



WATER TREATMENTS

Boiler's Water Treatments' Technology

Nov 2007

CHIMEC S.p.A. – Water Technology Unit



WATER TREATMENTS

Water Usage in Industry

➤ Overview

Water Properties Fundamentals

➤ Physical and Chemical background

Boilers' Technology and Products for Boiler's Water



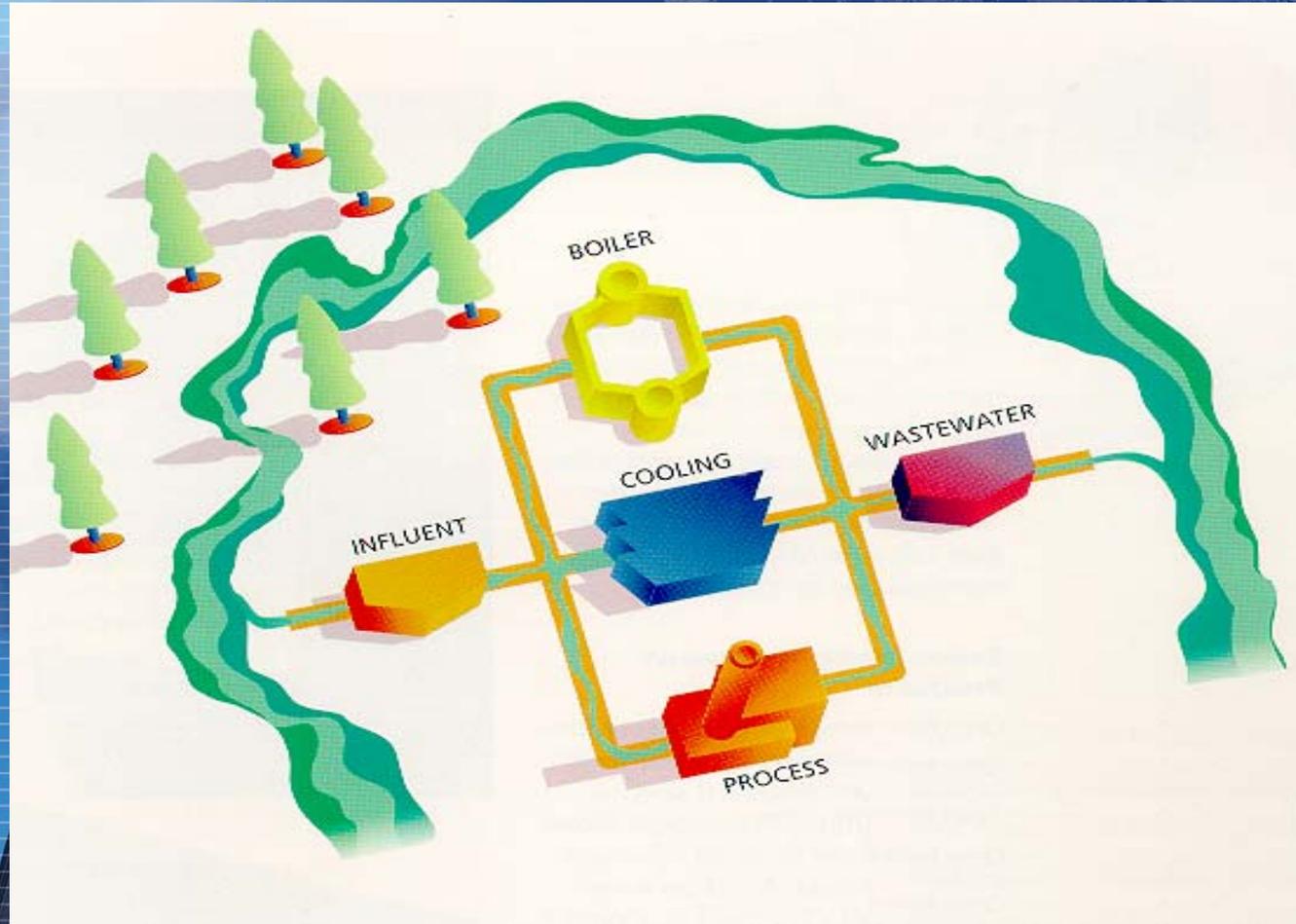
WATER TREATMENTS

☐ Water Usage in Industry

- *60 to 70 % of industrial water is used for cooling purposes*
- **10 to 15% is used in Boilers**
- *up to 15% is used in Processes, Services, and other purposes*

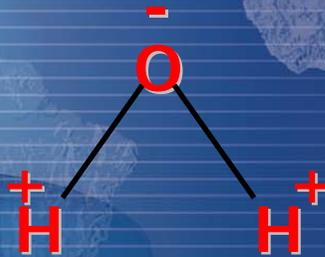


WATER TREATMENTS



□ Water Properties Fundamentals

Water Molecule



Molecular Weight: 18

Specific Heat: 4.18 kJ/kg°C

Latent Heat: 2260 kJ/kg

➤ *Strong Polar Solvent*

➤ *Involved almost in any Reaction*

□ Water Properties Fundamentals

CONCENTRATION can be expressed in several useful ways:

- *Percentage – grams of solute in 100 g of Solution*
- *ppm “parts per million” – mg of solute in 1L of Solution (1L=1000g for common applications)*
- *Molarity – moles of solute in 1 Litre of Solution*

□ Water Properties Fundamentals

CHEMICAL EQUILIBRIUM – condition at which, many reactions taking place in Water, lead:



- *Equilibrium Constant "K" defined by:*

$$K = \frac{[\text{H}^+] * [\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

Shows how a reaction proceeds, the higher "K", the higher the products of reaction

□ Water Properties Fundamentals

pH, WATER ION PRODUCT

- *pH is defined as the negative log (base 10) of H^+ ion concentration:*

$$pH = -\log[H^+]$$

- Water Ion Product $H_2O = H^+ + OH^-$

its equilibrium constants is $K_w = 10^{-14}$

at neutral conditions $[H^+] = [OH^-]$ so $pH = 7$

□ Water Properties Fundamentals

ACIDS and BASES

- ACID is a substance that releases H^+ ions in water $HCl \rightarrow H^+ + Cl^-$ pH < 7
- BASE is a substance that releases OH^- ions in water $NaOH \rightarrow Na^+ + OH^-$ pH > 7

□ Water Properties Fundamentals

IONS – *charged particles:*

Cations are positive, Anions are negative

→ HCO_3^- , CO_3^{2-} , OH^- responsible for Water Alkalinity

Common
Ions in water

→ Na^+ , K^+ , Fe^{2+} , Fe^{3+} , Cl^- , NO_3^- , SO_3^{2-} and others

→ Ca^{2+} , Mg^{2+} responsible for Water Hardness

□ Water Properties Fundamentals

ALKALINITY – is the capacity of a water to accept Hydrogen ions;

is a measure of its acid neutralizing capacity (ANC).

Alkalinity is often described as the Buffering capacity

Ions Contributing to Alkalinity:



□ Water Properties Fundamentals

HARDNESS - is the sum of the metallic cations Ca^{2+} and Mg^{2+} ;

These cations, react and form precipitates with other ions in water, to form scale in boilers (mainly as $CaCO_3$ and $MgCO_3$)

Hardness is expressed in mg/L $CaCO_3$



WATER TREATMENTS

□ Water Properties Fundamentals

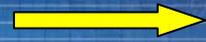
CONDUCTIVITY – measures the ability of an aqueous solution to carry an electric current; the higher the number of ions, the higher the conductivity.

Conductivity is expressed in $\mu\text{S}/\text{cm}$

□ Water Properties Fundamentals

SOLIDS – one of the most significant parameters

SOLIDS are
Classified
as:



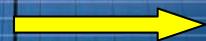
Total "TS": all the residue remaining after evaporation @ 105°C



Suspended "SS": the particles retained by a membrane of pore size 0.44 µm



Total Dissolved "TDS": TS - SS



Expressed in mg/L

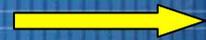
□ Water Properties Fundamentals

SOLIDS – further characteristics

SOLIDS are
Classified as:



Suspended



Dissolved may also include



COLLOIDAL: of clay origin and
of size from 10^3 to $1 \mu\text{m}$.

Colloidal do not dissolve,
remain as a solid phase in
suspension



WATER TREATMENTS

□ Water Properties Fundamentals

COLOUR – caused by dissolved minerals, dyes or humic acids from plants

TURBIDITY – is a measure of cloudiness, caused by suspended matter which scatters and absorbs light

ODOUR and TASTE – caused by organic and some inorganic compounds, including algae and other organisms

These parameters apply mostly to Drinking Water



WATER TREATMENTS

End of Part 1



WATER TREATMENTS

BOILERS AGENDA

- ◆ *General Information*
- ◆ *Pretreatments*
- ◆ *Oxygen Removal*
- ◆ *Internal Treatments*
- ◆ *Condensate Circuit*



WATER TREATMENTS

BOILERS – *General Information*

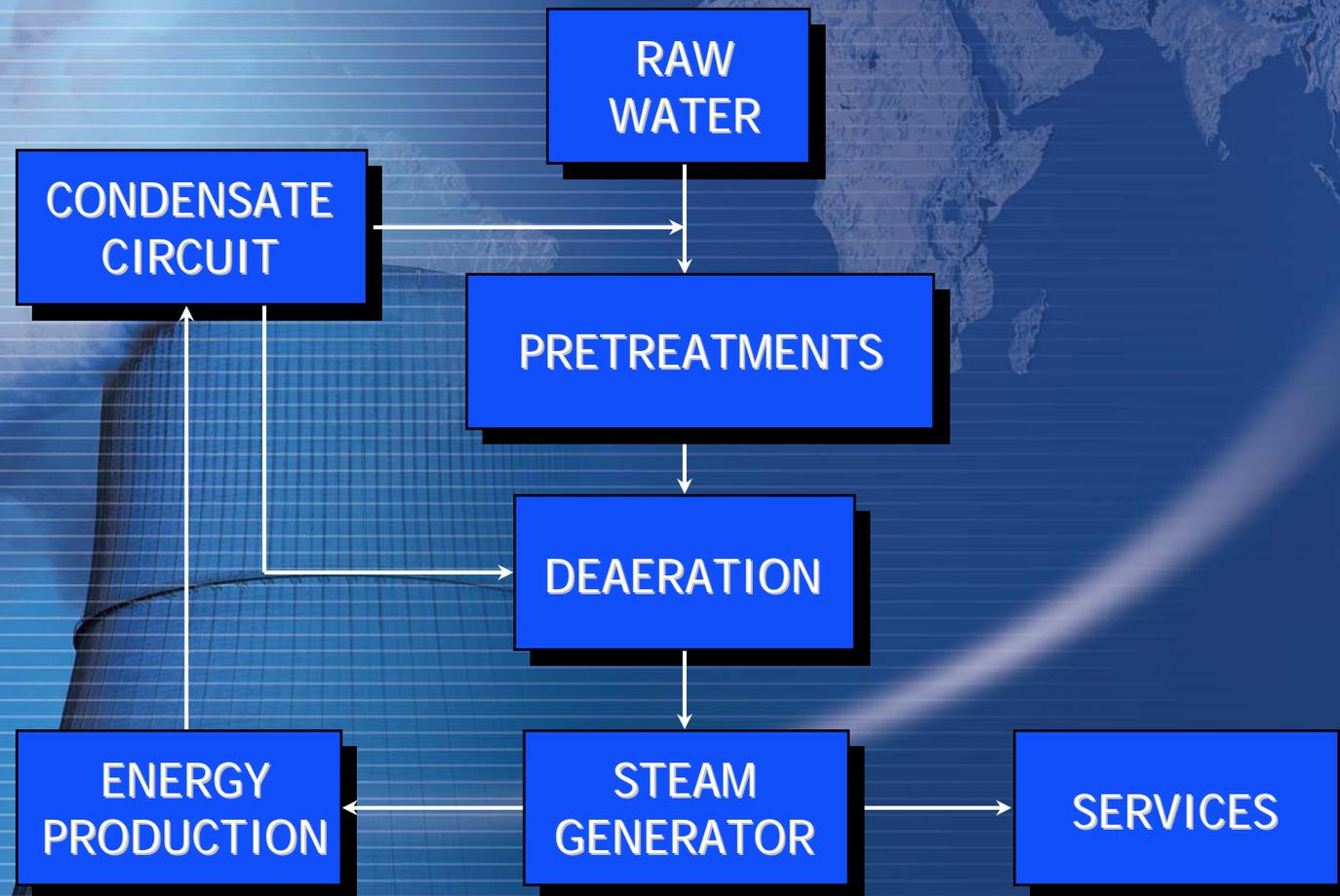
◆ *Steam Usage*

- *Heating medium*
- *Production of Electricity*
- *Processing*



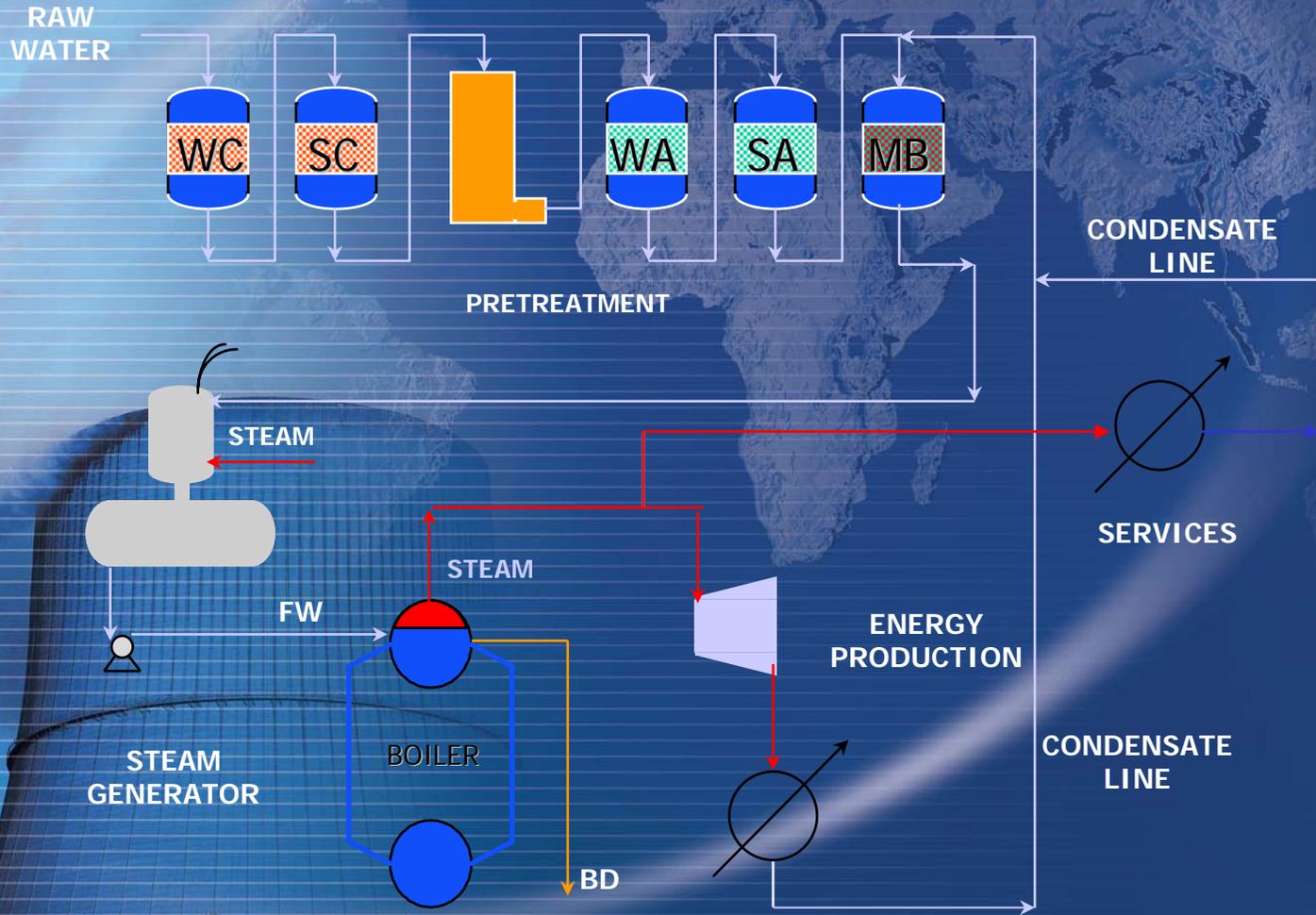
WATER TREATMENTS

BOILERS – *Water Flow Diagram*





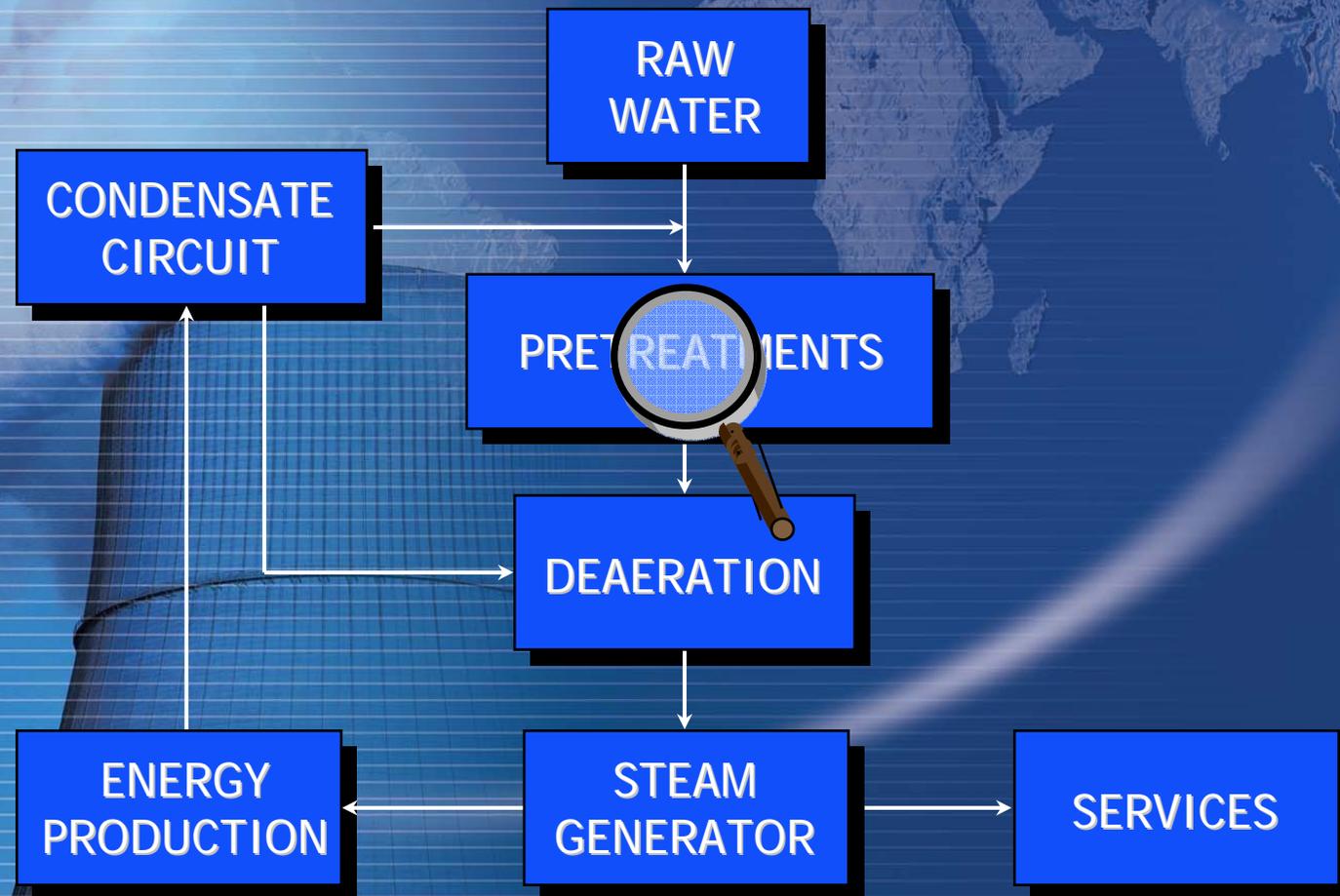
WATER TREATMENTS





WATER TREATMENTS

BOILERS – *Water Flow Diagram*





WATER TREATMENTS

BOILERS – *Water Pretreatments*

Pretreatment of Raw Water is necessary to eliminate Dissolved Solids

↳ Sodium based **Softening**
(Eliminates Ca e Mg)



↳ **Deminerlization**
(Eliminates all salts)

**ION
EXCHANGE**



WATER TREATMENTS

BOILERS – Water Pretreatments 1

ION EXCHANGE - is BASED on some RESINS' ABILITY TO HOLD CATIONS AND ANIONS and EXCHANGE them WITH H^+ and OH^- IONS RESPECTIVELY.

- ↪ Strong Acid Cation (SAC) exchange all Cations
- ↪ Weak Acid Cation (WAC) " ions due to Hardness
- ↪ Strong Basic Anion (SBA) " all Anions
- ↪ Weak Basic Anion (WBA) " weak Anions



WATER TREATMENTS

BOILERS – *Water Pretreatments*

ION EXCHANGE RESINS



Gellular Cationic Resins



Macroporous Anionic
Resins



WATER TREATMENTS

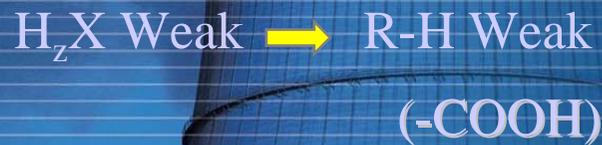
BOILERS – Water Pretreatments

ION EXCHANGE RESINS Reactions

CATION exchange reaction



Formation of $\text{H}_z \text{X}$:



ANION exchange reaction



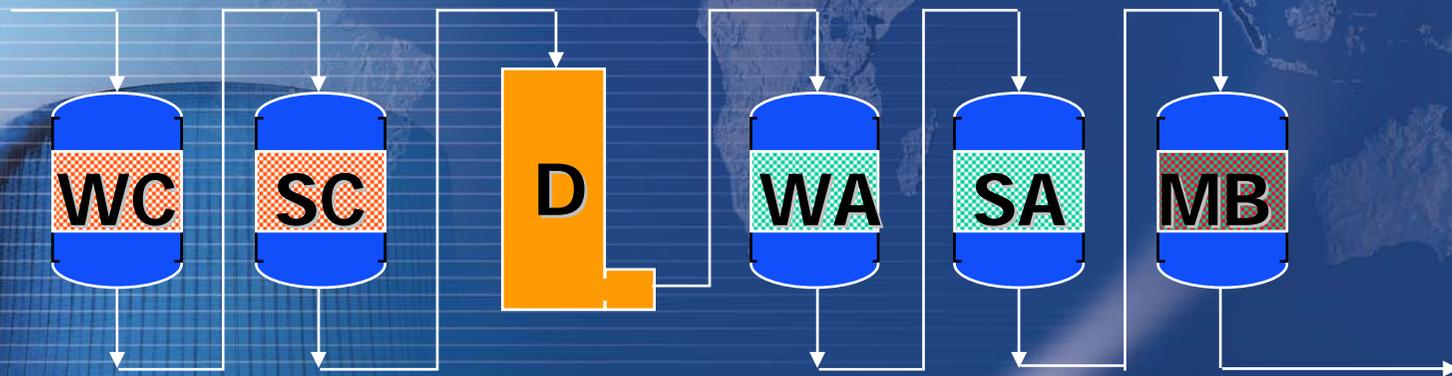
Dissociation of $\text{H}_z \text{X}$:



BOILERS – *Water Pretreatments*

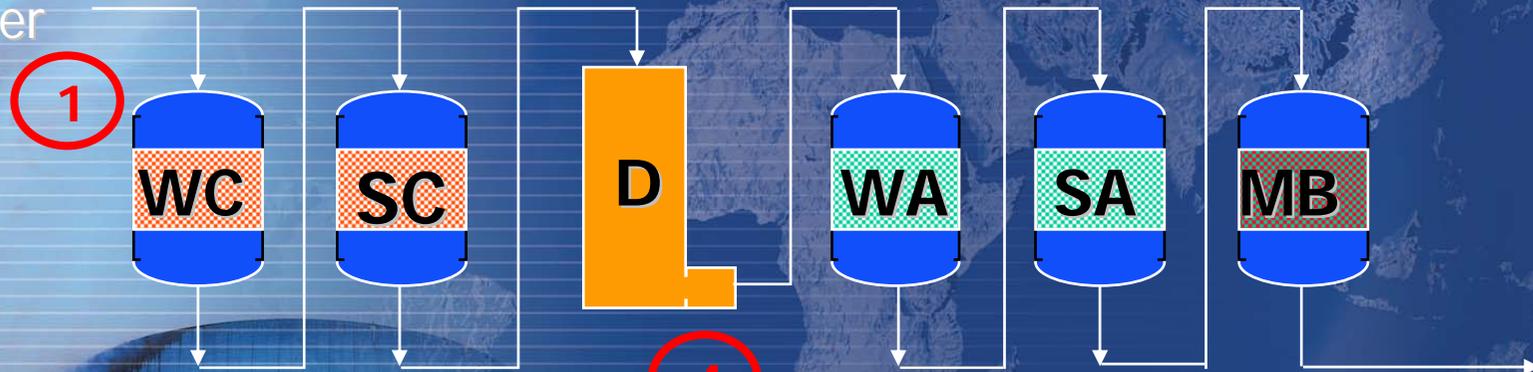
Ion Exchange and CO₂ Removal

Raw Water



CO₂ removal moves equilibrium to the left, alkalinity is consumed

Raw Water



2

3

4

5

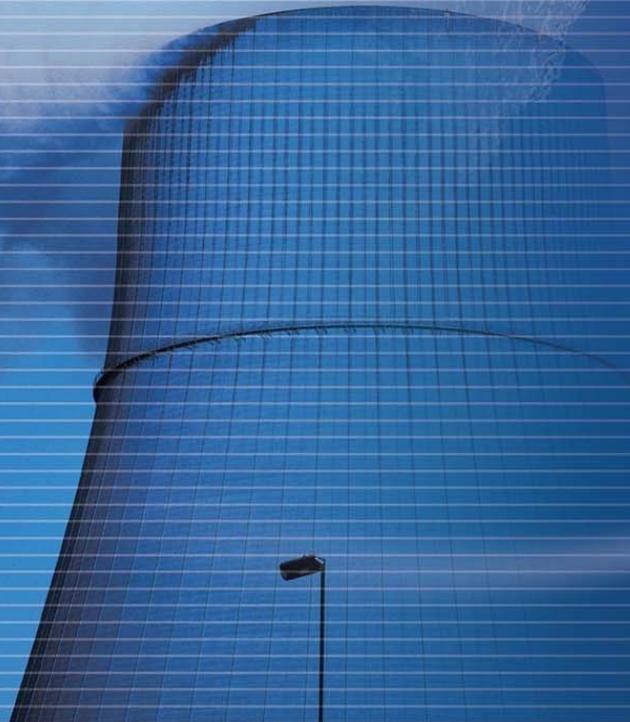
6

	Ca	Mg	Fe	Na	Malk	pH	SO ₄	Cl	NO ₃	SiO ₂
1	150	100	7	3	220	7	20	10	10	5
2		37		3	220	4 - 5	20	10	10	5
3					220	2 - 3	20	10	10	5
4					25-35	2 - 3	20	10	10	5
5					25-35	4 - 5				5
6						6,5 - 7,5				



WATER TREATMENTS

End of Part 2





WATER TREATMENTS

BOILERS – *Water Pretreatments*

DEAERATION – *is necessary to prevent corrosion problems due to Oxygen in Feedwater*

Methods for Oxygen Removal are mainly:

- *Physical* – *deaerating device*
- *Chemical* – *oxygen scavenging*



WATER TREATMENTS

BOILERS – *Water Pretreatments*

Physical Deaeration – based on the following principles:

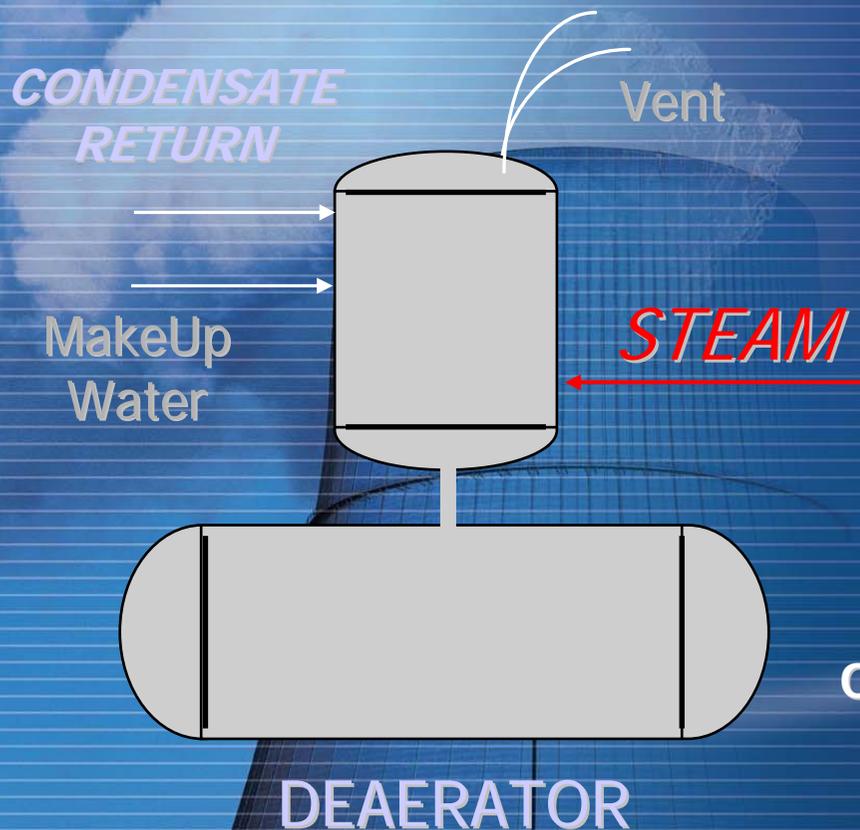
- *Solubility of a gas in a liquid medium is directly proportional to its partial pressure at the liquid surface (Henry's Law)*
- *Solubility of a gas in a liquid medium decreases as the temperature increases*
- *Efficiency of removal increases with mixing*



WATER TREATMENTS

BOILERS – Water Pretreatments

Physical Deaeration – Steam Stripping



- ↪ Temperature
- ↪ Degree of water drops atomisation
- ↪ Adequate venting

$O_2 < 7$ ppb Chemical Removal is necessary



WATER TREATMENTS

BOILERS – *Oxygen Scavengers Products*

Inorganics

➤ *Sodium Sulfitite/Bisulfitite* →

- Max Pressure 42 Bar
- Residue Easy to Analyse
- Increases Solids Content

Organics

➤ *Hydrazine*

➤ *Hydroquinone*

➤ *Carbohydrazide* →

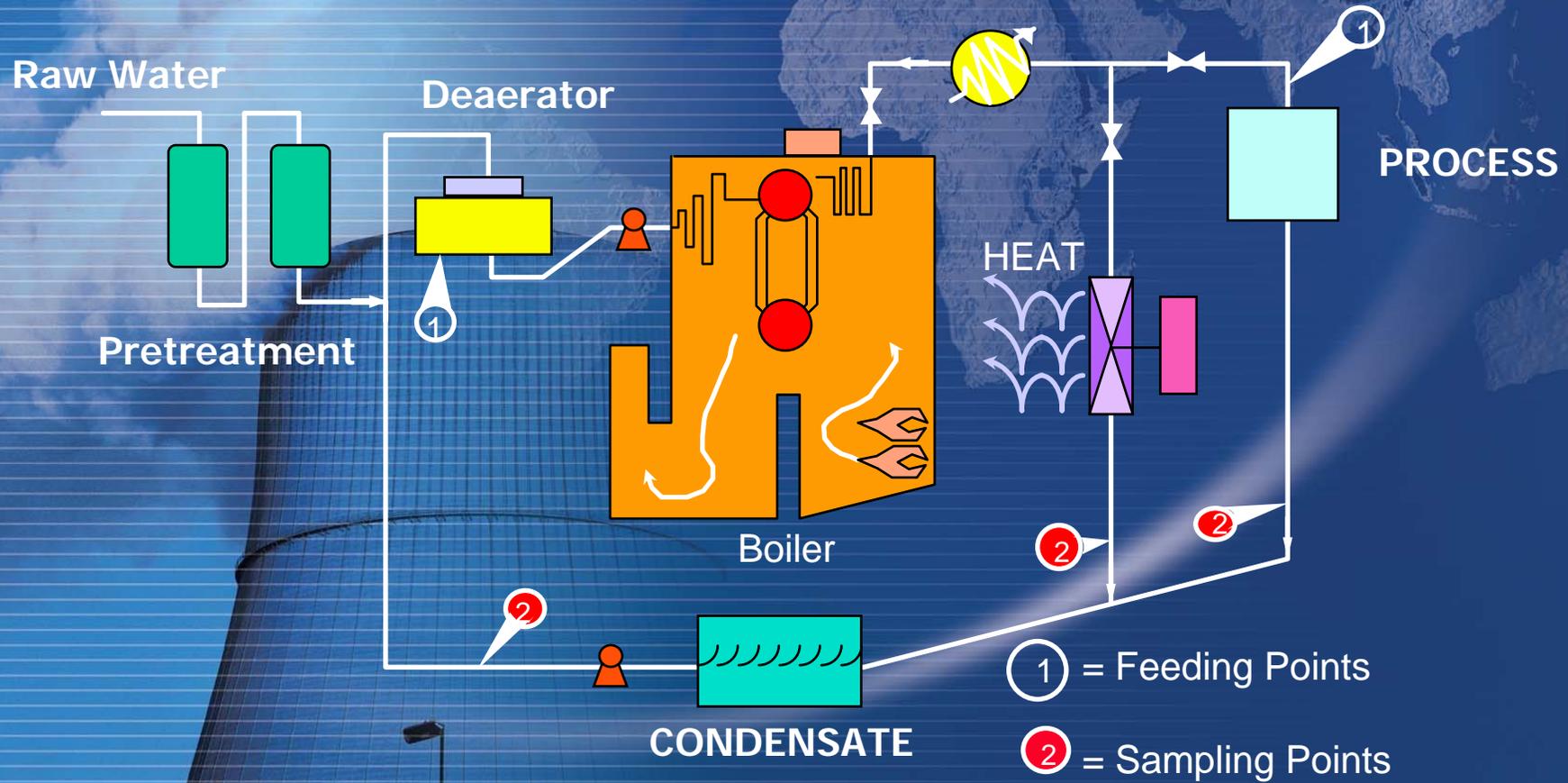
➤ *Ascorbic and Erythorbic acid*

- Promotes Magnetite Layer
- Residue Easy to Analyse
- Does not add Solids
- Suitable for Attemperating Water



WATER TREATMENTS

BOILERS – *Layout*





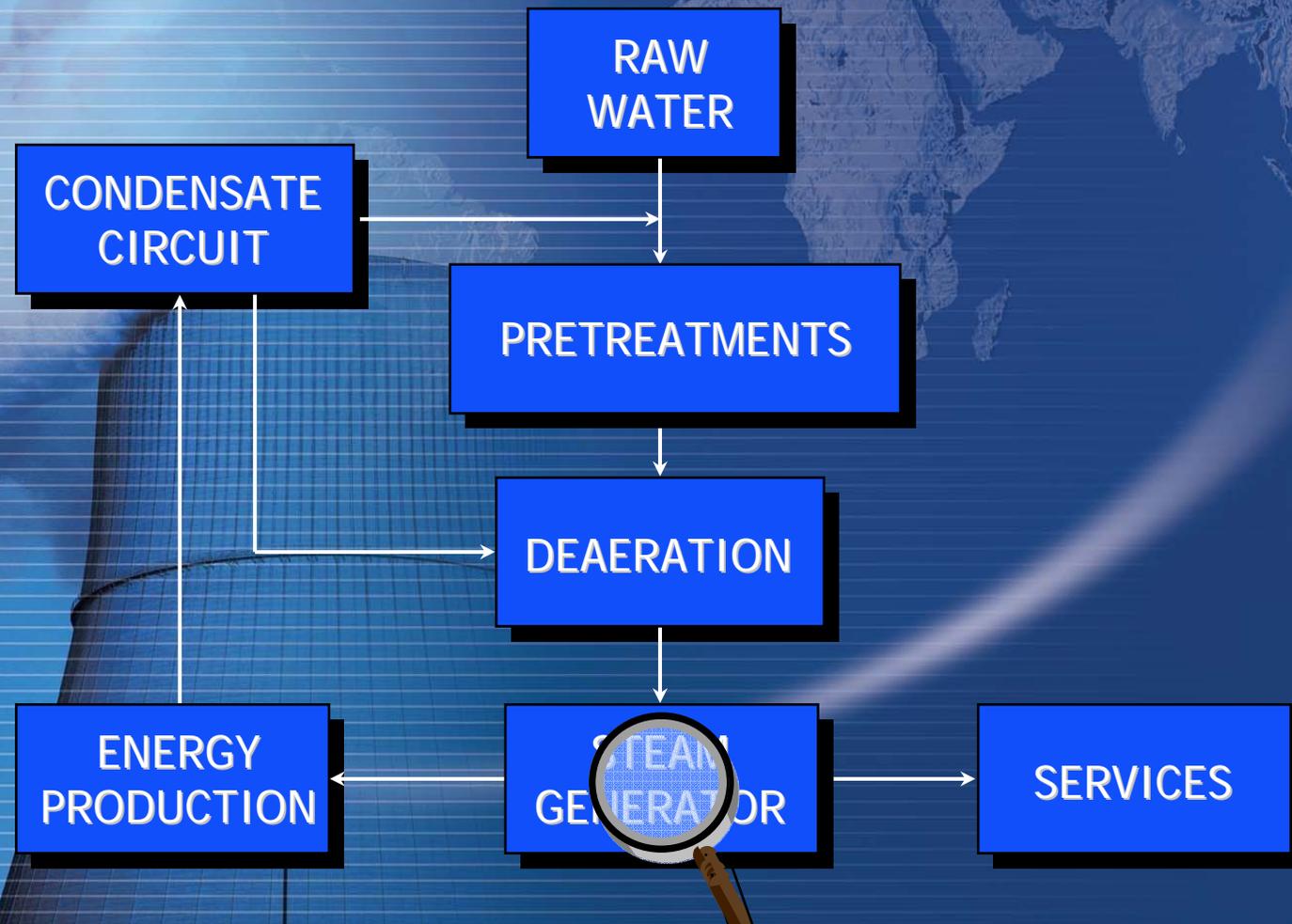
WATER TREATMENTS

End of Part 3



WATER TREATMENTS

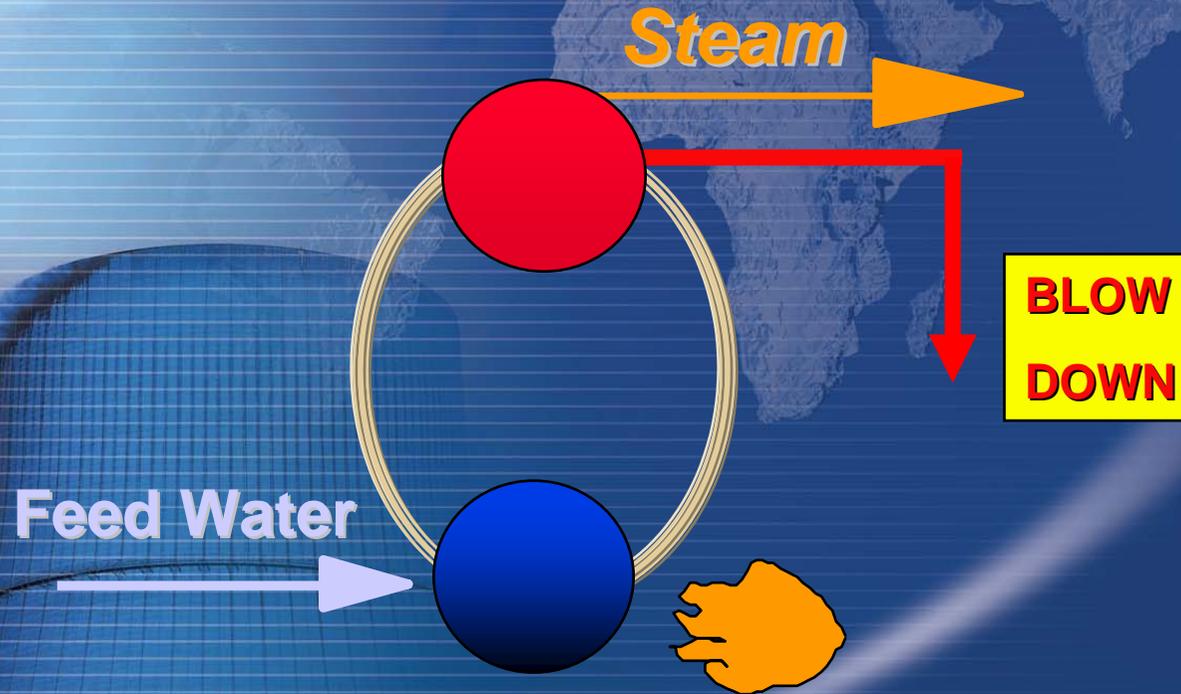
BOILERS – *Water Flow Diagram*





WATER TREATMENTS

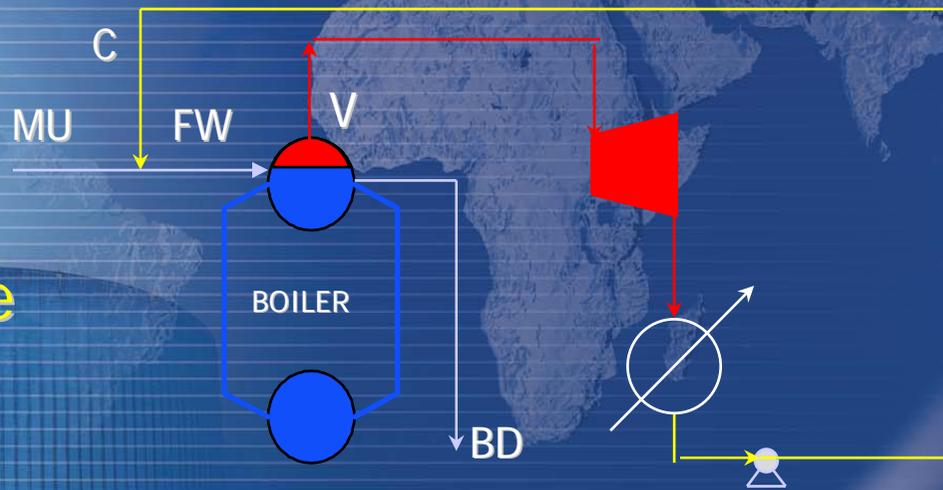
BOILERS – *Steam Generation Systems*





WATER TREATMENTS

BOILERS – *Steam Generation Systems*



Global Mass Balance

$$FW = V + BD$$

$$FW = C + MU$$

Single Species Mass Balance

$$X_{FW} \times FW = X_{BD} \times BD$$

$$\left\{ \begin{array}{l} \frac{X_{BD}}{X_{FW}} = \frac{FW}{BD} = N_C \\ BD = \frac{V}{N_C - 1} \\ BD = \frac{FW}{N_C} \end{array} \right.$$



WATER TREATMENTS

BOILERS – *Steam Generation Systems*

Firetube

↪ Water flows outside the tubes

↪ Low capacity (20 ton/h)

↪ Low heat exchange efficiency

↪ Low installation costs

Watertube

↪ Water flows inside the tubes

↪ High capacity (100 ton/h)

↪ High heat exchange efficiency

↪ High installation costs

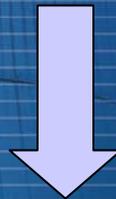


WATER TREATMENTS

BOILERS – *Steam Generation Systems*

↳ *Corrosion phenomena*

↳ *Deposition phenomena*



*Enhanced by Working Conditions
(Temp, Press, Thermal flux)*



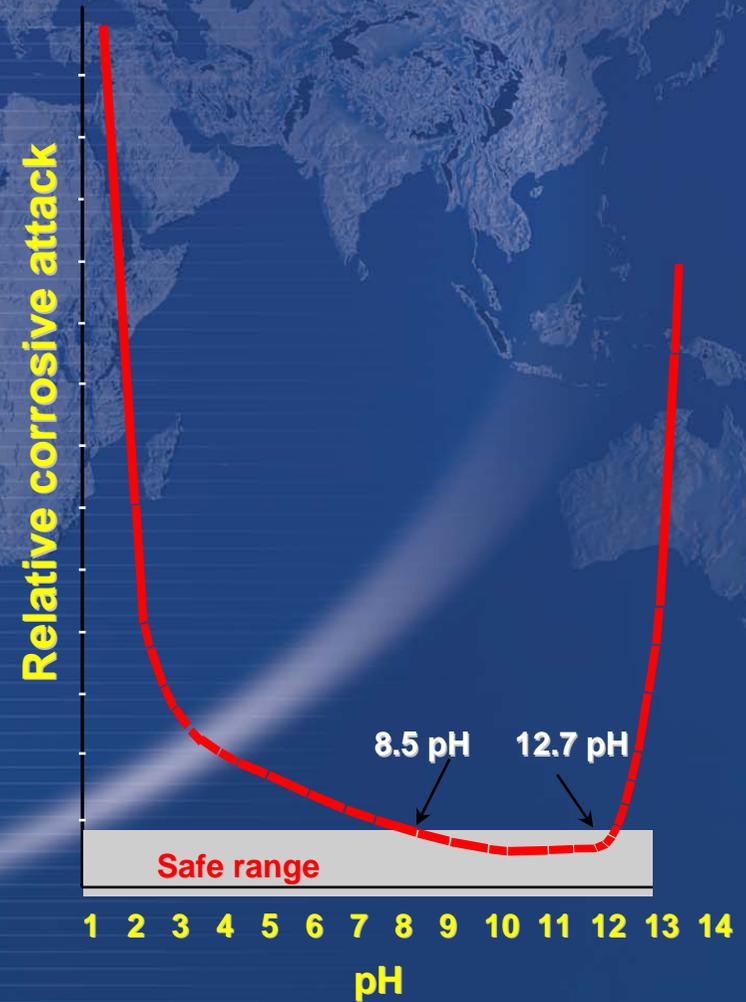
WATER TREATMENTS

CORROSION in BOILERS

- Maintenance Costs
 - Equipments spoiling
- Keeping Targeted Production
 - Unscheduled shutdown

TYPES of CORROSION

- *Oxygen Attack*
- *Acid Corrosion*
- *Caustic Corrosion*



TYPES of CORROSION

➤ *Oxygen Attack*

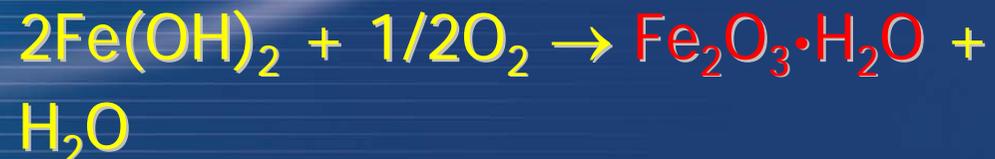
Anode Reaction (Oxidation):



Cathode Reaction (Reduction):



Fe precipitates as $\text{Fe}(\text{OH})_3$ and



Oxygen Pitting

(self activating mechanism)

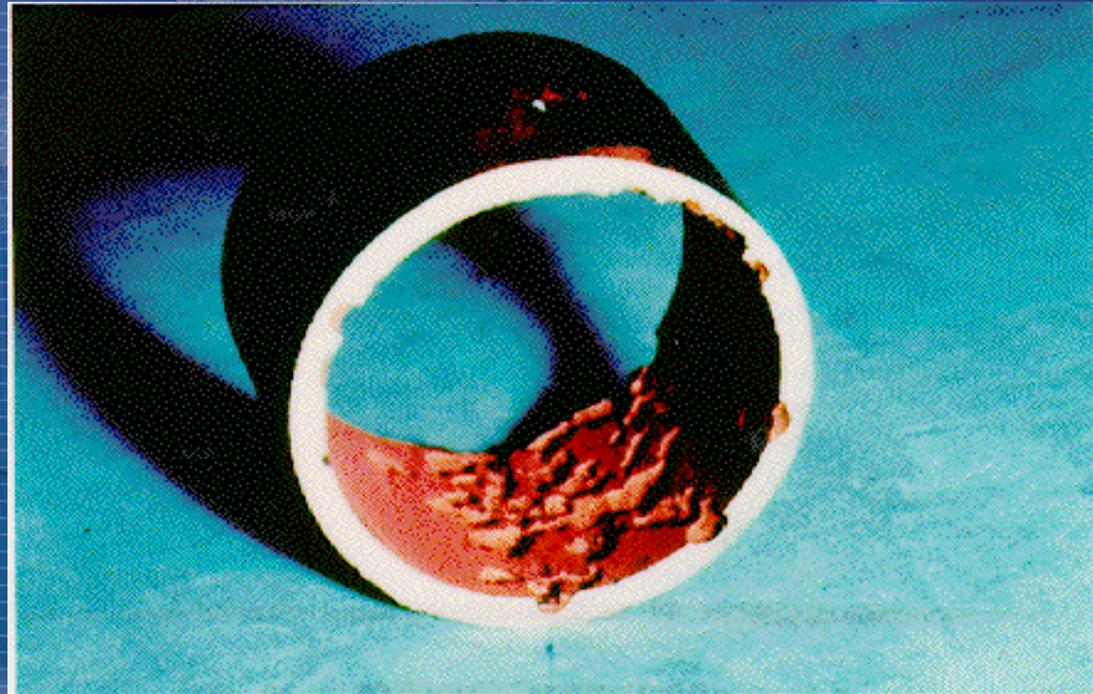


WATER TREATMENTS

TYPES of CORROSION

➤ *Oxygen Attack*

Oxygen Pitting
(self activating mechanism)



TYPES of CORROSION

➤ *Acid Corrosion*

↳ *Improper operation or control of demineralization anionic unit, inlet of acidic hydrolysis' salts (e.g.):*



↳ *Contaminated cooling water*

↳ *Feedwater at low pH*



WATER TREATMENTS

TYPES of CORROSION

➤ *Acid Corrosion*



Internal Wall Surface Corrosion

TYPES of CORROSION

➤ *Caustic Corrosion*

↳ *Takes place with high caustic concentration*



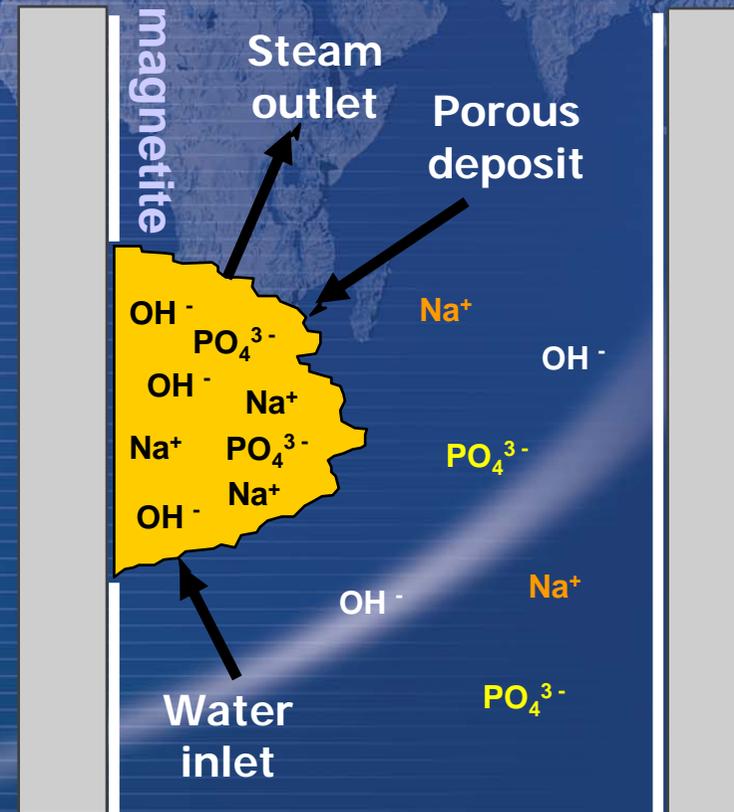
Magnetite protective layer is dissolved

➤ *Caustic Corrosion*

In presence of deposits results in:

↳ Steam nucleation areas

↳ Slits and cracks allowing steam to flow





WATER TREATMENTS

TYPES of CORROSION

➤ *Caustic Corrosion*



Caustic Corrosion due to high pH

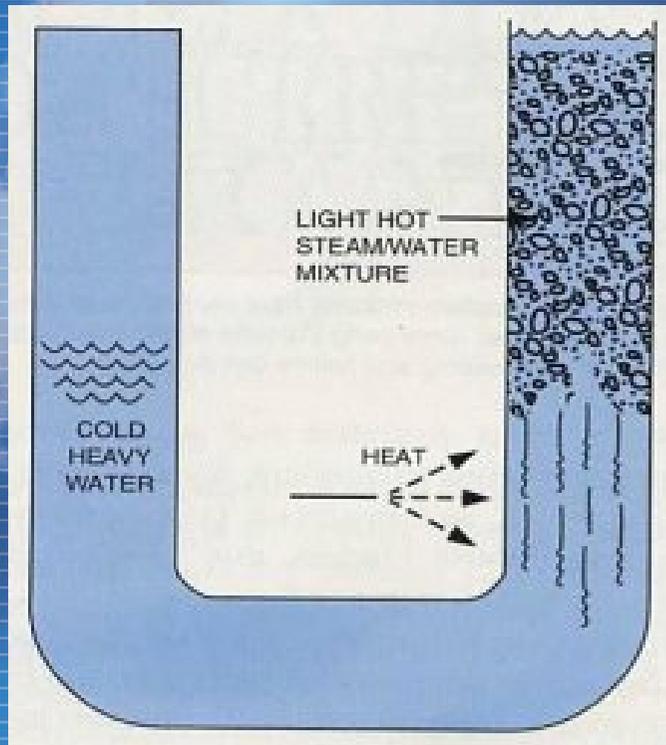


WATER TREATMENTS

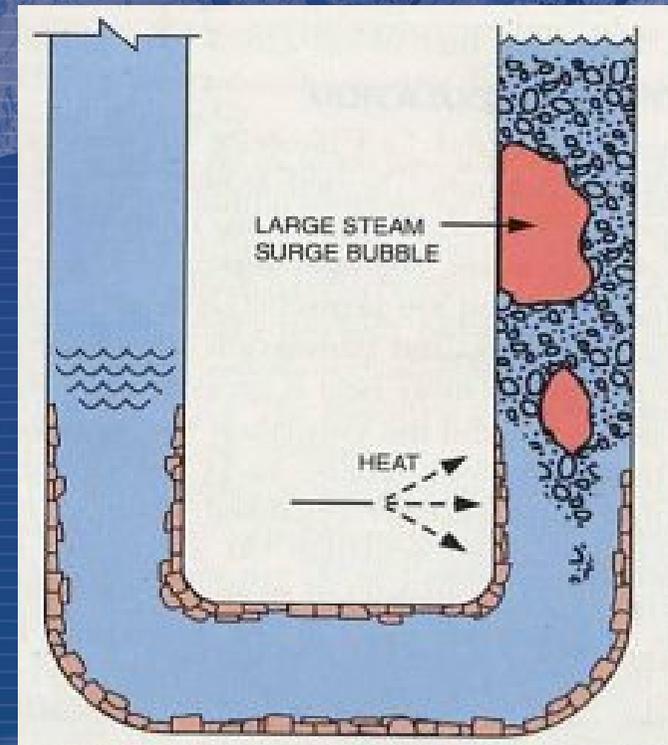
DEPOSITION in BOILERS

- Maintenance Costs
 - *Breaking down for local overheating*
- Keeping Targeted Production
 - *Unscheduled shutdown*
- Energy Costs
 - *Lower heat exchange efficiency*

DEPOSITION in BOILERS



Clean Tubes: correct water/steam formation



Deposits in Tubes: incorrect water/steam formation



WATER TREATMENTS

DEPOSITION in BOILERS



Deposition leads to clogging of Tubes and Pipes



WATER TREATMENTS

DEPOSITION in BOILERS

Generated by

- *Feedwater's salts content*
- *Chemicals used for pretreatment*
- *Corrosion byproducts*
- *Contaminants*



WATER TREATMENTS

DEPOSITION in BOILERS

Suspended Solids

WATER

Dissolved Solids

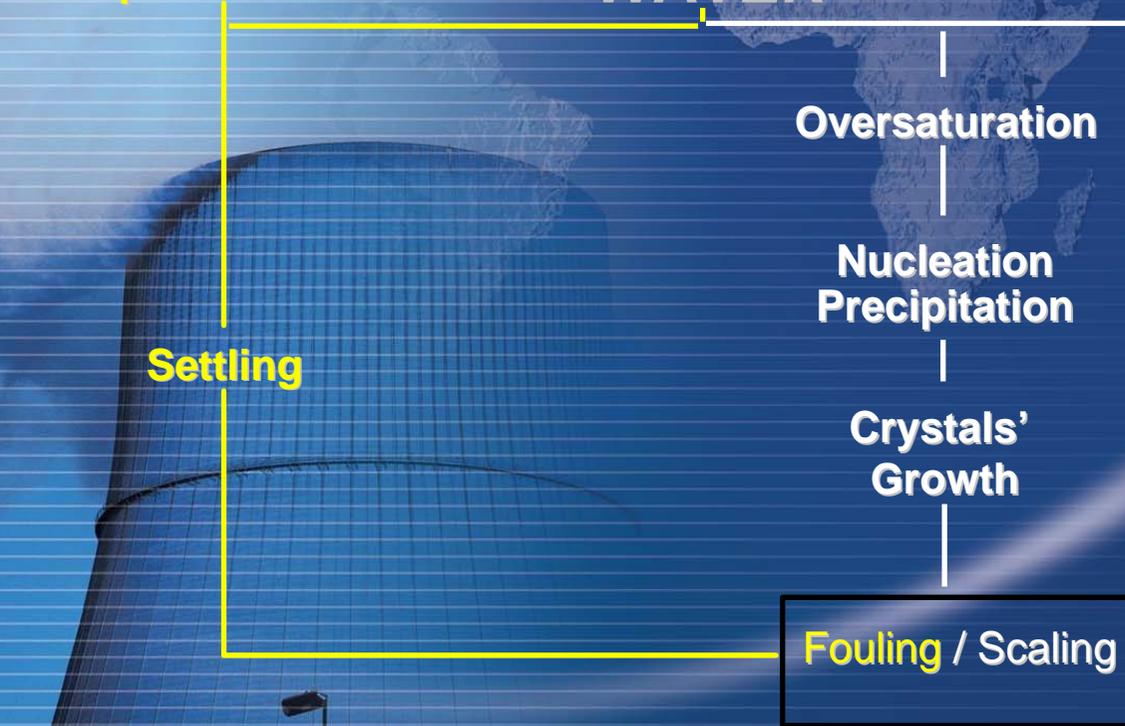
Oversaturation

Nucleation
Precipitation

Crystals'
Growth

Fouling / Scaling

Settling





WATER TREATMENTS

INTERNAL TREATMENTS

◆ *Coordinated phosphate/pH control*

↪ *Can control corrosion*

↪ *Uses Phosphates to control pH and neutralizes NaOH excess*

↪ *Contains deposition control polymers*

◆ *Phosphate dispersant*

↪ *Precipitating treatment*

↪ *Polymers keep sludges and metal oxides suspended*

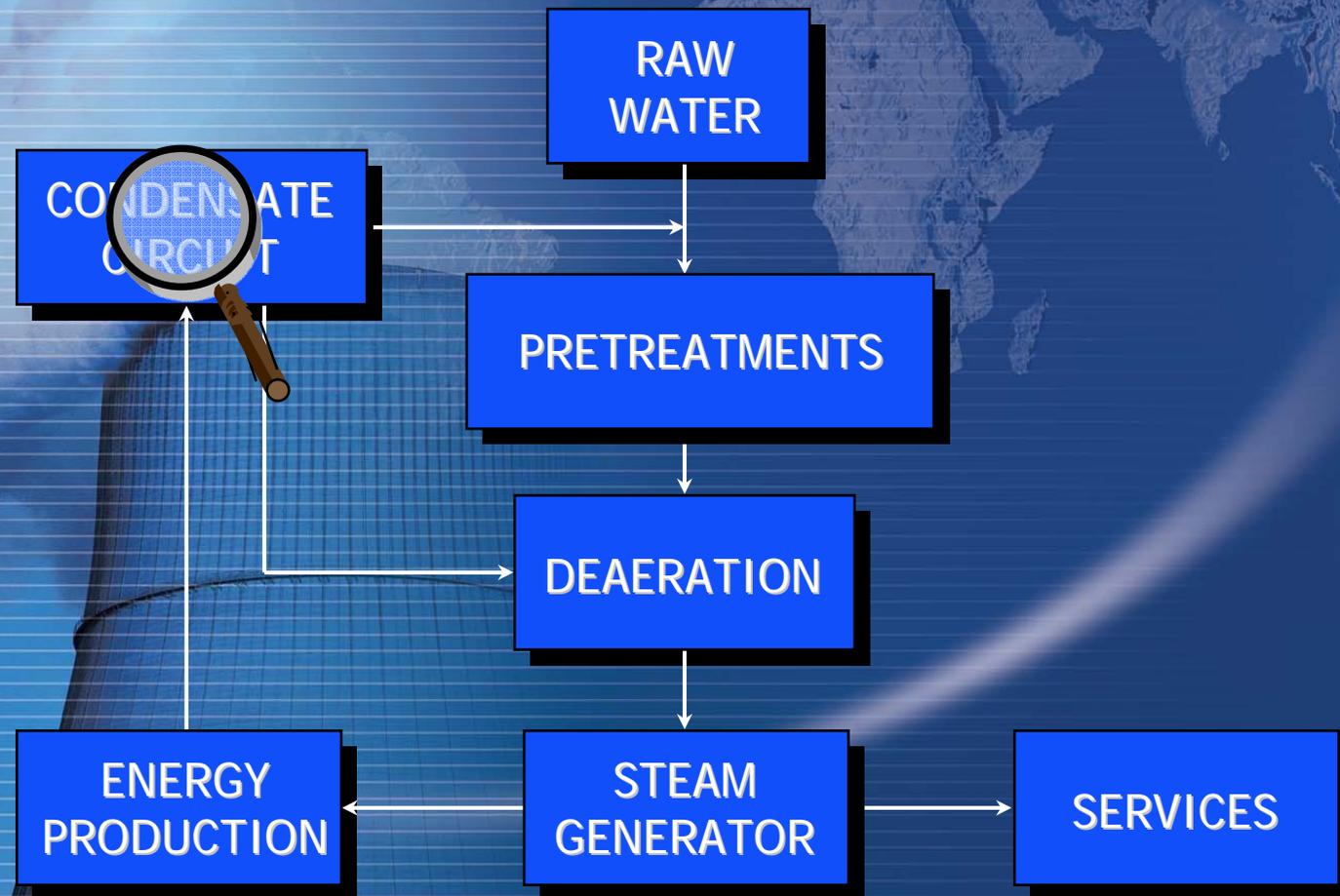
↪ *Uses phosphates residues for treatment's control*

◆ *All polymer*



WATER TREATMENTS

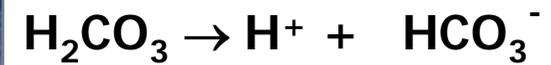
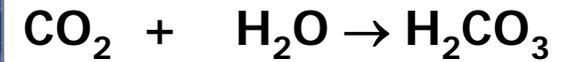
BOILERS – *Water Flow Diagram*





WATER TREATMENTS

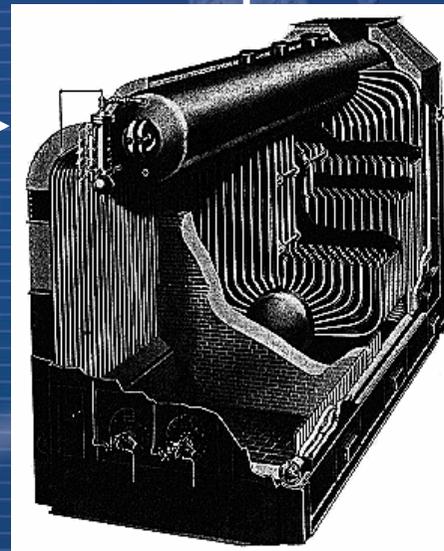
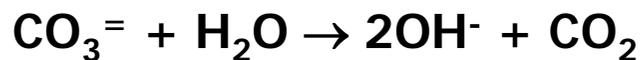
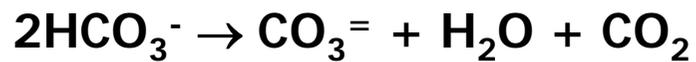
CONDENSATE CIRCUIT



STEAM
CO₂

FEED WATER
HCO₃⁻
CO₃⁼

At Boiler working conditions:



BLOWDOWN
OH⁻



WATER TREATMENTS

CONDENSATE CIRCUIT

O₂ BOOSTS CORROSION

↳ Air Inlet

Vacuum systems

Subcooled systems

↳ Raw Water Inlet

Condenser losses

↳ Poor Oxygen Removal



WATER TREATMENTS

CONDENSATE CIRCUIT - *Treatments*

◆ Neutralizing Amines

Hydrolysis Reaction: $R-NH_2 + H_2O \leftrightarrow R-NH_3^+ + OH^-$

Neutralization Reaction: $R-NH_2 + H_2CO_3 \leftrightarrow R-NH_3^+ + HCO_3^-$

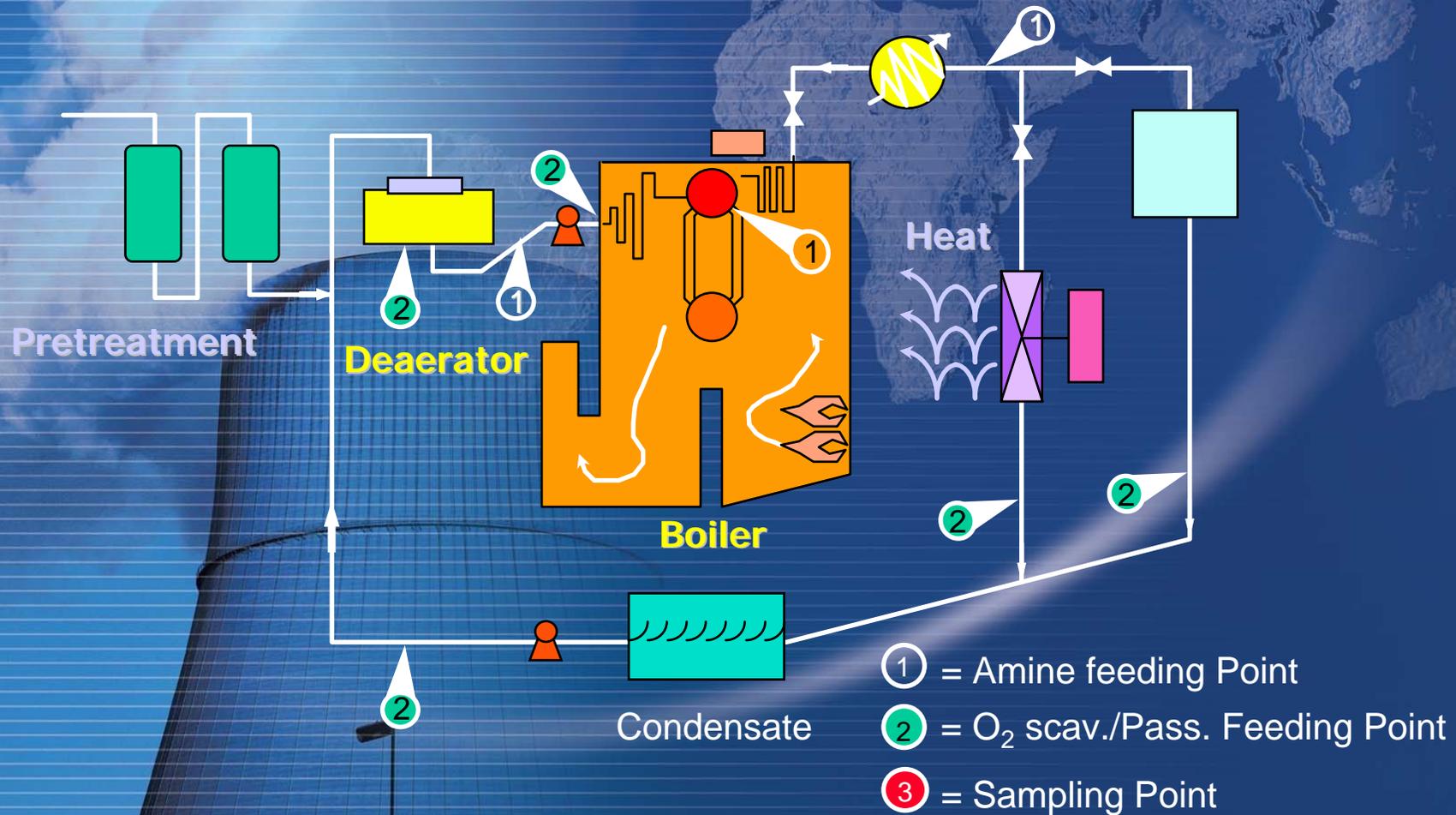
◆ Filming Amines

Create a Monomolecular layer on metal surface, avoiding contact with Water (hydrophilic/hydrophobic parts)

◆ Oxygen Scavenging / Passivation

Reaction with O_2 in feedwater and condensate
Neutralization of condensate acidity

BOILERS – Layout Condensate Circuit





WATER TREATMENTS

CHIMEC selected programme consists of:

- ◆ CH 4263: Carbohydrazide Oxygen Scavenger
- ◆ CH 3665: Coordinated pH / Phosphate corrosion inhibitor and dispersant
- ◆ CH 1764: Neutralising Amines Blend for Condensate Circuits



WATER TREATMENTS

CHIMEC Products: Health & Safety

- ◆ All the selected chemicals might be considered safe if handled correctly.
- ◆ CHIMEC highly recommends to:
 - ◆ properly store & handle the chemicals
 - ◆ follow the safety practices
 - ◆ wear always the most suitable personal protective equipment, be sure you know the basic chemical properties of the Product (its recovery measures etc.)
- ◆ *Be Safe, Work Safe*



WATER TREATMENTS

Boiler's Water Treatments' Technology

Nov 2006

*...Thank You for Your
Attention...*

CHIMEC S.p.A. – Water Technology Unit