica contributes to the difficulties commonly associated with impure steam; the other constituents are of concern only where they interfere with the measurement of steam purity.

METHODS OF STEAM PURITY MEASUREMENT

Several methods of measuring steam purity have been available and used for many years. Each offers its own distinct advantages.

Specific Conductance

Specific conductance is one of the most commonly used methods. The specific conductance of a sample, measured in microsiemens (μS) or micromhos (μmho), is proportional to the concentration of ions in the sample. When boiler water is carried over in steam, the dissolved solids content of the boiler water contaminates the steam, and steam sample conductivity increases. Measurement of this increase provides a rapid and reasonably accurate method for determining steam purity.

One of the disadvantages of using specific conductance is that some gases common to steam (such as carbon dioxide and ammonia) ionize in water solution. Even at extremely low concentrations, they interfere with measurement of dissolved solids by increasing conductivity. This interference can be appreciable in a high-purity steam sample.

For example, in a sample containing less than 1 ppm dissolved solids, specific conductance may be in the range of 1.0-2.0 μS . The presence of any ammonia or carbon dioxide in this sample significantly increases the conductance reading:

- ammonia by 8.0-9.0 μS per ppm of ammonia
- carbon dioxide by 5.0 μS per ppm of carbon dioxide

Neither of these gases is a dissolved solid. In order to obtain a proper measure of dissolved solids, the influence of each gas must be determined, and conductivity readings must be corrected for their presence. When the ammonia and carbon dioxide contents of the sample are known, accurate conductivity correction curves may be obtained to allow proper corrections to be made.

Equipment is available to degas a sample prior to measurement of conductance. Hydrogen-form cation exchange resin columns are used to reduce ammonia and amines to negligible levels. Cation conductivity analyzers apply this technology to detect acid-producing anions, such as chlorides, sulfates, and acetates. They also take advantage of the high conductance of solutions containing hydrogen ions. [These solutions have a conductivity several times greater than that of a solution with an equal concentration of ions formed by a neutral salt \(Figure 17-1\).](#)

[In a Larson-Lane analyzer \(Figure 17-2\), a condensed steam sample is passed through a hydrogen-form cation exchange resin column.](#) This resin column removes ammonia, amines, and sodium hydroxide from the sample. The sample then flows through a reboiler, which removes carbon dioxide. Conductivity is measured after this process and may also be measured at the analyzer inlet and ion exchange column outlet. When conductivity is measured at all three points, a fairly complete picture of steam composition is provided.

Sodium Tracer Technique

Another commonly used method for measuring steam purity is the sodium tracer technique. This technique is based on the fact that the ratio of total solids to sodium in the steam is the same as the ratio of total solids to sodium in the boiler water for all but the highest-pressure (greater than 2400 psig) boiler systems. Therefore, when the boiler water total solids to sodium ratio is known, the total solids in the steam can be accurately assessed by measurement of sodium content. Because sodium constitutes approximately one-third of the total solids in most boiler waters and can be accurately measured at extremely low concentrations, this method of steam purity testing has been very useful in a large number of plants.

Sodium Ion Analyzer. [The instrument most frequently used for sodium measurement is the sodium ion analyzer \(Figure 17-3\).](#) A selective ion electrode similar to a pH electrode is used to measure the sodium content of the steam sample.

In typical operation, a regulated amount of an agent such as ammonium hydroxide is added to a regulated amount of condensed steam sample to raise pH and eliminate the possibility of hydrogen ion interference. A reservoir stores the conditioned sample and feeds it at a constant flow rate to the tip of the sodium ion electrode and then to a reference electrode. The measured electrode signal is compared to the reference electrode potential and translated into sodium ion concentration, which is displayed on a meter and supplied to a recording device.

Good results have been reported with various sodium ion analyzers. According to the manufacturers, the instruments operate in a concentration range of 0.1 ppb to 100,000 ppm of sodium ion with a sensitivity of 0.1 ppb. Recalibrated on a weekly basis, these instruments are valuable for continuous, long-term testing and monitoring.

The acceptance of the sodium ion analyzer as an accurate, reliable steam purity evaluation instrument is evidenced by its widespread use for continuous monitoring as well as for field

testing. Many steam generating plants have switched from previously accepted methods to sodium ion analysis in order to improve accuracy.

Although sodium ion analyzers measure total contamination, they do not show rapid changes in sodium concentration. This is due to a lag in electrode response and the dilution effect of the reservoir, which dampens sharp, momentary changes in conditions. Because of this, peaks that exceed boiler guarantee limits or a known carryover range may not show up on the analyzer.

This would affect interpretation of test results.

Flame emission spectroscopy and flame spectrophotometer testing. Flame spectrophotometer testing is much more sensitive to quick changes in operating conditions and detects peaks in solids concentration. Flame emission spectroscopy also provides accurate measurement in the low parts per billion range despite quick variations. Neither method is suitable for continuous, unattended monitoring.

Interpretation of Sodium Test Results. The exact ratio of sodium to dissolved solids in the boiler water and consequently in the steam can be determined for each plant but is approximately 1:3 for most plants (i.e., for each 0.1 ppm of sodium in the steam there is approximately 0.3 ppm of dissolved solids present).

Initially, the use of the sodium tracer technique for steam purity evaluation required collecting sample bottles and transporting them to the laboratory for analysis. This technique is still a valuable tool for steam purity measurement. Samples are gathered in special laboratory-prepared, polyethylene bottles, and care is taken to protect against contamination.

In the preferred sampling procedure, three or four samples are drawn within a 15-minute period to ensure representative sampling. If there are excess solids in the steam, the bottle samples are used to define the range of the problem before implementation of an in-plant study with continuous analyzers. Bottle samples can also be used to monitor steam purity on a periodic basis.

Experience has shown that solids levels as low as 0.003 ppm can be measured with either shipped bottle samples or in-plant testing.

Anion Analysis

Occasionally, it is of interest to determine the amount of anions (chlorides, sulfates, acetates, etc.) in the steam. Degassed cation conductivity provides a measure of the total anion concentration in the sample. In addition, chloride-specific ion electrodes and ion chromatography are used to detect low levels of specific contaminants.

REPRESENTATIVE STEAM SAMPLING

In order to ensure accurate analysis, samples must be truly representative of the steam being generated. When the sampling procedures are not followed properly, the steam purity evaluation is of little or no value.

Sampling nozzles recommended by the ASTM and ASME have been in use for many years. The nozzles have ports spaced in such a way that they sample equal cross sectional areas of the steam line. Instructions for these nozzles can be found in ASTM Standard D 1066, "Standard Method of Sampling Steam" and ASME PTC 19.11. Field steam studies have shown that sampling nozzles of designs other than these often fail to provide a reliable steam sample.

Isokinetic flow is established when steam velocity entering the sampling nozzle is equal to the velocity of the steam in the header. This condition helps to ensure representative sampling for more reliable test results. The isokinetic sampling rate for many nozzles that do not conform to ASME or ASTM specifications cannot be determined.

Accurate sampling of superheated steam presents problems not encountered in saturated steam sampling. The solubility of sodium salts in steam decreases as steam temperature decreases. If a superheated steam sample is gradually cooled as it flows through the sample line, solids deposit on sample line surfaces. To eliminate this problem, the steam can be desuperheated at the sampling point

Chapter 18 - Steam Turbine Deposition, Erosion, And Corrosion

The development of modern, high-efficiency steam turbines has led to an increase in deposition, erosion, and corrosion problems. Close tolerances in the turbines, the use of high-strength steels, and impure steam all contribute to these conditions.

TURBINE DEPOSITION

Although several factors influence the formation of deposits on turbine components, the general effect is the same no matter what the cause. Adherent deposits form in the steam passage, distorting the original shape of turbine nozzles and blades. These deposits, often rough or uneven at the surface, increase resistance to the flow of steam. Distortion of steam passages alters steam velocities and pressure drops, reducing the capacity and efficiency of the turbine. Where conditions are severe, deposits can cause excessive rotor thrust. Uneven deposition can unbalance the turbine rotor, causing vibration problems.

As deposits accumulate on turbine blades, stage pressures increase. [Figure 18-1 shows the effect of gradual deposit buildup on stage pressure](#). The deposits were caused by the use of contaminated water to attemperate the steam. In a fouled condition, this 30-MW turbine lost over 5% of its generating capacity.

Turbine deposits can accumulate in a very short time when steam purity is poor. The turbine shown in [Figure 18-2](#) was forced off-line by deposition only 3 months after it was placed in operation. Carryover of boiler water, resulting from inadequate steam-water separation equipment in the boiler, caused this turbine deposit problem.

The nature of silica deposits found on turbine blades varies greatly. Table 18-1 lists a number of silica compounds that have been identified in various studies of turbine blade deposition. Of these, amorphous silica (SiO_2) is the most prevalent.

Table 18-1. Silicate deposits found in steam turbines.

SiO_2	silica
Na_2SiO_3	sodium silicate
$\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$	sodium metasilicate pentahydrate
$\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$	sodium metasilicate nonahydrate
NaAlSiO_4	sodium aluminum silicate
$\text{Na}_4\text{AlSi}_3\text{O}_{12}(\text{OH})$	sodium aluminum silicate hydroxide
$\text{Na}_4\text{Al}_6\text{SO}_4(\text{SiO}_4)_8$	sodium aluminum sulfate silicate
$\text{NaFeSi}_2\text{O}_6$	sodium iron silicate
$\text{Na}_3[\text{Cl}(\text{AlSiO}_4)_6]$	sodium chlorohexaaluminum silicate
KAlSi_3O_8	potassium aluminum silicate
$\text{KNa}_3(\text{AlSi}_4)_6$	potassium trisodium aluminum silicate
$\text{Mg}_6[(\text{OH})_8\text{Si}_4\text{O}_{10}]$	magnesium octahydrate silicate
$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	magnesium silicate hydrate
$\text{Ca}_2\text{Si}_2\text{O}_4$	calcium silicate
$\text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})$	calcium aluminum silicate hydroxide
$3\text{Al}_2\text{O}_3 \cdot 4\text{Na}_2\text{O} \cdot 6\text{SiO}_2 \cdot \text{SO}_3$	noselite



iron magnesium hydroxide silicate



sodium aluminum molybdenum oxide silicate

Causes of Turbine Deposition

Entrainment. Some mechanical entrainment of minute drops of boiler water in the steam always occurs. When this boiler water carryover is excessive, steam-carried solids produce turbine blade deposits. The accumulations have a composition similar to that of the dissolved solids in the boiler water. Priming and foaming are common causes of high levels of boiler water carryover. Because of the high levels of carryover often encountered, these conditions often lead to superheater tube failures as well.

Attemperating Water Impurity. Turbine deposits are also caused by the use of impure water for steam attemperation and by leakage in closed heat exchangers used for attemperation. If a boiler produces pure steam and turbine deposits still occur, the attemperating system should be investigated as a possible source of contamination. Attemperating water should be of the same purity as the steam. Any chemical treatment in the attemperating water should be volatile.

Vaporization of Boiler Water Salts. Another source of turbine deposition is the vaporization of salts present in boiler water. With the exception of silica, vaporization of boiler water salts is usually not significant at pressures below 2400 psig. Silica can vaporize into the steam at operating pressures as low as 400 psig. This has caused deposition problems in numerous turbines. The solubility of silica in steam increases with increased temperature; therefore, silica becomes more soluble as steam is superheated. As steam is cooled by expansion through the turbine, silica solubility is reduced and deposits are formed, usually where the steam temperature is below that of the boiler water. To minimize this problem, the quantity of silica in the steam must be controlled. Silica deposits are not a problem in most turbines where the silica content in the steam is below 0.02 ppm. Therefore, it has become customary to limit silica to less than 0.02 ppm in the steam. Sometimes, because of the more stringent operating conditions of certain turbines, vendors specify that steam silica be maintained at less than 0.01 ppm.

The conditions under which vaporous silica carryover occurs have been thoroughly investigated and documented. Researchers have found that for any given set of boiler conditions using demineralized or evaporated quality makeup water, silica is distributed between the boiler water and the steam in a definite ratio. This ratio, called the distribution ratio, depends on two factors: boiler pressure and boiler water pH. The value of the ratio increases almost logarithmically with increasing pressure and decreases with increasing pH.

The effect of boiler water pH on the silica distribution ratio becomes greater at higher pH values. A pH increase from 11.3 to 12.1 reduces the ratio by 50%, while a pH increase from 7.8 to 9.0 has no measurable effect. [For any boiler pressure and pH, the distribution ratio for silica can be determined from Figure 18-3.](#) The amount of silica vaporized with the steam can be determined by measurement of boiler water silica. [The proper boiler water silica level necessary to maintain less than 0.02 ppm silica in the steam is shown in Figure 18-4.](#)

When soluble, the silica present in boiler feedwater does not influence the amount of silica present in the steam. When added to boiler water in separate experiments, equivalent quantities of silicic acid and sodium silicate produced the same amount of silica in the steam. Because the amount of silica in the steam is greatly affected by pH, it is likely that silicic acids are involved in the vaporization mechanism.

Silica has a higher solubility in superheated steam than in saturated steam for any given pressure. If mechanical carryover contributes to the silica content of the saturated steam, the silica will be dissolved during superheating, provided that the total silica present does not exceed the solubility of silica in the superheated steam. Therefore, silica deposits are seldom found in superheater sections of a boiler.

After steam reaches a turbine it expands, losing pressure and temperature. As a result, the solubility of the silica decreases. Studies have shown that with a maximum of 0.02 ppm of silica in the steam, a pressure of less than 200 psig is reached in the turbine before silica starts to condense from the steam. Therefore, silica preferentially deposits in the intermediate-pressure and low-pressure sections of the turbine where the specific volume of the steam varies from approximately 1 to 10 ft³/lb. [Solubility data shown in Figure 18-5 helps to explain the distribution of silica deposits in the turbine.](#)

Localized Silica Saturation. Turbine deposits are also formed where localized silica saturation occurs and silica condenses from the steam in those areas of the turbine. Partial evaporation of the precipitated silica can then occur with only a portion of the silica being dissolved by the continuous steam flow. Deposits remain as a result.

Turbine Velocity. Another factor affecting the location of turbine deposits is the velocity in the turbine. Steam flows from the inlet to the outlet of the turbine in only a fraction of a second. Consequently, deposition is shifted downstream from the saturation point by the high steam velocities.

Prevention of Silica Deposits

The most significant factor in minimizing turbine silica deposits is the maintenance of low silica concentrations in the boiler water. External treatment equipment must be operated carefully to limit the amount of silica entering with the makeup water, and the condensate must be monitored to minimize contamination. After silica enters the boiler water, the usual corrective action is to increase boiler blowdown (to decrease the boiler water silica to acceptable levels) and then to correct the condition that caused the silica contamination.

Removal of Deposits

When a turbine becomes fouled with water-soluble salts as a result of boiler water carryover or attemperating water contamination, turbine capacity can often be restored by water washing. Because it can cause severe turbine damage, water washing should be supervised carefully and the recommendations of the turbine vendor should be followed.

When the turbine becomes fouled with compounds that are not water-soluble (including silica), water washing rarely restores capacity. Out-of-service cleaning by blasting with aluminum oxide or other soft grit material is required to remove these deposits.

EROSION

Erosion of turbine blades results in rough, uneven surfaces that alter steam flow paths. This reduces turbine efficiency and can also limit capacity. Erosion at the high-pressure end of a turbine is usually caused by solid particles (usually iron oxide) present in the steam. Iron oxide particles are present if they were not removed by steam blows during system start-up. They can also result from exfoliation of superheater or main steam header oxides or can be introduced into the steam by contaminated attemperating water.

Erosion of intermediate and low-pressure blades is usually caused by water in the steam. Operation below design inlet steam temperature or at low load can cause condensation in these stages, leading to erosion problems.

Carbon dioxide or other acidic species present in the condensate can accelerate the damage. Some protection against erosion-corrosion can be provided by low distribution ratio amines, which neutralize the acidity and elevate the pH of the condensate.

CORROSION

Pitting, corrosion fatigue, and stress corrosion cracking problems all occur in steam turbines. The major corrodents are sodium hydroxide, chloride, sulfate, and sulfides. Usually, the level of contaminants present in steam is not high enough to corrode the system components. As steam expands through a turbine, the solubility of contaminants in the steam decreases. They condense onto surfaces at solution concentrations much higher than the original contaminant concentration in the steam. These concentrated solutions promote system corrosion.

Pitting is commonly associated with chloride deposits and occurs on rotors, disks, and buckets. Pitting attack often occurs when a moist, oxygen-laden atmosphere develops in out-of-service turbines. Damage is most severe when chloride deposits are also present. An oxygen-free or condensate-free atmosphere should be maintained to protect out-of-service turbines from corrosion.

Corrosion fatigue and stress corrosion cracking of blades and disks are commonly associated with sulfides (see Figure 18-6), chlorides, and caustic. The problems are most common in low-pressure sections of large power plant turbines, which are characterized by high stresses, crevices, and operating temperatures conducive to the condensation of concentrated solutions of steam contaminants. Problems also occur in high-pressure sections and smaller industrial-sized turbines, usually when substantial levels of steam contamination occur. These problems can be mitigated by designs that prevent crevices, lower stresses, and/or employ lower-strength materials. It is also important to avoid unnecessary stresses and to maintain high-purity steam during operation.

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Problems caused by iron and copper corrosion in condensate systems are not restricted to piping and equipment damage or to the loss of high-quality water and heat energy when condensate is lost. If returned to the boiler, corrosion products and process chemicals from corrosion-caused leaks contribute to the formation of damaging boiler deposits, boiler carryover, and steam-driven equipment deposits. Their presence reduces system reliability and increases operation and maintenance costs.

CORROSION OF IRON

Iron corrodes in water even in the absence of oxygen. An iron oxide surface acts like a car battery, with the surface divided into microscopic anodes (+) and cathodes (-). In condensate systems, iron acts as an anode so that it is oxidized (i.e., gives its electrons to the cathode).

The cathode in pure water is a proton or hydrogen ion (H^+). When iron metal is oxidized, electrons are passed from the iron surface to hydrogen ions as shown in the reactions below.

Oxidation:



ferrous ion

Reduction:

$2e$

electrons

Overall:

«

The fate of the ferrous ion (Fe^{2+}) depends on condensate temperature, pH, and flow conditions. At low temperatures, Fe^{2+} reacts with water to form insoluble ferrous hydroxide, $Fe(OH)_2$. If the condensate stream velocity is high enough, colloidal $Fe(OH)_2$ is swept into the water and carried downstream to deposit elsewhere. In low-flow areas of the condensate system, $Fe(OH)_2$ deposits near the oxidation site, forming a porous oxide layer.

At temperatures above 120°F the deposited ferrous hydroxide reacts further to form surface-bound magnetite (Fe_3O_4) crystals.

+

At even higher temperatures (above 300°F), Fe^{2+} spontaneously forms magnetite without first forming $Fe(OH)_2$. This magnetite forms a nonporous, tightly adherent layer on the metal surface.

«

In most condensate systems, two or three forms of iron oxide are present. In pure water, a tightly adherent magnetite layer is formed, which is indicative of a well passivated iron surface. In the absence of contaminants, this oxide layer greatly retards any further oxidation reactions.

Oxygen Corrosion of Iron

In the presence of oxygen, the corrosion process described above is modified. Dissolved oxygen replaces hydrogen ions in the reduction reaction. The reactions are as follows:

Oxidation:

Fe^{2+}

ferrous ion

Reduction:

$2e$

electrons

Overall:

$2H^+$

«

hydrogen ion

This reaction occurs more readily than the direct reaction between iron and protons. Therefore, corrosion rates are accelerated in the presence of oxygen.

Two types of corrosion can occur with oxygen present. The first, generalized corrosion on the metal surface, causes a loss of metal from the entire surface. The second, [oxygen pitting \(Figure 19-1\)](#), causes a highly localized loss of metal that results in catastrophic failure in a short time.

Oxygen pitting begins at weak points in the iron oxide film or at sites where the oxide film is damaged. Instead of growing along the metal surface, the corrosion penetrates into the surface, effectively drilling a hole into (or through) the metal.

Pits are active only in the presence of oxygen. There is a visible difference between active and inactive pits. An active oxygen pit contains reduced black oxide along its concave surface, while the surrounding area above the pit is covered with red ferric oxide. If a pit contains red iron oxide, it is no longer active.

Sources of Oxygen. Oxygen usually enters the condensate by direct absorption of air. It can also flash over with the steam when the feedwater contains oxygen. With effective mechanical deaeration and chemical oxygen scavenging, all but a trace of oxygen is eliminated from boiler feedwater, so this source is not significant in most systems.

In a good system design, the air-condensate contact is minimized to prevent oxygen absorption. The condensate receiving tank can be designed with a cover to reduce air contact and a steam heating coil within the tank to elevate condensate temperature and thereby reduce oxygen solubility.

Under certain conditions, gross oxygen contamination of the condensate may be unavoidable. For example, condensate from warm-up steam for equipment used only intermittently should not be saved. Its dissolved oxygen attacks systems between the point of condensation and the deaerating heater. This contaminated condensate can return large amounts of corrosion products to the boiler.

In most cases, proper feedwater deaeration and elimination of air infiltration into the condensate substantially reduce oxygen corrosion.

CORROSION OF COPPER

Although copper is similar to iron in chemistry, the form of the resulting oxide layer is very different. Both copper and iron are oxidized in the presence of hydrogen ions and oxygen and can undergo oxygen pitting.

«

CU

or in alkaline solution:

«

Iron forms intact oxide layers. The oxide layers formed by copper and its alloys are porous and "leaky," allowing water, oxygen, and copper ions to move to and from the metal surface (Figure 19-2).

The rate of movement is controlled by the copper oxide film thickness. As the oxide layer grows in thickness, the copper oxidation rate is slowed. As the oxide layer becomes thicker, the outer layers begin to slough off as particles of copper oxide. The resulting oxide layer is a much more dynamic system than that of iron. Soluble copper ions and particulate copper oxides are also formed by the normal oxidation processes.

EFFECT OF pH ON CORROSION OF IRON AND COPPER

The stability of the passivating iron or copper oxide layer is critically dependent on condensate pH. Any contaminants in the condensate system that cause the pH to decrease cause dissolution of the oxide layer and increased corrosion.

Carbon dioxide (CO₂) is the primary cause of decreased condensate pH. Carbon dioxide enters the system with air leaking into the condenser or from decomposition of feedwater alkalinity. Although part of the feedwater alkalinity is removed by a properly operated deaerating heater, most is converted to CO₂ in the boiler and released into the steam.

In boilers, carbon dioxide is liberated as shown by the following reactions:



+

sodium carbonate

«

The first reaction proceeds to completion while the second is only (approximately) 80% completed. The net results are release of 0.79 ppm of carbon dioxide for each part per million of sodium bicarbonate as CaCO₃ and 0.35 ppm of carbon dioxide for each part per million of sodium carbonate as CaCO₃.

As the steam is condensed, carbon dioxide dis-solves in water and depresses the pH by increasing the hydrogen ion concentration as shown in the following reaction sequence:



water



+

hydrogen ion



hydrogen ion

Carbonic acid promotes the iron corrosion re-action by supplying a reactant, H^+ . The overall reaction is:



iron

Low pH causes a generalized loss of metal rather than the localized pitting caused by oxygen corrosion. Pipe walls are thinned, particularly in the bottom of the pipe. [This thinning often leads to failures, especially at threaded sections \(Figure 19-3\).](#)

In order to reduce low pH-induced condensate system corrosion, it is necessary to lower the concentration of acidic contaminants in the condensate. Feedwater alkalinity can be reduced by means of various external treatment methods. Less feedwater alkalinity means less carbon dioxide in the steam and condensate. Venting at certain points of condensation can also be effective in removing carbon dioxide.

EFFECT OF OTHER CONTAMINANTS

Other contaminants in the condensate system can affect corrosion rates of iron and copper even when the pH is correctly maintained. By complexing and dissolving iron and copper oxides, contaminants such as chloride, sulfide, acetate, and ammonia (for copper) can dissolve part or all of the oxide layer.

Ammonia is the most common contaminant and is usually present in low concentrations.

Ammonia contamination is usually caused by the breakdown of nitrogenous organic contaminants, hydrazine, or amine treatment chemicals. Sometimes, ammonia is fed to control condensate pH. In these systems, [ammonia feed rates must be carefully controlled to minimize the attack of any copper-bearing alloys \(Figure 19-4\).](#)

CHEMICAL TREATMENT OF CONDENSATE SYSTEMS

Condensate systems can be chemically treated to reduce metal corrosion. Treatment chemicals include neutralizing amines, filming amines, and oxygen scavenger-metal passivators.

Neutralizing Amines

Neutralizing amines are used to neutralize the acid (H^+) generated by the dissolution of carbon dioxide or other acidic process contaminants in the condensate. These amines hydrolyze when added to water and generate the hydroxide ions required for neutralization:

«

The overall neutralization reaction can be written as shown:



«

carbonic acid

By regulating the neutralizing amine feed rate, the condensate pH can be elevated to within a desired range (e.g., 8.8-9.2 for a mixed copper-iron condensate system).

Many amines are used for condensate acid neutralization and pH elevation. The ability of any amine to protect a system effectively depends on the neutralizing capacity, recycle ratio and recovery ratio, basicity, distribution ratio, and thermal stability of the particular amine.

Neutralizing Capacity. Neutralizing capacity is the concentration of acidic contaminants that is neutralized by a given concentration of amine. The neutralizing capacity of an amine is inversely proportional to molecular weight (i.e., lower molecular weight yields higher neutralizing capacity) and directly proportional to the number of amine groups. Neutralizing capacity is important in treating systems with high-alkalinity feedwater. Table 19-1 provides a measure of the neutralizing capacity of commonly employed amines. Neutralizing capacity is not the only measure of a required product feed rate.

Table 19-1. Relative neutralizing capacities

Amine	ppm Neutralizing Amine/ppm CO ₂
Cyclohexylamine	2.3
Morpholine	2.0
Diethylaminoethanol	2.6
Dimethyisopropanolamine	2.3

Recycle Ratio and Recovery Ratio. In determining product feed rates, recycle and recovery ratio are important factors. In Figure 19-5, the recycle factor is the concentration of amine at point x divided by the amine feed rate at point z. Because some amine is returned with the condensate, the total amine in the system is greater than the amount being fed. Recovery ratio is a measure of the amount of amine being returned with the condensate. It is calculated as the amine concentration at site y divided by the amine concentration at site z.

Basicity. An amine's ability to boost pH after neutralizing all of the acid species is termed "basicity." In chemical terms, it is a measure of an amine's ability to hydrolyze in pure water. The dissociation constant K_b is a common measure of basicity.

$$K_b = \frac{[R-NH_3^+][OH]}{[R-NH_2]}$$

As the value of K_b increases, more OH is formed (after all of the acid has been neutralized) and pH increases.

Examples of neutralizing amine K_b values at various temperatures are provided in Table 19-2.

Table 19-2. Relative basicity

Amine	Relative Basicity $K_b \times 10^6$		
	72 °F	298 °F	338 °F
Cyclohexylamine	489	61	32
Morpholine	3.4	4.9	3.8
Diethylaminoethanol	68	11.3	9.2
Dimethybispropanolamine	20.6	6.9	4.6

Distribution of Amines between Steam and Liquid. In condensate systems, the distribution of amines between steam and liquid phases is as significant as basicity or neutralizing capacity. As the steam condenses, acidic contaminants can either remain in the steam or dissolve in the liquid phase. Some contaminants, such as carbon dioxide, stay mainly in the steam phase while others, such as hydrochloric acid, go largely into the liquid phase.

Neutralizing amines must be chosen according to their distribution characteristics to "chase" acidic contaminants. This choice must be tailored to the condensate system and the process contaminants.

For example, morpholine is an amine that primarily distributes into the liquid phase. If this amine is fed into a CO_2 laden steam system with three consecutive condensation sites, it will go into the liquid phase at the first condensation site while most of the carbon dioxide remains in the steam. With a high concentration of morpholine, the liquid phase has a high pH. At the next condensation site, the concentration of morpholine is lower, so the condensate pH is lower. At the last condensation site, where the remaining steam is condensed, little morpholine is left but most of the CO_2 is still present. The high CO_2 concentration depresses the pH, promoting acidic attack of the metal oxide layers.

An amine that is more likely to distribute into the steam, such as cyclohexylamine, is a better choice for the system described above. However, amines with a high tendency to distribute into the steam are not always the best choice.

For example, if cyclohexylamine is used in a second condensate system with two consecutive condensation sites having acetic acid as a contaminant, most of the acetic acid goes into the liquid phase at the first condensation site, while most of the cyclohexylamine remains in the steam. This results in low pH in the first condensation site liquid phase. At the second site, where total condensation takes place, the pH is high. A morpholine-cyclohexylamine blend is a better choice for this system.

In practice, the best protection is provided by blended products containing a variety of amines with differing steam/liquid distributions.

To compare the relative steam/liquid distribution of amines, the distribution ratio (DR) is traditionally used. The distribution ratio of an amine is:

$$\text{DR} = \frac{\text{amine in vapor phase}}{\text{amine in liquid phase}}$$

Amines with a DR greater than 1.0 produce a higher concentration of amine in the vapor phase than in the liquid phase. Conversely, amines with a distribution ratio less than 1.0 produce a higher concentration of amine in the liquid phase than in the vapor phase.

[Distribution ratios are not true physical constants but are a function of pressure \(Figure 19-6\) and pH.](#) The effect of temperature and pH of the condensation site must also be considered. In a complex condensate system, the distribution of chemicals between different condensation sites is difficult to estimate without the use of computer modeling packages specifically designed for this purpose.

Thermal Stability. All organic chemicals exposed to a high-temperature, alkaline, aqueous environment eventually degrade to some degree. Most amines eventually degrade to carbon dioxide and/or acetic acid and ammonia. The time required varies greatly with different amines. The most stable amines commonly used are morpholine and cyclohexylamine. These remain substantially intact at pressures up to 2500 psig.

Quantity. The quantity of neutralizing amine required depends on the carbon dioxide content of the condensate at specific locations and the degree of corrosion protection desired. Complete neutralization is achieved if the condensate pH in all portions of the system is above 8.3. From a practical standpoint, it is necessary to establish a pH control range that provides the desired protection for the most critical system components.

The degree of protection can be monitored by various means. Corrosion test specimens installed in bypass racks, corrosion product analyses, corrosion rate meters, and submicron corrosion product filtration are some of the effective monitoring tools that may be employed.

The behavior of amine bicarbonate in the deaerator affects amine requirements for the system.

Although they are soluble in most cases, amine bicarbonates remain associated in the condensate. In an ideal situation, the amine bicarbonate entering the deaerator breaks down with subsequent venting of carbon dioxide to the atmosphere and recirculation of the amine back to the boiler. Actual behavior involves some loss of amine additive and some recirculation

of carbon dioxide. The amounts of lost amine and retained carbon dioxide are a function of the amine bicarbonate stability in the deaerator.

Filming Amines

Another approach to controlling condensate system corrosion is the use of chemicals that form a protective film on metal surfaces (Figure 19-7). This approach has come into widespread use with the development of suitable products containing long-chain nitrogenous materials.

Filming amines protect against oxygen and carbon dioxide corrosion by replacing the loose oxide scale on metal surfaces with a very thin amine film barrier. During the period of initial film formation, old, loosely adherent corrosion products are lifted off the metal surface due to the surfactant properties of the amine. The metal is cleansed of oxides, which normally cling very tightly and can build up over long periods of time. Excessive initial filming amine treatment of old, untreated or poorly treated condensate systems can cause large amounts of iron oxide to be sloughed off, plugging traps and return lines. Therefore, treatment must be increased gradually for old systems.

When contaminants are present in the condensate, filming amines have a tendency to form deposits by reacting with multivalent ions, such as sulfate, hardness, and iron. Overfeed of filming amines and excessive oxygen contamination can also contribute to deposit formation.

For maximum efficiency, filming amines should be fed directly to the steam header.

Advances have been made in formulating filming amine treatments. Straight filming amines containing one ingredient, such as octadecylamine, are effective but often fail to cover the entire system and can produce fouling. Emulsifiers and, in some cases, small amounts of neutralizing amines can be added to improve film distribution by providing more uniform coverage. This increases system protection and reduces the fouling potential. Application experience has shown that combination amines (filming and neutralizing amines with dispersant aids) provide a superior film bond, reduce deposit problems, and provide better system coverage and thus provide more complete and economical corrosion protection (Figure 19-8).

The feed of filming amines is usually based on steam throughput. Different levels of treatment are required, depending on the particular blend in use. As in the case of neutralizing amines, various methods are used to monitor the effectiveness of the treatment, including corrosion test specimens installed in bypass coupon racks (Figure 19-9), iron analyses, corrosion rate meters, and submicron corrosion product filtration.

Oxygen Scavenging and Metal Passivation

Where oxygen invades the condensate system, corrosion of iron and copper-bearing components can be overcome through proper pH control and the injection of an oxygen scavenger.

One important factor to consider in choosing an oxygen scavenger for condensate treatment is its reactivity with oxygen at the temperature and pH of the system. A scavenger that removes oxygen rapidly provides the best protection for the condensate metallurgy. Hydroquinone has been shown to be particularly effective for most systems.

Like those of neutralizing amines, the steam/liquid distribution of each scavenger has a unique temperature dependence. Some scavengers, such as ascorbic acid and hydrazine, have a very

low volatility. Therefore, it is necessary to feed them close to a problem area. An example of this is the injection of hydrazine to the exhaust of a turbine to protect the condenser. Other scavengers, such as hydroquinone, are relatively volatile and can be fed well upstream of a problem area.

The use of neutralizing amines in conjunction with an oxygen scavenger/metal passivator improves corrosion control in two ways. First, because any acidic species present is neutralized and pH is increased, the condensate becomes less corrosive. Second, most oxygen scavenger/passivators react more rapidly at the mildly alkaline conditions maintained by the amine than at lower pH levels. For these reasons, this combination treatment is gaining wide acceptance, particularly for the treatment of condensate systems that are contaminated by oxygen.

Chapter 20 - Fireside Preboiler Systems

The heart of any boiler is its fuel system. Fuel handling and storage problems can limit the efficiency of the entire boiler.

There are three forms of boiler fuel: liquid, solid, and gas. Methods of handling and storage vary according to the type of fuel used.

GASEOUS FUELS

Clean and relatively moisture-free gaseous fuels present little difficulty in handling. Natural gas is a prime example of clean fuel and is the one most commonly used in boiler systems.

Dirty gas, such as refinery gas, blast furnace gas, carbon monoxide gas, and other waste gases from processes, can cause significant handling problems. Special measures must be taken to prevent escape to the surrounding atmosphere, fire, fuel line deposition, moisture, and incomplete combustion. The severity of the problem depends on the specific contaminants in the gas. Methods of handling are selected according to the nature of the specific gas and local regulations.

Wet scrubbers, electrostatic precipitators, chemical dispersants, and suitable pipe and tank lagging may be used to eliminate problems. Wet scrubbers and electrostatic precipitators remove contaminants mechanically. Chemical dispersants have been used in conjunction with wet scrubbers and electrostatic precipitators to handle troublesome contaminants. Because leakage is one of the major concerns in handling gases, some method of leak detection is essential. The selected method may be as simple as detector-type sprays or as sophisticated as combustible detectors with alarms, which may be connected to automatic fire control systems.

SOLID FUELS

Solid fuels (including coal, wood, and solid waste) present some of the same handling difficulties. Problems occur unless a free-flowing, continuous supply of fuel that is properly sized for the specific type of combustion equipment is provided. The problems include sizing, shredding or pulverizing, consistency of moisture content, freezing or lumping, dusting, fires in storage due to spontaneous combustion, and fires in the feed or ash handling systems.

Most problems can be minimized or eliminated through proper selection of fuel handling equipment. Specific types of equipment for handling, storage, and preparation depend on the characteristics of the solid fuel used.

Because the proper equipment is not always available, fuel additives or aids have been used in the attempt to minimize problems. These additives include grinding aids, moisture improvers, dusting aids, freezing inhibitors, and catalysts to minimize combustibles in ash and fly ash handling systems.

LIQUID FUELS

Liquid fuels include waste oils, light oils, heavy oils, and other combustible liquids. Because of the problems of liquid residue disposal, an increasing variety of combustible liquids is being considered and tested. Figures 20-1 and 20-2 illustrate key components found in a typical [liquid fuel handling system](#) and [fuel oil storage system](#), respectively.

Problems encountered in the handling, storage, and preparation of liquid fuels include water contamination, sludge formation, resistance to flow, biological growths, instability, and corrosive-ness. Generally, these conditions are manifested as excessive strainer plugging, poor flow, increased loading on the fuel pump, heater deposits, fuel line deposits, loss of storage space, burner tip deposits, burner fouling, leakage due to storage tank corrosion, poor atomization, and other combustion problems. Table 20-1 summarizes the nature and cause of problems associated with key liquid fuel handling system components; some of these conditions are illustrated in [Figures 20-3 - 20-4](#) and [20-5 - 20-6](#).

Table 20-1. Preboiler problems and their causes.

Location	Problem	Cause
Storage Tank	sludge reduces available volume of fuel oil storage	sludge may have resulted from more than 7 days' storage or from using several oil sources
Suction Strainers	frequent cleaning necessary	sludge is being carried over from storage tank
	loss of oil pump suction plugging	sludge is being carried over from storage tank
Oil heater	loss of oil temperature varying oil temperature	sludge is being carried over from storage tank; oil has become polymerized
	poor atomization	
	distorted flame patterns	
Burner	reduced maximum load frequent cleaning necessary	high oil viscosity; sludge is being carried over from storage tank; high burner temperature; water in oil
	difficulty cleaning burner	
	oil flow discontinuity	

WATER

Water can become emulsified in oil during processing and can also be introduced into oil during handling by condensation, contamination, or leakage. The presence of water can lead to many problems:

water that separates from oil is generally acidic and can readily corrode storage tanks, particularly at the oil/water interface

separated water occupies useful storage space

water at the burner can cause oil flow discontinuity

if it enters the firing system in sufficient quantity, water may cause thermal shock, leading to refractory damage

Most water can be eliminated by means of careful shipping and handling procedures. Proper design and maintenance of equipment can also minimize water leaks, such as those resulting from steam heater or tank leaks. To minimize condensation, proper lagging and heating of the tank are necessary.

Properly selected additives can be used to emulsify small amounts of water (up to approximately 1%) economically. Large quantities of water should be removed physically from the tank by draining or pumping. When large amounts of water are detected, the source should be identified and corrected.

Water in storage tanks can be detected by means of a Bacon Bomb. This device is lowered into a tank and opened to allow sampling at any point beneath the surface. The sample can then be evaluated by testing for bottom sediment and water (BS&W). Testing for water can be as simple as waiting for the sample to settle in a graduate.

SLUDGE

Sludge is composed of settled heavy agglomerates combined with suspended matter from an oil or liquid fuel. Sludge formation increases when fuel oils of different crudes or liquid fuels of different sources are mixed. When fuel oils are heated in a tank to ensure good flow, the likelihood of sludge formation is increased. If the heat is high enough to break the water in oil emulsion, the heavier agglomerates may settle. Sludge formation in the tanks reduces storage space for usable fuel and removes part of the high energy containing components of the fuel.

Frequent strainer cleaning is required to prevent high pressure drops and ensure good flow. Sludge formation can also cause heater burner tip fouling. Sludge can be detected in a storage tank by Bacon Bomb sampling of the tank.

In order to mix settled sludge with new fuel, it helps to fill the storage tank from the bottom. A tank with effective lagging (outer insulation) is less susceptible to sludge buildup. Long-term storage (over 7 days) should be avoided and some method of recirculation employed to keep the heavy agglomerates mixed. Where mechanical methods are not completely effective and/or some degree of help is desired, additives are effective in dispersing sludge, even at low use rates. The additives help clean fouled storage tanks and heater and burner assemblies, on-line or off-line.

Many advantages result when fuel sludge is minimized:

- > Increased energy content in the fuel increases efficiency.
- > Clean tanks afford maximum utilization of storage space.
- > Clean feed lines, heaters, and burners are essential to good flow and good combustion.
- > Proper fuel conditioning produces good flame patterns, reducing the chances of flame impingement.

Proper fuel flow allows the boiler to operate at maximum capacity and helps control the formation of burner deposits. It also allows operation at minimum excess air, which helps control slagging and high-temperature corrosion.

FUEL FLOW

The resistance to flow of a liquid fuel is a function of viscosity and pour point. A higher temperature lowers viscosity and increases the ability of the fuel to flow. It is important to

maintain the correct temperature range in a storage tank to ensure good fuel flow and prevent vaporization of the light oil fraction.

One method used to control pour point involves blending of oils with differing pour points. Care must be taken because the pour point of a mixture can be higher than that of either of the two components. As a result, solidification and crystallization can occur in the fuel, which can completely plug a fuel pump. Such plugging is almost impossible to remove through normal cleaning methods. High temperature and constant motion are advisable when high pour point fuels are used.

Viscosity also affects atomization of the oil by the burner. Proper atomization requires lower fuel viscosities than those needed for good fuel flow. This lower viscosity is obtained by heating. Only preliminary heating may take place while the oil is in its storage tanks, to prevent vaporization of the lighter oil fractions. Following preheating, the oil flows to an in-line heater where it is heated to a temperature suitable for good atomization.

CORROSION OF TANKS AND BACTERIAL GROWTH

Water that separates from fuel oils is almost always acidic. Although most hydrocarbons are protective by nature, corrosion can still be found at the water/oil interface. In practice, an alkaline material or amine-type additive is added to protect metal surfaces.

Because heavier fuel oils do not provide life-sustaining nutrients, they rarely experience bacterial growths. In lighter fuel oils, such as diesel fuels, bacteriological growth has been found at the water/oil interface. In order to prevent this occurrence, it is necessary to use water-free fuel oils or to prevent separation of water from the fuel. When bacteriological growths are not prevented, they can be controlled by antimicrobials.

Corrosion test specimens can be installed at the water/oil interface to monitor corrosion, eliminating the need for periodic equipment inspections. Bacterial growth monitoring requires sampling at the water/oil interface and testing for bacteria count.

SPECIFIC EQUIPMENT PROBLEMS

Fuel strainers protect the fuel system from problems with heavy agglomerates and suspended matter. The strainers are relatively coarse, because fine straining can retard fuel flow and increase required cleaning frequency.

Fuel oil pump selection should be based on the anticipated suspended solids in the fuel, along with the type of additive to be used for fireside protection. For example, a constant differential pump operates at a constant rate, and varying amounts of unused oil are recirculated as loads vary. This recirculation, together with certain additives, may increase the amount of suspended solids in the fuel, thereby increasing the clearance tolerances needed. Naturally, the tolerances can be much closer for very light, clean oils than for heavier fuels or fuels carrying more suspended solids.

Burner nozzles are affected by suspended matter and are subject to wear. The effect of wear on the nozzles can be determined by observation of the flame pattern or by means of "go or no-go" gauges.

In-line heaters and burner tips develop clogging problems due to high temperatures, which cause some solidifying of heavier hydrocarbons. Problems with the in-line heater are revealed

by pressure drop across the heaters, a decrease in fuel oil temperature, or an increase in the steam pressure required to maintain the same oil temperature. Burner tip deposits are indicated by distorted flame patterns or inability to achieve maximum load due to restricted flow.

Proper fuel handling must be maintained to ensure optimal conditions and thereby minimize these problems. In addition, periodic cleaning is often necessary. When the required frequency of cleaning is excessive, an additive may be used to help keep the heavy agglomerates dispersed and flowing easily.

SAFETY

Liquid fuels require care in handling to maximize safety. Potential problems include contamination from spills or leaks and escape of combustible vapors. Tank areas should be diked to contain any spills. To guard against fire, special tank construction is necessary and combustible vapor monitors should be used. Combustible monitors may be integrated into fire control systems.

Chapter 21 - Boiler Fireside Deposit And Corrosion Control

Impurities in fuels can cause deposit formation and fireside metal surface corrosion. Compounds of aluminum, barium, copper, iron, magnesium, manganese, and silica have all been used to control combustion fouling and corrosion. The most severe problems are generally found in combustion equipment firing fuels that significantly deviate in composition from the fuel on which the equipment design was based.

SOURCE AND NATURE OF FIRESIDE DEPOSITION

Fireside fouling of combustion equipment is caused by the deposition of fuel ash components. Table 21-1 shows analyses of typical high, medium, and low ash liquid fuels. Oils containing more than 0.05% ash are considered high ash oils; those containing less than 0.02% ash are considered low ash oils.

Table 21-1. Typical residual oil analyses.

	High Ash	Medium Ash	Low Ash
Specific Gravity, at 60 °F	0.9548	0.9944	0.9285
Viscosity SSF at 122 °F, sec	240	200	100.5
Calorific Value, Btu/gal	147,690	152,220	147,894
Bottom Sediment & Water, %	0.1	0.4	0.1
Sulfur, %	1.93	2.26	0.62
Ash, %	0.06	0.04	0.02
Vanadium, ppm	363	70	6
Sodium, ppm	16	50	9
Nickel, ppm	48	19	14
Aluminum, ppm	9	1	10
Iron, ppm	12	3	1

Sulfur emission regulations have severely restricted the use of high sulfur oils. Generally, high sulfur oils (greater than 1.0% sulfur) have high ash contents. These oils are usually imported from the Caribbean area. Prior to 1972, most East Coast boilers were burning high sulfur, high ash oils.

The combustion of high ash oils produced troublesome deposits on boiler convection surfaces such as steam generating, superheat, reheat, and economizer sections. The firing of high ash oils (even in those units which were originally designed to burn coal) produced convection surface deposition that was difficult to remove by soot blowing.

The most troublesome oil ashes are those which contain a vanadium/sodium ratio of less than 10:1. In Table 21-1, the fuel with the medium ash content has a relatively low vanadium/sodium ratio and produced an [extremely tenacious deposit on superheater surfaces \(as shown in Figure 21-1\)](#).

Vanadium reacts with oxygen to form various oxides in the furnace. When formed, vanadium pentoxide condenses within the furnace when gas temperatures approach its solidification point.

Sodium also reacts with oxygen and sulfur trioxide to form fouling compounds. Thermodynamics favor the formation of sodium sulfate rather than the relatively unstable sodium oxide.

Nickel can also contribute to deposition by forming oxides. Aluminum can be present in the oil in the form of cracking catalyst fines (aluminum that is introduced during the refining of oil). Although it is generally not a troublesome component, iron is occasionally present in fuels at relatively low levels. When waste fuels are burned, some contaminants (such as lead) can cause extremely dense and tenacious deposits.

Black liquor has been used as a boiler fuel for many years in the Kraft paper industry. It contains a significant amount of combustible material, along with sodium salts. Black liquor burning can produce relatively adherent, low bulk density sodium sulfate deposits on recovery boiler convective surfaces. In some instances, it is advisable and economically beneficial to control or limit deposition with magnesium-based additives. These materials are blended compounds which contain magnesium oxide and/or aluminum oxide.

The combustion of coal tar in boilers often produces objectionable amounts of sodium salts and/or iron compounds on boiler convective surfaces. Often, ash deposits are similar in composition to coal ash.

Combustion of solid fuels such as coal and bark (also referred to as "hog fuel") can also lead to fireside slagging. Sodium, calcium, silica, iron, and sulfur content are of primary concern in the burning of solid fuels. Other metal oxides, such as alumina, titania, and potassium oxide, can also aggravate slagging. [Figure 21-2 shows a heavy accumulation of slag in a coal-fired boiler.](#)

In addition to proper boiler furnace design, operational considerations should be explored to prevent fireside slagging. [Ash fusion testing has been used by boiler manufacturers to assess slagging potential \(see Figure 21-3\).](#) Where design and operational improvements are impractical or insufficient, chemical treatments (such as combustion catalysts and antifoulants) should be considered.

TREATMENT FOR FOULING

Additives are used to control fouling by elevating the melting point of the deposits, by physically diluting deposits, or by providing a shear plane to assist in removal by soot blowing. Additives used to control fouling contain magnesium, silica, manganese, and/or aluminum. [Figure 21-4 illustrates the effect of treatment.](#)

The melting point of untreated ash constituents can be as low as 1000°F. The introduction of appropriate metal oxides elevates the melting point of ash components by several hundred degrees. The additive components most commonly used to raise the deposit melting point are magnesium and/or aluminum. Dosages depend on ash levels in the fuel and the ratio of various ash components.

Fuel additives are intended to control fouling by forming a friable, nonadherent deposition that can be removed by soot blowing.

When melting temperatures are raised, the physical characteristics of the deposits are altered. Often, the heaviest deposition occurs in areas where the gas temperature is lower than the melting temperature of a deposit. Therefore, a treatment program designed solely to elevate the melting point of the deposit will not solve the problem, and it is necessary to introduce additive components that change the physical characteristics of the deposit, making it more friable. Additives used for this purpose contain compounds of magnesium or aluminum.

Aluminum is usually the most effective material for increasing friability of deposits.

Newer technology has been developed that offers certain advantages over magnesium or magnesium/aluminum combination treatments. Silicon-based materials have been used to control fouling and form friable nonadherent oxides. The silicon component acts like a sponge to adsorb low melting point oxides, preventing their agglomeration and subsequent deposition. The silicon-based materials contribute far fewer solids than traditional treatment. This reduces fouling and minimizes loading on the solids collection system.

Additive dosage should be fixed at the minimum level necessary for proper conditioning of deposits. Overfeeding of additives, particularly magnesium oxide, can cause troublesome deposition. Magnesium oxide can react with sulfur trioxide in the flue gas to form magnesium sulfate deposits. These deposits generally form in convection areas, such as primary superheaters, steam generating sections, and economizers.

Boiler design has proven to be a very important consideration in the determination of magnesium additive levels. The addition of aluminum to magnesium-based additives reduces magnesium sulfate deposition.

The greatest need for fuel additives to control deposition is in boilers previously used to fire other fuels, such as natural gas or coal. Generally, units used to fire coal have sufficient soot blower placement for adequate removal of properly conditioned deposits.

Natural gas-burning units generally do not have the desired soot blowing equipment. It is advisable to contact the manufacturer so that the proper number of soot blowers and their location can be specified. It is virtually impossible to burn a fuel containing greater than 0.2% ash without the use of soot blowers, even with the aid of a conditioning additive.

Boilers designed for oil firing incorporate design parameters that allow for relatively trouble-free operation from a fireside standpoint. Combustion gas velocity, tube spacing, furnace gas exit temperature, and economizer configuration are adjusted to account for oil ash characteristics. The most common problems associated with oil-design boilers are air preheater fouling and corrosion. Deposition and corrosion can occur when the oil used is of lesser quality than specified for the boiler, or if multiple oils are used.

HIGH-TEMPERATURE FIRESIDE CORROSION

Fuel ash corrosion in high-temperature areas can cause extensive boiler damage. The corrosion is caused principally by complex oxide-slugs with low melting points. Corrosion by slag components, such as sodium vanadyl vanadate, progresses rapidly between 1100 and 1650°F.

Sodium sulfate is also a primary corroding medium that can be present with sodium vanadyl vanadate. It also is the primary corroding material of gas turbine blades. High-temperature corrosion can proceed only if the corroding deposit is in the liquid phase and the liquid is in direct contact with the metal. [The liquid-phase deposits corrode by fluxing of the protective](#)

oxide layer on the metal surface as shown in Figure 21-1. Deposits also promote the transport of oxygen to the metal surface. Corrosion is caused by the combination of oxide layer fluxing and continuous oxidation by transported oxygen.

Tube spacers, used in some boilers, rapidly deteriorate when oil of greater than 0.02% ash content is fired. Because these spacers are not cooled and are near flue gas temperatures, they are in a liquid ash environment. Fuel oil additives can greatly prolong the life of these components.

High-temperature corrosion caused by sulfidation is a common problem in gas turbines. The corroding medium is sodium sulfate. Sodium enters the gas turbine either with the fuel or combustion air. The sodium content of the fuel can be lowered by means of water washing. It is relatively difficult to remove all sodium-containing mists or particulates at the intake of the gas turbine. Due to salt water mist ingestion, blade sulfidation problems are common in gas turbines used for marine propulsion.

Reheating furnaces in the iron and steel industry have suffered wastage of metallic recuperators. The problem is more prominent where steel mills have converted reheat furnaces from natural gas to residual oil firing. The gas inlet temperature at the recuperator is high enough to provide an environment for high-temperature corrosion.

Firing of residual oil in refinery process heaters has caused numerous corrosion failures of convection tube support members. The tube supports are generally not cooled by water or air and, therefore, are at a temperature close to that of the gas. In some cases, tube supports fabricated from nickel and chromium alloys have been installed to alleviate this problem.

Additives containing magnesium and aluminum oxides have been successful in controlling these and other high-temperature corrosion problems. The additives function by elevating the melting point of the deposits. Enough magnesium oxide must be added to enable the metallic constituents to remain in the solid phase as they contact the metal surface.

In conjunction with an additive program to control high-temperature corrosion, it is advisable to operate the unit at minimum excess air levels. The corrosion rate is influenced by the oxygen content of the combustion gas. The second phase of the corrosion mechanism is oxidation; therefore, the partial pressure of oxygen in the combustion gas can be lowered to reduce corrosion rates.

In residual oil-fired equipment, it is often necessary to feed a 1:1 ratio of magnesium and vanadium to achieve low corrosion rates. This level of feed is generally higher than that which is necessary to control fouling.

COMBUSTION CATALYSTS

Combustion catalysts have been used for all types of fuels. The combustion catalyst functions by increasing the rate of oxidation of the fuel. Some fuels are difficult to burn within a given fixed furnace volume. Combustion catalysts are applied to these fuels to comply with particulate and opacity regulations. Combustion catalysts are also used to improve boiler efficiency by reducing carbon loss in the flue gas.

FUEL ADDITIVES

Most soluble fuel additives contain metallo-organic complexes such as sulfonates, carbonyls, and naphthenates. These additives are in a very convenient form for feeding. Most dry fuel additive preparations are used to treat fuels with high ash content, such as coal, bark, or black liquor. Metal oxides are used for this purpose.

Chapter 22 - Cold-End Deposition And Corrosion Control

Cold-end corrosion can occur on surfaces that are lower in temperature than the dew point of the flue gas to which they are exposed. Air heaters and economizers are particularly susceptible to corrosive attack. Other cold-end components, such as the induced draft fan, breeching, and stack, are less frequently problem areas. The accumulation of corrosion products often results in a loss of boiler efficiency and, occasionally, reduced capacity due to flow restriction caused by excessive deposits on heat transfer equipment.

Acidic particle emission, commonly termed "acid smut" or "acid fallout," is another cold-end problem. It is caused by the production of large particulates (generally greater than 100 mesh) that issue from the stack and, due to their relatively large size, settle close to the stack. Usually, these particulates have a high concentration of condensed acid; therefore, they cause corrosion if they settle on metal surfaces.

The most common cause of cold-end problems is the condensation of sulfuric acid. This chapter addresses problems incurred in the firing of sulfur-containing fuels. Sulfur in the fuel is oxidized to sulfur dioxide:



oxygen

A fraction of the sulfur dioxide, sometimes as high as 10%, is oxidized to sulfur trioxide. Sulfur trioxide combines with water to form sulfuric acid at temperatures at or below the dew point of the flue gas. In a boiler, most of the sulfur trioxide reaching the cold end is formed according to the following equation:



oxygen

The amount of sulfur trioxide produced in any given situation is influenced by many variables, including excess air level, concentration of sulfur dioxide, temperature, gas residence time, and the presence of catalysts. Vanadium pentoxide (V_2O_5) and ferric oxide (Fe_2O_3), which are commonly found on the surfaces of oil-fired boilers, are effective catalysts for the heterogeneous oxidation of sulfur dioxide. Catalytic effects are influenced by the amount of surface area of catalyst exposed to the flue gas. Therefore, boiler cleanliness, a reflection of the amount of catalyst present, affects the amount of sulfur trioxide formed.

The quantity of sulfur trioxide in combustion gas can be determined fairly easily. The most commonly used measuring techniques involve either condensation of sulfur trioxide or adsorption in isopropyl alcohol. [Figure 22-1 is a curve showing the relationship of sulfur trioxide concentration to dew point at a flue gas moisture content of 10%.](#) Higher flue gas moisture increases the dew point temperature for a given sulfur trioxide-sulfuric acid concentration. Cold-end metal temperatures and flue gas sulfur trioxide content can be used to predict the potential for corrosion problems.

At the same sulfur content, gaseous fuels such as sour natural gas, sour refinery gas, and coke oven gas produce more severe problems than fuel oil. These gases contain more hydrogen than fuel oil, and their combustion results in higher flue gas moisture. Consequently, dew points

are raised. With any type of fuel, corrosion and fouling potentials rapidly increase below gas temperatures of 140 degrees F (60 degrees C), which is the typical water dew point for flue gases.

Cold-end corrosion and deposition are usually much less severe in coal-fired boilers than in oil-fired units. Usually, coal ash is alkaline, so it increases the pH of the deposits formed in cold-end sections. Thus, the extent of the corrosive attack by sulfuric acid is diminished. Also, the high level of ash present when coal is fired results in a lower concentration of acid in the ash particle. At the same sulfur content, coal firing dew points are generally 20-40 degrees F lower than oil firing dew points.

The most common cause of deposition within air preheaters is the accumulation of corrosion products. Most air preheater deposits contain at least 60% iron sulfates formed by the corrosion of air heater tube metal. Therefore, a reduced corrosion rate frequently reduces the fouling of air preheaters.

MECHANICAL AND OPERATIONAL SOLUTIONS

Air Preheaters

A regenerative air preheater can reduce cold-end problems when installed instead of a recuperative air preheater on a new or existing boiler. In the regenerative air preheater design, heat transfer surfaces are below the acid dew point for much shorter periods of time.

Most modern regenerative air preheaters are equipped with steam or compressed air sootblowers and fixed or oscillating water washing nozzles. In boilers equipped with multiple units, individual air preheaters can be isolated and washed on-line. Suitable drain connections must be provided as well as a system for treating the wash water prior to disposal. Washing is generally continued until the pH of the wash water is above 4.5. The wash water effluent is a relatively low pH stream with a high soluble iron content. Most air preheaters are washed with untreated water. Some operators add caustic soda or soda ash to neutralize the deposits and lower the loss of air heater metal during washing.

The average cold-end temperature of an operating air preheater is the sum of combustion air inlet temperature and flue gas outlet temperature, divided by two. The average cold-end temperature is generally used in the assessment of potential problems and the selection of air preheater size and materials of construction. The average cold-end temperature of an operating air preheater must be maintained in accordance with the manufacturer's specifications. Corrosion-resistant materials are used in some regenerative air preheater cold sections to obtain the lowest possible stack gas temperature and consequently the highest boiler efficiency.

Steam Coil Air Preheaters

In some installations, heating coils are placed between the forced draft fan outlet and the air preheater inlet to accommodate seasonal fluctuations in incoming combustion air temperature. These heat exchangers are commonly termed "steam coil air preheaters." They maintain the average cold-end temperature of the air preheater above the acid dew point. Where steam coils are used, the temperature of the combustion air entering the air heater is independent of the ambient temperature.

Steam coil air preheaters are also installed when boilers are changed from coal or gas firing to oil firing. Steam coils are installed because oil firing requires maintenance of an air preheater average cold-end temperature that is higher than that normally specified for the firing of natural gas or coal. The operation of steam coil air preheaters results in an increase in the heat rate of the steam plant. Combustion air bypasses around the air heater and hot air recirculation have also been used to control average cold-end temperatures. Both of these methods reduce boiler efficiency.

Minimizing Air Infiltration

The operation of a boiler at or below 5% excess air can result in a marked reduction in flue gas sulfur trioxide content and dew point. An experimentally determined relationship for one boiler is shown in Figure 22-2. The infiltration of air into the flame zone or into an area where the catalytic oxidation of sulfur dioxide is occurring increases the potential for cold-end problems. Therefore, maintenance and inspection procedures should be directed toward minimizing air infiltration.

Minimizing Flue Gas Moisture Content

As previously stated, the dew point is not only affected by the partial pressure of sulfuric acid in the flue gas but also by the partial pressure of water in the flue gas. The minimum obtainable flue gas moisture content is determined by the moisture content of the fuel and combustion air and by the hydrogen content of the fuel.

The moisture content of coal is somewhat controllable through proper handling and storage procedures. Handling and storage specifications can be written limiting the moisture content of fuel oil. Factors that increase flue gas moisture content include:

- > boiler tube leaks
- > steam coil air preheater leaks
- > excessive boiler or air heater soot blowing
- > leaking water wash nozzles
- > instrumentation leaks

When two fuels (such as coal and oil, oil and natural gas, or blast furnace gas and coke oven gas) must be fired simultaneously, certain ratios produce the highest dew points. The worst ratio on a Btu-fired basis is 1:1.

When a fuel is fired that has a higher hydrogen content than the base fuel normally used, the flue gas produced has a higher moisture content, resulting in an increased dew point. When possible, fuels of different hydrogen content should be fired separately. Figure 22-3 graphically depicts the influence on sulfuric acid dew point that results when natural gas and a sulfur-containing fuel are fired simultaneously in a single boiler.

CHEMICAL TREATMENT

Many chemical solutions have been devised to control cold-end deposition and corrosion. These solutions can be divided into two broad classifications: fuel additives and cold-end additives. Fuel additives are compounds that are added directly to the fuel or combustion

process. Cold-end additives are fed into the back of the boiler after steam-generating surfaces so that they specifically treat only the lower-temperature areas.

Fuel Additives

Magnesium and magnesium/aluminum based fuel additives are used to reduce sulfur trioxide in the flue gas. These compounds function primarily by altering the effectiveness of the iron and vanadium catalysts. They are fed to liquid fuels, most commonly residual fuel oil. Alkaline fuel oil additives, such as magnesium, also increase the pH of deposits formed on cold-end surfaces, thereby reducing corrosion.

Cold-End Additives

Cold-end corrosion and deposition can be controlled more economically and effectively through the use of cold-end additives. Cold-end additives include sulfuric acid neutralizing agents and corrosion inhibitors.

Magnesium Compounds. Alkaline magnesium compounds, such as magnesium oxide and magnesium carbonate, are fed to reduce the sulfur trioxide content of flue gases. These compounds are fed in high-temperature areas, such as primary superheater sections. The reaction product formed, magnesium sulfate, often increases deposition within air preheaters.

The main benefit of magnesium compound injection is a reduction in air preheater corrosion. Often, the level of fouling is not appreciably altered, because the corrosion product fouling is replaced by magnesium sulfate fouling. Therefore, where magnesium compounds are used, suitable water wash nozzles must be present to permit periodic removal of magnesium sulfate.

Additives that remove sulfur trioxide from flue gas must be fed in stoichiometric quantities with respect to the amount of sulfur trioxide to be removed. Therefore, higher levels of sulfur in the fuel require higher feed rates for protection. Coal-fired boilers require less treatment than oil-fired boilers for a given sulfur level in the fuel.

Corrosion Inhibitors. Corrosion inhibitors can be added to the cold end of the boiler to alleviate problems associated with the condensation of sulfuric acid. These materials do not neutralize the sulfuric acid in the flue gas; they prevent surface corrosion where the sulfuric acid condenses. Fouling of the air preheater is reduced because the quantity of corrosion products is reduced. Although the dosage of inhibitor required to achieve the desired effect increases with increasing acid content in the flue gas, the relationship is not linear.

The compositions of inhibitor-type cold-end additives are usually proprietary. Products are available in powder and liquid form. Liquid solutions are injected upstream of the problem area with atomizing spray nozzles.

Justification for cold-end additives is generally based on the benefits obtained by higher unit heat rates and lower maintenance costs for the equipment in the cold-end section. The feed of cold-end additives enables the unit to operate with a lower rate of steam flow to the steam coil air preheaters, resulting in an increase in unit heat rate. If average cold-end temperature is controlled with bypasses, the bypassed air flow can be reduced so that an improvement in boiler efficiency is obtained. A smaller improvement in heat rate is gained through reduction of fan horsepower, which reduces the average pressure drop across the air preheater.

Acid Smut Control. Cold-end additives can be used to reduce acid smut problems. In some in-stances, it is believed that smut is created when fly ash particles agglomerate to form larger particles. These particles adsorb sulfuric acid mist and become highly acidic. Fly ash deposits often accumulate in low-temperature areas of breeching. During soot blowing or load changes, some of the deposited fly ash can be entrained in the flue gas stream and carried out the stack. The large particles then settle in the vicinity of the stack. Magnesium-based fuel additives have been beneficial in reducing acid smut problems by increasing the pH of the deposits.

Evaluation and Monitoring Techniques

Corrosion Rate Measurement. Various devices are available to assess the impact of additive application on corrosion rates. Table 22-1 shows a selection of monitoring methods. In some cases, problems in the breeching, induced draft fans, and stack can be measured by corrosion coupons placed within the flue gas stream.

For air heater corrosion and fouling problems, some provision must be made to maintain a corrosion specimen temperature that is within the ranges typically found in the operating air preheater. Corrosion probe methods (see Table 22-1) are used to simulate corrosion rates in an operating air preheater. [Figure 22-4 shows a multipoint corrosion probe. The temperature to be maintained on the specimen is determined by calculation of average cold-end temperature and measurement of dew point.](#)

Table 22-1. Comparison of corrosion rate assessment methods

Method	Variable Measured	Time Required	Instrument		
			Cost	Advantages	Limitations
Corrosion coupon installed on surfaces	loss of weight of coupon	1-4 week	low	simple; measures corrosion directly	not clear if location of coupon represents entire surface
Air-cooled corrosion probe for flue gas test	loss of weight of coupon	1-4 week	low	simple; can determine corrosion as a function of temperature	temperature cannot be closely controlled without relatively high expense
Multipoint corrosion probe	short-range loss of iron	5-7 hour	low to moderate	can determine corrosion over a wide temperature range; rapid indication	difficulty extrapolating short-range to long-range results
Sampling of flue gas	flue gas sulfur trioxide	4-5 hour	high	direct measurement of SO ₃ ; then dew point temperature is accurate	more technical knowledge required to operate equipment; not a direct indication of corrosion
Electrical	temperature	2-4 hour	high	quick; gives	low sulfur trioxide gives

conductivity, dew point and rate of acid buildup meter	at which acid condenses on probe; rate of acid deposition below the dew point	some idea of corrosion problem	inaccurate and nonreproducible results; high dust loadings interfere with rate of acid buildup measurements; does not measure surface coating additive effect
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The electrical conductivity dew point meter is useful in problem assessment work and some results monitoring. In addition to corrosion monitoring, this meter provides an indication of the deposition rate by measuring the increase in the conductance of an acid-containing film with respect to time. The electrical conductivity meter is acceptable for results monitoring only where a sulfur trioxide removal additive is used. [The dew point meter is shown in Figure 22-5.](#)

Normally, direct measurement of sulfur trioxide is used only for Environmental Protection Agency tests because of its cost and complexity. All of these evaluation techniques and tools are used by suppliers of proprietary cold-end treatments. They enable the engineer to define the problem and measure results properly.