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Scaling, Corrosion and Water Treatment on Steam Generator Systems < 30 bar

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Introduction of Referent

The referent is senior expert with over 40 years experience in Materials Investigation, Failure Analysis, Water Chemistry and Corrosion in TÜV SÜD Industry Service, Munich, Germany.

1   Basics in Scaling, Corrosion and Water Constituents

1.1   Scaling

Scale in steam generators first must be divided into

- essential necessary dark brown to black, very thin (< 0.1 mm), dense, protective iron oxide layer (of magnetite), like very thin mill scale, which leads *not* to increased wall temperature,

- undesired, mostly grey or brownish white, porous scale of water impurities (mostly hardness scale or silica scale), which leads to more or less elevated wall temperature

- light brown to red brown deposits of porous iron corrosion product (mostly due to the iron content in boiler feedwater [BFW]) – heavily avoidable – and/or

- local blisters or bark like deposits due to oxygen corrosion during shut down.

All well-designed steam generators and hot water boiler - shell boiler and water tube boiler - achieve satisfying lifetime *only* if the boiler steel is able to develop and to maintain the mentioned thin protective magnetite (Fe_3O_4) layer during operation and shut down.

Undesired deposits of water constituents and/or corrosion product increase the wall temperature of furnaces depending on layer thickness, composition and porosity and may to lead material over-heating, subsequent loss in material strength, boiler damages or explosion. Particularly dangerous is silicate scale (**Fig. 1**) and scale containing oil or fat.

Fig. 1 Thin silicate scale on a fire tube of a shell boiler
led to a severe fire tube deformation due to over heating

1.2   Corrosion

Corrosion is the - mostly electro-chemical - reaction of a metallic material with its environment that results in a damage of the material or component before its regular lifetime.

The area where a metal corrodes respectively is going into solution in form of metal cations, like iron (Fe^{++}), is called *anode.*

The area where the ambient electron conductive medium (electrolyte, mostly water) reacts with the electrons of the anodic reaction is called *cathode.* For this reaction e.g. oxygen (O_2) is reduced to hydroxyl (OH^-) anions (oxygen corrosion type) or hydrogen (H^+) cations from an acid are reduced to atomic hydrogen (hydrogen corrosion type).

In boilers, the mainly observed corrosion is predominantly the result of different conditions of the protective magnetite layer (e.g. porous spots and dense layers), defects in the magnetite layer (e.g. cracks due to different strain) or different aeration conditions of the magnetite layer (e.g. on top and underneath of deposits, above and below water level lines). It is important to know that the magnetite protective layer is more brittle than steel and more noble than steel!

The reactions on the most common *oxygen corrosion* on iron or steel are shown in **Fig. 2**.

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Fig. 2   Principles of oxygen corrosion

Oxygen corrosion, which leads to local corrosion (pitting), can be frequently observed
- during stand still of boilers (if the pressure is 0 and steam is replaced by air), **Figs. 3+4** and
- as atmospheric corrosion on carbon steel.

Fig. 3   Oxygen corrosion on fire tube   **Fig. 4**   Oxygen corrosion on smoke tube
              of a horizontal shell boiler   of a horizontal shell boiler

Fresh oxygen corrosion appears yellow-brownish, older corrosion and already heated corrosion spots brown to dark brown. Corrosion effects are intensified by increasing conductivity. Other form of corrosion on lower pressure boiler systems is

- *acid corrosion* due to carbonic acid within steam and condensate lines, see **Figs. 5+6**, because corrosion on carbon steel is as higher as lower the pH, and

- *erosion corrosion* or *flow assisted corrosion (FAC)* and *cavitation,* both significantly affected by flow conditions.

Figs. 5 + 6 Carbonic acid corrosion on condensate return tube (right = enlargement)

FAC may be observed on pumps and pump impellers as well as on water pipes and valves as the result of a too low pH in combination with too high flow rate, see **Fig. 7**.

Cavitation is the result of steam bubble formation and their subsequent implosion (distinct audible!), e.g. on top of condensate pipes with condensate/steam mixtures, see **Fig. 8** or pumps operating in hot water. Elevated pressure at pump inlet solves the problem.

Fig. 7 Erosion corrosion on a steam   **Fig. 8** Cavitation on top side (12:00
              block valve used as control valve   position) of condensate return pipe

1.3   Water Constituents, Definitions

Natural waters (rain water, river water, well water, domestic water etc.) have, depending of its origin, very different composition. The most clean natural water is rain water. All other waters have undissolved (e.g. river water) and more or less dissolved constituents, like hardness, silica, iron, manganese, organics, oxygen etc.

Following definitions are frequently used to determine waters. Common impurities of waters and its effects and risks to boiler operation are explained.
1.3.1   Conductivity

The sum of all dissolved (electrical conductive) substances in water can be measured by the *electrical conductivity* (standard reference temperature 25 °C).
The conductivity depends on temperature and increases significantly with the temperature, e.g. 100 µS/cm at 25 °C increases to approx. 440 µS/cm at 100 °C.
SI-Unit / Definition: Siemens (S),   S = 1**:** Ohm (Ω, resistance),   1 S = 1,000,000 µS.

Water became electrical conductive due to dissolved salts, acids (also carbonic acid), lye (bases) and some organics, see **Fig. 9** – but silica doesn't affect conductivity!

Fig. 9 Specific conductivity at 25 °C of some solutions of acids (1,2), bases (3,4) and salts (5-10) in water.

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Dissolved in water, the above mentioned substances dissociate into ions with different electrical charge depending of their valence. The ions are divided into *cations* with positive charge, like mono-valent sodium ion (Na^+), bi-valent calcium ion (Ca^{++}) or tri-valent iron ion (Fe^{+++}) and *anions* with negative charge, like mono-valent chloride ion (Cl^-), bi-valent sulphate ion (SO_4^{--}) or tri-valent phosphate ion (PO_4^{---}).

Also water (H_2O) dissociates in traces into one mono-valent hydrogen (H^+) cation and one mono-valent negative hydroxyl ion (OH^-), which leads to a very little electrical conductivity. Purest water shows a conductivity at 25 °C of ca. 0.055 µS/cm corresponding to a specific resistance of about 18.2 MΩ·cm = 18,200,000 Ω·cm!

For comparison, in Asia rain water may have a conductivity about 10-20 µS/cm, river water (unaffected from sea water) 100 - 300 µS/cm and well water or domestic similar values. River water near the sea and brackish water may have conductivity up to 10,000 - 20,000 µS/cm. The conductivity of waters affects corrosion activities, as higher the conductivity as higher the corrosion rate.

1.3.2   pH-Value

The very low dissociation of pure water defines the neutral pH of 7.0, values below pH 7 characterise acidic conditions with increasing acidity down to pH 0 and pH values above 7 that of basic or alkaline conditions up to pH 14. Attention: Any single pH-step results to a 10 fold concentration change! For instance, 0.4 mg/l caustic soda (NaOH) in pure water result to a pH of 9, a content of 4 mg/l NaOH to pH 10, 40 mg/l to pH 11 and 400 mg/l NaOH to a pH of 12 etc. A caustic alkalinity of 1 mmol/l corresponds to 40 mg/l caustic soda (NaOH).

Moderate alkaline water conditions (pH 9-12) are important to protect iron from corrosion! Acid or acidic water dissolves the magnetite protective layer and attacks iron/steel.

1.3.3   Hardness

The total hardness of water (mainly calcium and magnesium compounds) must be divided into *carbonate hardness* and *non-carbonate hardness*.

Carbonate hardness (calcium-/magnesium-bi-carbonate) is only soluble in water together with a specific amount of carbonic acid (carbon dioxide dissolved in water). If this amount of carbon dioxide is removed due to boiling or reduced by spraying on air or heating, calcium carbonate (lime stone) will precipitate and forms carbonate scale.
In tropical and sub-tropical countries with heavy rain falls and little lime stone formation, the carbonate hardness of raw water is relatively low.

Non-carbonate hardness (calcium-/magnesium-chloride, -sulphate, -nitrate etc.) itself is well soluble in water, only calcium sulphate (gypsum) forms scale if its concentration exceeds about 2 g/l = 2,000 mg/l. Raw water - particularly river water contaminated with sea water - or brackish water, shows high non-carbonate hardness because sea water contains - beside very high sodium chloride content - also much calcium and magnesium chloride.

In presence of silica (silicon acid, silicon oxide) both, carbonate and non-carbonate hardness are forming scale of calcium-/magnesium-silicate (silicate scale), which reduces heat transfer extremely.

The most easy, safe and common way to remove hardness is application of a softener. It exchanges calcium and magnesium compounds to highly water soluble sodium compounds.

1.3.4   Alkalinity

Alkalinity allows determination of different water constituents, which are important for boiler operation, by an easy titration method using 0.1 N acid for (positive) + M/P-values and 0.1 N

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base for (negative) – P/M values. Alkalinity is divided into *total alkalinity*, *composite alkalinity* and *caustic alkalinity.*

The *total alkalinity* (+ M-alkalinity) indicates bicarbonates (e. g. from carbonate hardness, or sodium bi-carbonate [reaction product of carbonate hardness in softeners] and includes the composite alkalinity (+ P-alkalinity) and caustic alkalinity - if any. As far as water shows only + M-alkalinity, only bi-carbonates exist (like carbonate hardness or sodium bi-carbonate, which is typical for raw water).

A negative M-value (– M-value) indicates acidic conditions at a pH below 4.3 and must be titrated with 0.1 N NaOH.

The *composite alkalinity* (+ P-alkalinity) indicates all alkaline compounds above a pH 8.2 like sodium carbonate, tri-sodium phosphate and free caustics (e.g. caustic soda) and has replaced measurement of *caustic alkalinity.* Composite alkalinity includes caustic alkalinity!

A negative P-value (– P-value) indicates a pH below 8.2 and weak alkaline and acidic conditions respectively and must be titrated with 0.1 N NaOH.

The *caustic alkalinity* indicates the content of free caustics only, but needs a special procedure before titration against P-indicator (Phenolphthalein).

The M-indicator (Methylorange) changes its colour at pH 4.3, the P-indicator (Phenolphthalein) at pH 8.2, which means in presence of P-alkalinity the water is alkaline! The connection between +/ – P -value, +/ – M-value and pH and the changes of the indicators can be seen in **Fig. 10**.

For shell boiler, the boiler water should be at least tested for composite alkalinity (P-alkalinity) and total alkalinity (M-alkalinity).

Fig. 10

1.3.5   Silica / Silicate

In tropical and sub-tropical countries with heavy rain falls, raw water has regularly medium to high concentrations of silica (silicon oxide) and/or silicates (compounds of silica with e.g. calcium, magnesium, aluminium, e. g. alumo-silicates = clay), particularly river after heavy rain fall. Both, silica and silicates origin from under-ground materials like granite, mica, clay, basalt etc.; lime stone (calcium carbonate) contains only little silica and has been mostly dissolved by rain water.

Silica and silicates can be present in dissolved and quasi dissolved (colloidal) form and are not easy to eliminate or to reduce by water treatment. Mechanical filters and softener are unable to eliminate e.g. calcium-silicate and silica.
The solubility of silica (silicon oxide) in water increases strongly by temperature and alkalinity. In neutral or weak alkaline water the solubility is relatively low, which results to formation of silicon scale.
Silicates are almost insoluble in water, except alkali (Na, K) silicates, which leads to silicate scale if silica and hardness comes together in absence of phosphate.

1.3.6   Iron, Manganese

Iron and manganese compounds are frequently present in ground water or well water, if their oxygen content is low. This happens mostly in undergrounds with organic substances like river sediments - in some cases presence of hydrogen sulphide is likely.
Iron and manganese compounds may lead to scaling in piping systems due to iron ochre. After

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contact with oxygen (air) brown flocks are formed that may cause deposits in softeners and reduce the activity of softener resin. Iron compounds lead to brown stains on fabrics.
In many cases aeration makes iron compounds removable in mechanical filters. For manganese compounds aeration is often insufficient and stronger oxidation measures are necessary.

1.3.7   Organics

Organics in raw water may origin from nature (e.g. rotted leaves, peat) or human or industrial sources (e.g. waste water, industrial effluents), also condensate return can be contaminated through product (e.g. milk, vegetable oil, solvents). Many organics lead to foam formation in steam generators that affects the steam quality due to carry over of boiler water. Some organics, like sugar and alcohols decompose to organic acids and lower the pH of the boiler water. Oil and fat is able to set level control systems out of order, to block side glasses and may form dangerous scale. Hydro carbons with boiling point below approx. 130 °C regularly do not have negative effects to boiler.

1.3.8   Gases (Oxygen, Nitrogen, Carbon dioxide etc.)

Oxygen, nitrogen and carbon dioxide is always dissolved in water if it is or was exposed to air. The solubility of all gases in water depends strongly on temperature, see **Fig. 11**. Oxygen leads to oxygen corrosion on carbon or low-alloyed steel if the pH is too low and/or the steel can not form or maintain a protective layer of magnetite. Nitrogen does not harm boiler operation. Carbon dioxide lowers the pH-value and leads to acid corrosion on carbon steel.

Fig. 11: Solubility of oxygen and nitrogen in pure water at 1 bar absolute

Oxygen and nitrogen in water is easy to reduce by heating and becomes nearly zero at boiling conditions! Some chemicals, like sodium sulphite and hydrazine are able to bind oxygen chemically. Carbon dioxide can be only removed by heating if the water's pH is below 7-8 or at pH > 8, if the operation temperature of a thermal deaerator is above 135-140 °C.

2   Water Treatment

Water treatment in this paper means any method to minimise scaling or corrosion in boilers.
It can be done in form of an "*Inner water treatment*" or "*Extern water treatment*".

- *Inner boiler water treatment* or "chemical treatment" means treatment by exclusively dosing of chemicals to the boiler feedwater or boiler water with the consequence of sludge formation within the boiler itself. Presupposition for this kind of water treatment is limited heat transfer (steam production < 25 kg/m²·h), coal or wood firing (not oil!) and sufficient blow down. The inner side of the boiler must be easy accessible to remove sludge.
This method may be used for small vertical shell boiler only.

- *Extern boiler water treatment* applies at least softening to bind hardness on the softener resin and replace hardness by sodium, but can be improved by additional reverse osmosis (RO) units or e.g. demineralisation. This treatment can be used for any kind of steam boiler but requires also sufficient blow down to meet the related boiler feedwater and boiler water requirements. *It must be applied for water tube boiler!*
The treated water is mostly dosed (conditioned) with some chemicals to adjust e. g. pH or alkalinity. Thermal deaeration is also an external treatment step.

- *Physical water treatment*, using e.g. magnets, high frequency fields, high voltage fields etc. is a *not accepted method for boiler feed water or boiler water treatment*, because all this methods do *not* remove hardness and do *not* affect silica or silicates!

2.1   Inner boiler water Treatment

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Scaling doe to hardness and silicates can be significantly reduced if sufficient tri-sodium phosphate is dosed proportional to the fed hardness and feedwater flow. Carbonate and non-carbonate hardness react with phosphate and form calcium- and magnesium- phosphate sludge, which remains mostly in suspended form in the boiler water. During operation, the sludge must be removed by sufficient blow down. After operation, sediment sludge must be removed by additional blow down.

Phosphate has a higher affinity to calcium and magnesium than carbonate or silica and avoids formation of carbonate and silicate scale. In parallel carbonate hardness becomes exchanged to sodium carbonate, which is alkaline, increases alkalinity and the solubility of silica.
For one cubic meter (m^3) water with 1 meq/l hardness, an amount of 120 g tri-sodium phosphate (technical grade with 10 mol of crystal water, $Na_3PO_4 \cdot 10\ H_2O$ [20 % P_2O_5]) dissolved in at least 5 l water is necessary. For instance, to treat 1 m^3 feedwater with 3 meq/l = 1,5 mmol/l = 150 mg/l $CaCO_3$ total hardness an amount of ca. 350 g $Na_3PO_4 \cdot 10\ H_2O$ is necessary.
Inner boiler water treatment is easy, as far as the total hardness of the raw water is low (less than 1-1.5 mmol/l), or rain water is used.

2.2   Extern boiler water treatment

2.2.1   Softening

Softening is a simple and safe way to eliminate hardness from a clear water (turbid water must be treated before e. g. with sand filter) by using filters filled with softener resin (mostly honey-brown beats with 0.6-1.5 mm diameter made of strong acidic cation exchanger in sodium form). This resin is able to exchange hardness (calcium and magnesium salts) into sodium compounds, that are - in comparison to hardness - all highly soluble in water. The resin keeps the hardness ions and releases sodium ions, that means e.g. calcium bi-carbonate is exchanged to sodium bi-carbonate, magnesium chloride to sodium chloride etc. all other constituents were not changed. During operation cycle the hardness is < 0.02 mmol/l = < 2 ppm $CaCO_3$.
Common softener resins have a hardness capacity of 0.6-0.7 mol/l corresponding to 60-70 g $CaCO_3$ per litre resin. For instance 50 l sufficient regenerated resin can exchange ca. 3,200 g $CaCO_3$ or are able to soften approx. 30-32 m^3 water with 100 mg/l $CaCO_3$.

If the resin is loaded with hardness and not anymore able for the mentioned ion exchange (it is exhausted) operation must be stopped. It must be brought back into the required sodium form by application of an excess of salt (sodium chloride, NaCl) solution (brine), which is called regeneration. The salt must not have too much insoluble impurities to avoid blockage of the resin filter bed! Principles about softening and regeneration show **Figs. 12 & 13**.

Fig. 12:

Fig. 13

Regeneration takes ca. 60 minutes and includes following steps: Back washing (to remove unsolved particles from the resin bed, but not too fast - otherwise resin is lost!), application of clear brine for about 30 minutes, rinsing of the brine, final rinsing and testing for hardness.

Necessary equipment for continuous supply of softened water: 2 softener filter (or one and a storage tank) made of coated steel or glass fibre reinforced polyester, filter internals and resin, flow meter, water meter, sampling valve for softened water, brine tank with side glass or level control, injector to dilute brine to about 10 % salt solution and drain valve.

Attention: Softening is the minimal requirement for oil fired steam or hot water boiler with common heat transfer and for water tube boiler, if there are no further requirements to boiler operation and steam quality. Optimised quantity of condensate return is very advantageous.

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2.2.2 Reverse Osmosis (RO, Desalination)

Reverse Osmosis is an excellent physical method to reduce the content of all dissolved solids of water (e.g. total hardness, chlorides and silica) to a minimum that leads to a major reduction of its conductivity, principle is shown in Fig. 14.
RO is quasi an ultra filtration method that separates bigger water soluble ions from little water molecules but removes also undissolved matter (e.g. clay, iron oxide), organic substances and micro organism (e.g. bacteria and germs). The latter noted bigger size matter is able to block the pores of the polymer membranes of RO modules as well as hardness deposits and colloids. Micro organism likes to eat the polymer membranes and may damage the membranes irreversible. If not domestic water with restricted content of germs is used, the water must be disinfected with chlorine, hypo-chloride or better with ozone (it reduces also organics) but excess chlorine or ozone must be removed in an activated carbon filter.
The water for RO units must be really clear, must have only restricted amount of organic matter and micro organism and must be treated to avoid precipitation of concentrated water constituents in front of the membrane surface, like hardness.

About 70 % of the water to a RO unit can be received as treated water, 30 % must be drained.

An acceptable life time of 3 to 5 years of RO modules can be achieved only, if there is a sufficient, professionally operated water pre-treatment of the water before entering the membrane module and if the membrane is rinsed, cleaned and disinfected in periodical intervals, particularly for longer shut-down. RO units should operate continuous feeding a storage tank from where water is taken out on demand.
To avoid precipitation of hardness for smaller RO units (< 20-40 m³/day) upstream of a RO unit first softening of the raw water is recommended.

The water downstream of RO-units (so called permeate) that is fed with softened water is free of hardness, shows low conductivity (regularly < 20 µS/cm, mostly due to sodium bicarbonate) and silica < 0.2 mg/l SiO_2!

During thermal deaeration, residual sodium bicarbonate decomposes to alkaline sodium carbonate, increases the pH and leads to an excellent weak alkaline BFW for low and medium pressure boiler.
For pH adjustment in the BW dosing of tri-sodium phosphate is essentially!

RO-units need less control, space for installation, chemicals and are for a water demand < 20-40 m³/day much cheaper and easier to handle than other treatment methods, but once again the water pre-treatment must be done professionally.
Permeate is recommended if the conductivity of the raw water or boiler feedwater is high and if better steam quality is required, e.g. for food production, cosmetic or pharmacy industry.
Optimised quantity of condensate return is very advantageous.

Fig. 14
Principles of Osmosis and
Reverse Osmosis (RO).

Fig. 15
Partly unrolled cross flow membrane
module

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2.2.3   Deaeration

Thermal deaeration is the simplest way to minimise the content of dissolved gases in water like oxygen, nitrogen and carbon dioxide, because their solubility in water depends strongly on the temperature and becomes zero at boiling conditions, see **Fig. 11**.
Common are tray deaerator, sketch see **Fig.16** operating at over-pressure of 0.3-1 bar. They heat the BFW to temperatures > 100 °C and reduce oxygen to the limits < 0.02 mg/l as far as the deaerator has a sufficient number (at least 4-5) of trays, like vertical deaerator. Horizontal deaerator with 2-3 trays reduces the oxygen content only to about 0.1-0.3 mg/l.

For smaller plant at least partial thermal deaeration at temperatures between 50 and 80°C is recommended, which can be easy achieved with sufficient hot condensate return and *indirect* heating with blow-down water using a tube coil within the storage tank. Remaining oxygen can be eliminated by dosing of an oxygen scavenger like sodium sulphite.

Fig. 16

3   Boiler Types and Water Requirements

3.1   Boiler Types

The boiler types are divided into
- *Shell boiler* with boiler water around the fire box respectively flame tube as well as around the smoke tubes and flue gas within the tubes and
- *Water tube boiler* with boiler water within the tubes, and flue gas around the tubes.
  The water tubes are connected to a steam drum to separate water and steam (drum boiler).

Vertical Shell or Package Boiler are mainly coal fired one-pass steam generator with fire box and some horizontal smoke tubes, operate at a pressure up to 10 bars and have steam capacity less than 2,000 kg/hr. Their specific steam production is regularly < 25 kg/m²·hr. Only on that type of boiler inner water treatment is acceptable!

Horizontal Shell boiler are mainly gas or oil fired, see **Fig. 17**, three-pass steam generator with one or two fire tubes as first pass and smoke tubes for second and third pass. The design restricts the operation pressures to ca. 30 bars and steam capacity to about 25 t/h. They are equipped mostly with economiser but rarely with super-heater. They were delivered as package on a frame and supply steam to small and medium scale plants, but occasionally also to large-scale plants as auxiliary boiler for start up. If they are heated by solid fuel (coal, wood etc.) they may have in front of the fire tube a compartment with water tubes.

Fig.17:

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The smoke tubes are fitted into the front and rear tube-sheet with a gap between tube and tube-sheet and welded at the flue gas side only, which leads to heated gaps at these spots and to localised concentration of boiler water constituents within the gaps.

Water-tube boiler are mostly gas/oil/coal fired steam generators with natural or assisted circulation for pressures up to 180 bar and a steam production in industrial plants up to approx. 500 t/hr equipped with super-heater, de-super-heater and feedwater pre-heaters.

Quick start up boiler are mainly small gas or oil fired water tube boiler with natural or forced circulation that produce saturated steam in less than 30 minutes but with higher BW content in steam than other boiler.

3.2   Definition of Water Types

Raw water is any water before water treatment took place, like domestic water, well water, river water, rain water etc.

Filtered water is water after a mechanical filtration to remove undissolved matter.

Softened water is water or pre-treated water downstream a softener using strong acidic cation exchanger in sodium form and salt (sodium chloride) as regenerant. The water is free of hardness (< 1 ppm $CaCO_3$ or < 0.01 mmol/l) but silica and conductivity is unchanged.

Decarbonised water is treated water downstream a lime hydrate decarbonisation after filtration or decarbonised water downstream a weak acidic cation exchanger. Both waters must be softened if used as make-up water. The water is distinct lower in carbonate hardness and conductivity but silica is unchanged if ion exchanger is used. Hot lime decarbonisation may reduce silica for 10-30 %.

Desalinated water is water from Reverse Osmosis units (permeate), that must be softened as make-up water for boiler if the water before the RO unit is not softened. The water shows at least a direct conductivity at 25 °C < 30 µS/cm (mostly < 10 µS/cm) and silica content < 0.5 mg/l (ppm) SiO_2.

Make-up water is treated water used as substitute for the loss of condensate in the system.

Condensate return is clean condensate return from consumers. It should not be mixed with make-up water before thermal deaeration. Possible contamination with impurities from production requires adequate online quality control and e. g. condensate treatment.
Condensate is valuable because it is clean water (with low conductivity and without hardness and silica) it is hot and contains energy. A condensate return of e.g. 50 % reduces the feedwater conductivity for about 50 %!

Boiler Feedwater (BFW) is the treated, conditioned and deaerated water fed to the steam generator. It is mostly a mixture of condensate return and make-up water. For pH adjustment and oxygen scavenging mostly "conditioning" chemicals are added.

Boiler water (BW) is the water circulating within the boiler. It consists of concentrated BFW.

3.3   Boiler Feedwater and Boiler Water Requirements

3.3.1 Presuppositions

Water Requirements of the Boiler Manufacturer is warranty related!

Check the boiler feedwater and boiler water requirements of the boiler manufacturer referring to boiler pressure and design and compare it with the quality of the existing or planed water treatment plant and the realistic feedwater quality - including condensate return. Is it with the

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existing water treatment possible to meet the requirements under economical conditions?

Steam Purity and Steam Requirements is warranty related!

Check the boiler manufacturer's guarantee of the steam produced and compare it with the requirements or demand for processing. The BW content in steam should not exceed 0,1 - 0.2 %. As far as the steam is used for indirect heating only, up to 0.5 % BW content in steam is acceptable. The BW content in steam must be guarantied by the boiler manufacturer!

3.3.2   Water Requirements

International standards:

There are Standards from America (e.g. from ASME), Europe (EN 12 953-10 for Shell Boiler, EN 12 952-12 for Water Tube Boiler), Japan etc. as well as national standards.
The requirements do not differ very much, but refer basically to modern boiler - vertical shell boilers are not included in international standards.
The water requirements refer to steam generator & hot water boiler made of low-alloyed or carbon steel that are heated by combustion of one or more fuels or by hot gases.
Most Standards describe safety related minimum requirements and apply to components between the feedwater inlet and the steam outlet.

Applicable Feedwater and Boiler Water Requirements are shown in the following for:

3.3.2.1 Vertical Shell (Package) Boiler
With operation pressure > 0.5-10 bar(g) and ≤ 1,5 t/hr steam production

Preliminary Remarks:
These water requirements refer to steam generators that are heated by combustion of manually fed solid fuel. The boilers must have a specific steam production < 25 kg/m²·hr and must be equipped with at least one sufficient blow-down drain.
For boiler with specific steam production ≥ 25 kg/m²·hr, pressure >10 bar and/or steam production > 1.5 t/hr as well as for boiler being heated by combustion of liquid fuel or gas, the water requirements for "Shell Boiler" must be applied.

Water Treatment:

In general softening of the make-up water or boiler feedwater should be standard to avoid scaling and sludge formation within the boiler.
If there is no make-up or boiler feedwater treatment with a softener, at least "*Inner Boiler Water Treatment*" (IBWT) through dosing of suitable chemicals in sufficient amount must be applied.
Sufficient intermittent blow-down and rinsing of show glasses as well as external level controllers/indicators etc. is essentially, at least once per day, with IBWT every 8 hrs.

Requirements:

The following values show safety related minimum requirements for both softened boiler feedwater and not softened feedwater that becomes treated within the boiler itself ("Inner Boiler Water Treatment" (IBWT) to minimise corrosion and deposition.

Boiler Feedwater (BFW)		*Softened*	*with IBWT*
∗ Total Hardness (Ca + Mg) [a]	ppm $CaCO_3$	< 10	< 150
∗ pH value at 25 °C	—	(7.5) 8 - 9.5	7.0 - 9.5
∗ Composite Alkalinity (P-value)	ppm $CaCO_3$	2.5 - 25	0 - 25

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Oxygen [b]	mg/l	< 0.5	< 5

Boiler Water (BW) | | *From softened BFW* | *with IBWT* |

Undissolved matter [c]		almost clear	< 5 ml / 100 ml
∗ pH value at 25 °C	—	11 - 12.3	11 - 12.0
∗ Composite Alkalinity (P-value)	ppm CaCO$_3$	100 - 1500	100 - 500
∗ Total Hardness (Ca + Mg) [a]	ppm CaCO$_3$	< 10	< 50
∗ Direct Conductivity at 25 °C	µS/cm	< 5000	< 3000
∗ Phosphate (PO$_4$) [a]	mg/l	10 - 20	10 - 40

∗ Most important values;   mg/l is equal to ppm.

Notes
[a] Water samples must be clear filtered to get correct values!
[b] Oxygen content is reduced physically if water is heated at ambient pressure up to:
    - 85 °C the oxygen content is reduced to approx. 2 mg/l
    - 95 °C the oxygen content is reduced to approx. 0.5 mg/l.
    At lower temperatures the oxygen content can be reduced through dosing of oxygen
    scavenger e. g. sodium sulphite.
[c] Undissolved matter as sediment sludge after settling time of 1 hr.

Test of chemical composition

The noted parameters shall be checked periodically. The frequency of testing shall be specified in the boiler operating instructions. For feedwater and boiler water at least weekly tests of the most important values (∗) pH value *or* alkalinity, hardness, conductivity, phosphate and undissolved matter for IBWT operation are recommended.

3.3.2.2 Horizontal Shell (Package) Boiler and Water tube Boiler
With operation pressure > 0.5-30 bar(g)

Preliminary Remarks:

These water requirements refer to steam generator & hot water boiler > 110 °C that are heated by combustion of fuels or by hot gases. Shell boiler fired with solid fuel may have in front of the fire tube an external furnace possibly cooled with water tubes.

These requirements apply to components between the feedwater inlet and the steam outlet but do not cover the quality of steam produced and/or economical reasons etc.
For certain purposes, it will be appropriate to adapt the chemical requirements in order to optimise e. g. the steam purity (for super-heater operation) and plant reliability.

Water Treatment and Conditioning

Water Treatment: At least softening of the make-up water, boiler feedwater or circulating hot water has to be standard to avoid scaling and sludge formation; make-up water of higher quality may be necessary in particular cases.

Conditioning: The specific geometry of common shell boilers with heated gaps/crevices at joints between welded and/or rolled flue gas tubes and tube sheets or reverse chambers respectively requires particular conditioning of the feedwater and boiler water with phosphate.

Requirements:

The noted safety related minimum requirements for the boiler feedwater, boiler water or circulating hot water are set to reduce the risk of corrosion, sludge formation or deposition within

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the boiler. The values stated shall apply to continuous operation. During start-up, some values may deviate for a restricted period of time and to a limited extent to be specified by the boiler manufacturer.

A   Steam Generator

A 1   Boiler Feedwater (BFW)

For boiler with operation pressure	bar(g)	> 0.5 - 15	> 15 - 30
∗ Total Hardness (Ca + Mg)[a]	ppm CaCO$_3$	< 2	< 1
∗ pH value at 25 °C	—	(7.5) 8 - 9.5	8.5 - 9.5
∗ Oxygen [b]	mg/l	< 0.1	< 0.02

A 2.1 Boiler Water (BW)   Using BFW with direct Conductivity > 30 µS/cm

Boiler with operation pressure	bar(g)	> 0.5 - 15	> 15 - 30
∗ Direct Conductivity at 25 °C [c]	µS/cm	< 4 000	< 2 000
∗ pH value at 25 °C	—	10.5 - 12.0	10.5 - 11.8
∗ Composite Alkalinity (P-value) [c]	ppm CaCO$_3$	100 - 900	100 - 600
∗ Total Hardness (Ca + Mg) [a]	ppm CaCO$_3$	< 10	< 3
∗ Phosphate (PO$_4$) [a, d]	mg/l	10 - 30	10 - 30
∗ Silica (SiO$_2$)	mg/l	< 120	< 100

A 2.2 Boiler Water (BW)   Using BFW with direct Conductivity ≤ 30 µS/cm

Boiler with operation pressure	bar(g)	> 0.5 - 15	> 15 - 30
∗ Direct Conductivity at 25 °C	µS/cm	< 2 000	< 1 000
∗ pH value at 25 °C	—	10.5 - 11.5	10.5 - 11.3
∗ Composite Alkalinity (P-value)	ppm CaCO$_3$	25 - 250	10 - 100
∗ Total Hardness (Ca + Mg) [a]	ppm CaCO$_3$	< 3	< 1
∗ Phosphate (PO$_4$) [a, d]	mg/l	10 - 30	10 - 20
∗ Silica (SiO$_2$)	mg/l	< 100	< 80

B   Hot Water Boiler

B 1   Feedwater and Make-up Water

∗ Total Hardness (Ca + Mg) [a]	ppm CaCO$_3$	< 5
∗ pH value at 25 °C	—	> 7.0

B 2   Circulating Hot Water with temperature >110 °C

∗ Direct Conductivity at 25 °C	µS/cm	< 1 000
∗ Total Hardness (Ca + Mg) [a]	ppm CaCO$_3$	< 5
∗ pH value at 25 °C	—	9.5 -11.5
∗ Composite Alkalinity (P-value)	ppm CaCO$_3$	25 – 250

Notes

[a] Not really clear water samples must be filtered clear to get correct values!

[b] Oxygen content can be reduced physically almost to < 0.05 mg/l if water is heated to boiling temperatures, preferable using thermal deaerator. At lower temperatures the oxygen content can be reduced through dosing of an oxygen scavenger e. g. sodium sulphite.

[c] With super-heater operation consider 50 % of the noted upper value as maximum value.

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^d Tri-sodium phosphate dosing *must* be applied for shell boiler, if BFW with direct conductivity ≤ 30 µS/cm is used, but it is also recommended for BFW > 30 µS/cm!

∗ most important values;   mg/l is equal to ppm in water.

Test of chemical composition
The noted parameters shall be checked continuously or periodically. The frequency of testing shall be specified in the boiler operating instructions. For steam boiler at least daily, and for hot water boiler weekly tests of the most important values (∗) pH value *or* alkalinity, hardness, conductivity, oxygen *or* excess of oxygen scavenger, silica and phosphate are recommended.

4   General Comments and Recommendations

The mentioned BFW and BW requirements can be kept easier and more economical if there is sufficient condensate return – collect as much as possible! As noted, regularly the condensate is pure hot water with e.g. temperature > 80 °C that contains in this case an energy about 340 kJ/kg that corresponds, regarding the heat value, to about 10 kg coal per m³ condensate and considering the boiler's efficiency to 30-40 kg coal saving – already not considered the lower blow down rate.
Condensate with temperature > 100 °C, like condensate from ironing, releases steam that leads to high loss of energy! The steam can be cooled and condensed with spraying cool softened make-up into the steam flow of the vent of the condensate tank or installation of a cooling coil made of stainless steel.
The energy of 1 kg released steam is about 3,100 kJ, which is almost 10 times more than that of condensate of 80 °C and leads to 250-350 kg coal saving per 1000 kg steam!

Pumps for hot water must be connected in short distance to the hot water tank and must have a wide diameter at their inlet part (incl. block valve, best ball valve) to avoid pressure drop and cavitation at the pump. Hot water can be safely pumped if there is a little pressure at the inlet side of the pump, which can be easy achieved if the water level of a hot water tank is about 2-3 m above the pump inlet.

During boiler operation and steam production, the dissolved and undissolved water constituents become concentrated and must be kept within the limits of the BW requirements by discontinuous or continuous blow-down, that means some hot boiler water is taken out of the boiler and drained. This hot blow-down water contains energy, e.g. boiler water of 5 bar pressure 670 kJ/kg. A discontinuous blow-down makes it difficult to take the energy back because of the high flow rate in short time of some seconds. A continuous blow-down device takes a low flow rate of BW continuously out, which can be used to heat up BFW indirectly using a coil made of carbon steel. Discontinuous blow-down is economical with boiler > 10 bar and > 2 t/hr steam production.

5   Inorganic and Organic "Anti-Scalants" and "Dispersants"

These chemicals can be applied in shell and drum boilers to minimize scaling. Specific organic anti-scalants can be dosed also as preventive measure to clean a boiler from some thin scale during operation.

Inorganic anti-scalants like Tri-sodium / Tri-potassium phosphate, also used as alkalising chemicals, are applicable in boilers up to 180 bars. They react with hardness (Ca-, Mg-compounds) to hydroxyl apatite that remains mostly in suspension and avoids scale of limestone, gypsum and aluminium-silicate. Due to stronger affinity of phosphate to hardness than to silica, silicate scale can be significantly reduced in presence of phosphate.

Organic anti-scalants are mostly a mixture of poly-carbonic (poly-acrylic) acids or amides, as well as organo-phosphonates. Many products show a weak complex forming behaviour and

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keep Ca- /Mg-compounds in solution but are not too aggressive to iron oxides like chelants and applicable for boiler pressure < 120 bars.

Chelants are strong complex forming agents like EDTA, NTA and keep hardness and metal ions in solution. Too high concentrations attack the protective iron oxide layer and are not recommended in low pressure industrial boiler.

6   Preservation

Preservation means basically any method to avoid corrosion - mostly oxygen corrosion - on the waterside of boilers, parts of it or auxiliary components made of low-alloyed steel during shutdown and stand-by, but also during storage and transportation.

A sufficient and commonly present protective layer of iron oxides on the waterside of boilers (being in operation before shut down for at least 1 month) is able to protect low-alloyed steel in presence of humidity or moisture and air for restricted time only.
If softened water or permeate is used, the time without preservation is restricted to approx. 1 week, but with frequent shut-down times much shorter!

Exceeding times or frequent shut-down times requires preservation methods by either

- *Wet preservation* (in absence of air) e.g. by replacing of air by nitrogen or complete kept filling of the boiler with at least alkaline water, better containing oxygen scavenger, or

- *Dry preservation* (in absence of moisture) by drying with desiccants, e.g. silica gel or regenerative circulating dryers.

Wet preservation is recommended particularly for shorter downtime by e.g.:

- Completely filled boiler (and kept filled up to vent!) with alkaline boiler water (pH about 10) for some days or excess of oxygen scavenger and pH 10-11 for some weeks to few month. For short shut down, let the boiler cool down to approx. 1 bar and fill it with BFW up to the vent. Keep the boiler filled and check it every 2 days.

- Keeping steam pressure from other boiler in operation and maintain a steam blanket. That leads to condensate formation at the steam/water interface, lowers the BW pH and needs drainage to keep the water level in the boiler. Risky if the steam is not oxygen free!

- Application of inert gas (nitrogen) with partly filled or empty but wet boiler for some weeks to few months. Keep and check nitrogen over pressure of 10-20 mbar. Vent the boiler sufficiently before somebody is entering the boiler to avoid suffocation.

Dry preservation is recommended for longer downtime (some months) by either

- Desiccants e. g. silica gel (but avoid direct contact to steel!) or caustic lime (CaO) or

- Application of re-circulating dryer in case of preservation of bigger volume tanks.

Preservation on the flue gas side of boilers may be necessary too, particularly on coal and oil fired boilers.

7   Sampling of Boiler Feedwater and Boiler Water / On Line Control

Sampling pipes should be made of stainless steel (at least of TP 321 or 316), be as short as possible and in a diameter of approximately 10 x 1.0 – 1.5 mm or 12 x 2 mm.
Hot samples should be cooled down to ca. 25 -30 °C with a flow of at least 25 kg/hr. The cooler coil should be made from stainless steel. Cooler are urgently recommended for boiler with pressure > 10 bar and for oxygen measurement in BFW.
All sampling devices should have a straight blow out line before entering the cooler or the measuring equipment.

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7.1   Sampling of Water

No special design necessary, but a representative average (bulk) sample must be available. Sampling device for oxygen measurement must be gas tight by welding or particular high pressure fittings and valves!
Sampling points are recommended after any treatment step and chemical dosing point, which leads to a possible change of the water quality and are a must for BFW and BW, for instance:

- Raw water and water after pre-treatment (flocculation, filtration, de-chlorination).
- Treated water after softening or RO plant
- Raw condensate and/or from condensate tank,
- BFW after deaeration and chemical dosing - optimal at boiler inlet
- BW from continuous blow down (min. 100 l/hr) close to the drum or directly from the boiler opposite the feedwater inlet.

7.2   Chemical Control of Plant Circuits

Manually controlled must be at least Boiler Feedwater (BFW) and Boiler Water (BW) once per day for the following safety related parameters:

> Total and composite alkalinity (P- an M-value) or pH
> Total hardness
> Conductivity
> Phosphate / Anti-scalants - if dosed
> Silica 2 x per week

On-Line controlled should be conductivity of BW because it can be used as signal for automatic blow down. The conductivity measurement should be temperature corrected to standard reference temperature of 25 °C.

Measurement of hardness in make-up water and condensate return should be done on demand. Oxygen can be measured with "Karmina Chemets" in BFW.

8   Boiler Pre-Treatment and Chemical Cleaning of Boilers

8.1   Procedures for Boiler Cleaning

8.1.1   Alkaline boil out

Before alkaline boil out, new boiler, especially water tube boiler must be mechanically cleaned and rinsed with BFW or softened water - best alkalised to a pH around 9.5 with volatile chemicals - to remove solids until the drained water is almost clear! Rinse and check every drain for possible blockage.

New boiler should undergo at least an alkaline boil out to remove oily and fatty matter as well loose oxides and dust, commonly using tri-sodium phosphate, caustic soda, a mixture of both or other alkaline chemicals like dispersants *well dissolved in water* (boil out solution up to a pH of approx. 10 -10.5) at elevated temperature up to approx. 70 % of the normal operation pressure. During boil out any contamination of steam lines to consumer must be definitely avoided.

For boiler with *heated* crevices e. g. between tubes and tube-sheet, like shell boiler or process gas cooler the exclusively use of caustic soda is prohibited (may initiate caustic stress corrosion cracking, SCC) and tri-sodium phosphate recommended. Before operation the boil out solution must be drained and the boiler must be rinsed sufficiently through all drains to remove further solids and to dilute the boil out chemicals to conditions (pH, conductivity) close to that of the incoming rinsing water.

8.1.2   Chemical Cleaning during shutdown

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Acid Cleaning (Pickling)

Before any acid cleaning an alkaline boil out is necessary to get a "hydrophilic" (easy to wet) surface. Acid cleaning is recommended for new boiler in case of significantly corroded surfaces and for boiler with local heat flux > 250 kW/m², particularly if there are many welds in the area with high heat flux. On boilers already being in service, acid cleaning is necessary if inorganic scale is thicker than acceptable (depending on heat flux and composition > 0.1 to 1 mm). It is usually carried out with *inhibited* inorganic (preferable hydrofluoric or hydrochloric acid) or *inhibited* organic acids (citric acid, glycolic acid, formic acid etc.). Silicate scale can be dissolved only with hydrofluoric acid, which must be done by experts!

Inhibitors for acid cleaning are organic compounds that reduce corrosion to metallic surfaces drastically in specific media. They reduce the rate of the anodic processes of metal dissolution by the formation of an "organic protective film" on the exposed metal. Mill scale and other scale is not protected and will be dissolved as supposed.

Inhibitors must be adapted to the type of acid, the metal in service and to temperature. The inhibitor concentration and maximal application temperature (mostly not exceeding 60-80°C) must be kept within its correct range following supplier's application recommendation for optimal corrosion protection.

For any chemical cleaning the limits of the application conditions for the combination - solvent, e.g. acid, inhibitor, temperature and application time - must be kept exactly to avoid excessive material attack. The loss of base metal must not exceed 20 g/m² (= 2.5 µm loss of wall thickness) during application. A representative steel sample with different thick mill scale layers should be merged into the solvent to check the cleaning progress during application.
The cleaning process must be controlled by measuring at least acid and metal concentration.

For test cases an average sample of the applied solvent of at least 10 litres (e. g. 1-2 l from any batch) of the cleaning solution should be taken and kept to repeat corrosion tests.
For austenitic stainless steel, hydrochloric acid is not permitted! Ferritic stainless steel shows against some acids higher corrosion rate than mild steel!
Any acid cleaning should be finished with a passivation step to form a thin homogeneous oxide layer; cleaned boiler shall go into operation as soon as possible

Chemical Cleaning with other Chemicals

Chelants like EDTA or NTA where applied regularly in alkaline solution but should be rarely used for cleaning because of inhomogeneous cleaning and environment effects. They need application temperatures > 80 -100 °C, which is frequently adjusted by direct firing with a risk of heterogeneous temperature distribution, different cleaning effect and corrosion rate.

8.1.3   Chemical Cleaning during operation

Cleaning during operation (see also chapter 5) is possible as far as the scale thickness do not exceed 0.3 mm (localised max. 0.5 mm), thicker scale may peel off and may affect the boiler water circulation. Easy removable is scale consisting > 50 % of calcium and magnesium compounds without fat or oil. Application of aggressive chelants like EDTA or ETA is possible but difficult to handle and affects the environment.

Recently biological degradable organic anti-scalants and dispersants have been developed with lower complex forming strength than EDTA or NTA, which can be used for cleaning during operation. Producer of such weaker complex forming agents are international chemical treatment companies such as Betz, Drew, Grace-Dearborn, Kurita or Ondeo (Nalco). These chemicals should be used temporarily - may be one month per year - to remove thin scale preventively. As far as a boiler was operated according to the BFW and BW requirements, chemical cleaning is not necessary within less than 5 years. Frequent cleaning activities indicate clearly lack in BFW and BW treatment or insufficient preservation during stand still.

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