

## 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 Water Chemistry, Corrosion, Failure Analysis and Materials Investigation in TÜV SÜD Industrie 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, thin (< 0.1 mm), dense, protective iron oxide layer (magnetite layer), 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]) – mostly not avoidable – and/or
- local blisters or bark like deposits due to oxygen corrosion during shut down.

Well-designed steam generators - actually mostly vertical and horizontal shell boiler - achieve satisfying lifetime *only* if the boiler steel is able to develop and to maintain the mentioned thin protective magnetite ( $\text{Fe}_3\text{O}_4$ ) layer during operation and shut down.

Undesired deposits of water constituents or corrosion product increases the wall temperature of furnaces depending on layer thickness, composition and porosity and may 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

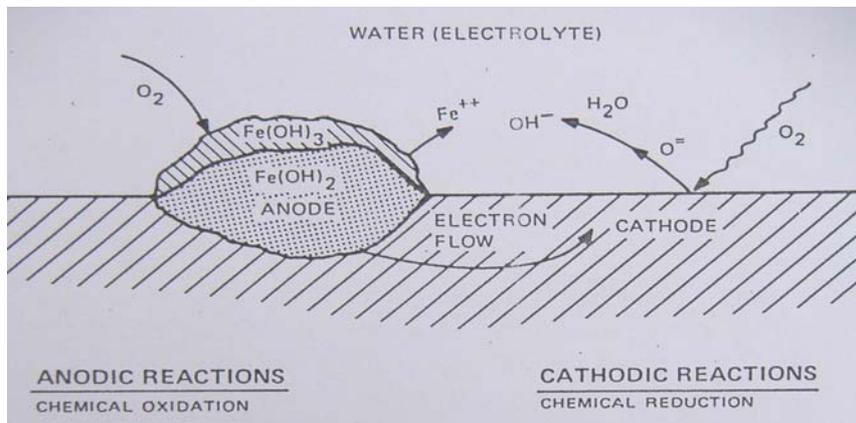
Corrosion is the - mostly electro-chemical - reaction of a metallic material with its environment that results in a damage of the material or component before its regular lifetime.

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 medium - 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 and dense layers), defects in the magnetite layer 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**.



**Fig. 2** Principles of oxygen corrosion

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



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



**Fig. 4** Oxygen corrosion on smoke tube

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**, and

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



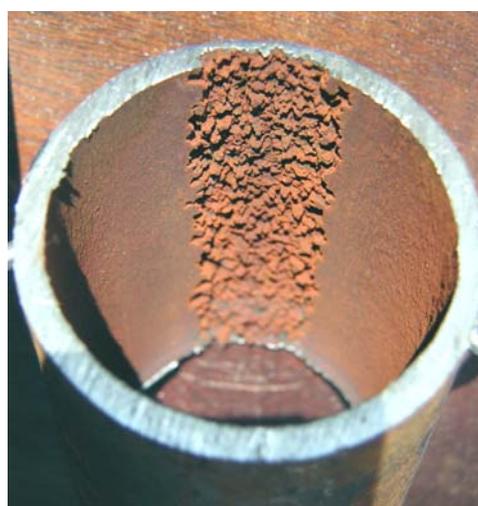
**Figs. 5 + 6** Carbonic acid corrosion on condensate return tube (right = enlargement)

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 connected condensate/steam mixtures, see **Fig. 8** or pumps operating in hot water or. Elevated pressure at pump inlet solves the problem.



**Fig. 7** Erosion corrosion on a steam block valve used as control valve



**Fig. 8** Cavitation on top side (12:00 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.

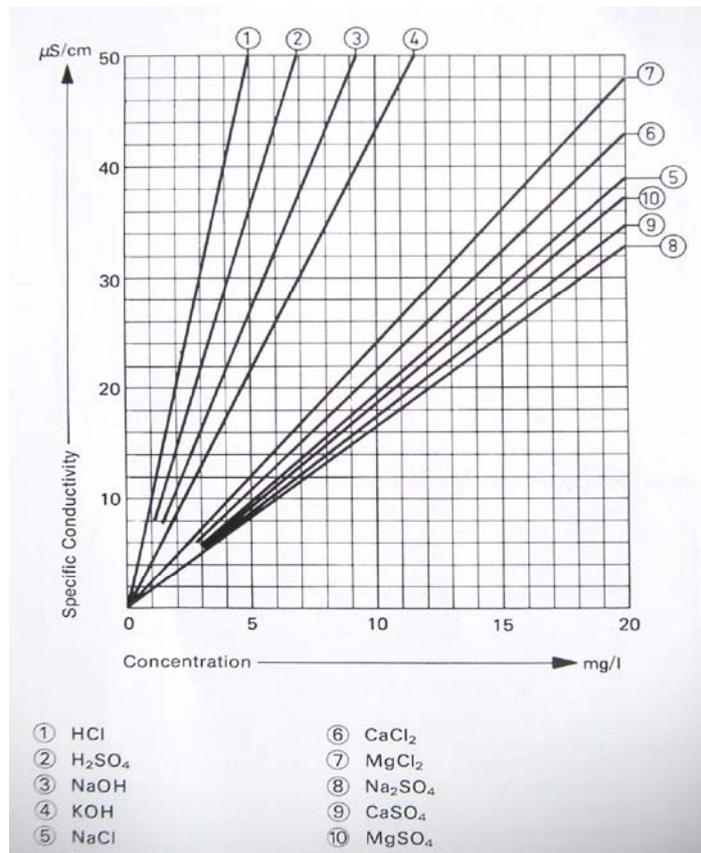
#### 1.3.1 Conductivity

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  $\mu\text{S}/\text{cm}$  at 25 °C increase to approx. 440  $\mu\text{S}/\text{cm}$  at 100 °C.

SI-Unit / Definition: Siemens (S),  $\text{S} = 1/\text{Ohm} (\Omega, \text{resistance})$ ,  $1 \text{ S} = 1,000,000 \mu\text{S}$ .

Water became electrical conductive due to dissolved salts, acids (also carbonic acid), lye (bases) and some organics, see **Fig. 9** – but silica don'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.

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 ( $\text{Na}^+$ ), bi-valent calcium ion ( $\text{Ca}^{++}$ ) or tri-valent iron ion ( $\text{Fe}^{+++}$ ) and *anions* with negative charge, like mono-valent chloride ion ( $\text{Cl}^-$ ), bi-valent sulphate ion ( $\text{SO}_4^{--}$ ) or tri-valent phosphate ion ( $\text{PO}_4^{---}$ ).

Also water ( $\text{H}_2\text{O}$ ) dissociates in traces into one mono-valent hydrogen ( $\text{H}^+$ ) cation and one mono-valent negative hydroxyl ion ( $\text{OH}^-$ ), which leads to a very little electrical conductivity.

Purest water shows a conductivity at 25 °C of ca. 0.055  $\mu\text{S}/\text{cm}$  corresponding to a specific resistance of about  $18.2 \text{ M}\Omega \cdot \text{cm} = 18,200,000 \Omega \cdot \text{cm}$ !

For comparison, in Asia rain water may have a conductivity about 10-20  $\mu\text{S}/\text{cm}$ , river water (unaffected from sea water) 100 - 300  $\mu\text{S}/\text{cm}$  and well water or domestic similar values. Brackish water may have a conductivity up to 10,000 - 20,000  $\mu\text{S}/\text{cm}$ .

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, if a pH of 7 corresponds to 1 mg/l, a pH of 8 corresponds to 10 mg/l, a pH of 9 to 100 mg/l, a pH of 10 to 1000 mg/l = 1 g/l, a pH of 11 to 10 g/l etc.

Moderate alkaline water conditions 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.

#### 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 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 or softened 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 like carbonate (soda), 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 or acidic conditions and must be titrated with 0.1 N NaOH.

The *caustic alkalinity* indicates content of free caustics only, but needs a special procedure before titration against p-indicator.

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

For shell boiler, the boiler water should be tested for composite alkalinity (p-alkalinity) and total alkalinity (m-alkalinity).

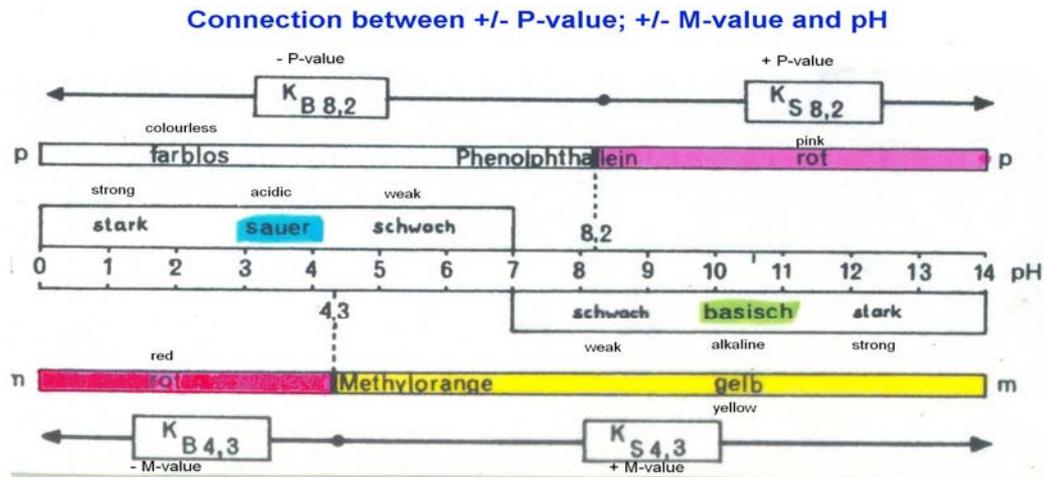


Fig. 10

### 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., because lime stone has been already 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, that results to formation of silicon scale.

Silicates are almost insoluble in water, 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 magnesium compounds may lead to scaling in piping systems due to iron ochre. After contact with oxygen (air) formation of brown flocks is common that may cause deposits in pipes as well and reduce the activity of softener resin due to brown turbidity.

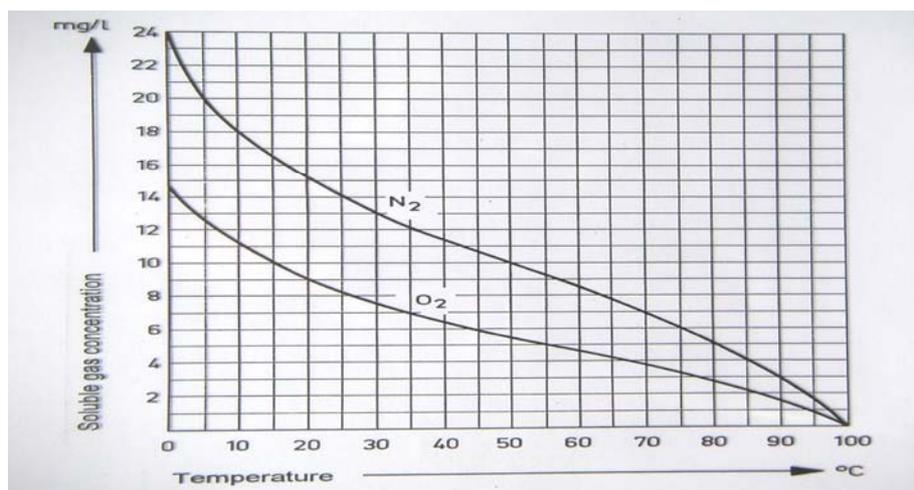
In many cases aeration make iron compounds removable in mechanical filters. For manganese compounds aeration is often insufficient and stronger oxidation measures are necessary.

### 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 a protective layer of magnetite. Nitrogen do nor 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.

## 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/m<sup>2</sup>·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 softener to bind hardness on the softener resin, 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. 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 water treatment, because all this methods do *not* remove hardness and do *not* affect silica or silicates!

### 2.1 Inner boiler water Treatment

Scaling due to hardness and silicates can be significantly reduced if sufficient tri-sodium phosphate is dosed proportional to the fed hardness respectively 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 should 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.

Per 1 cubic meter (m<sup>3</sup>) boiler feedwater with 1 meq/l hardness, an amount of 120 g tri-sodium phosphate (technical grade with 10 mol of crystal water, Na<sub>3</sub>PO<sub>4</sub>·10 H<sub>2</sub>O [20 % P<sub>2</sub>O<sub>5</sub>]) dissolved in at least 5 l water is necessary. For instance, to treat 1 m<sup>3</sup> feedwater with 3 meq/l or 1,5 mmol/l total hardness an amount of ca. 350 g Na<sub>3</sub>PO<sub>4</sub> ·10 H<sub>2</sub>O is necessary.

Inner boiler water treatment is easy, as far as the total hardness of the raw water is low (less than 1 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 e. g. with sand filter) by using filters filled with softener resin (mostly honey-brown beads 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 < 0.01 mmol/l = < 1 ppm CaCO<sub>3</sub>.

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**.

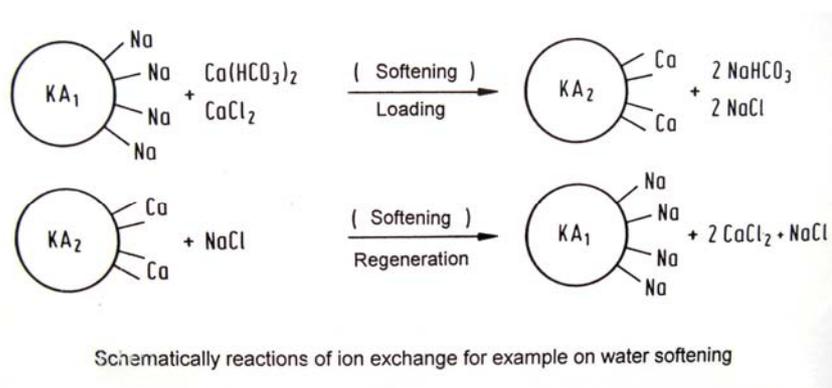


Fig. 12:

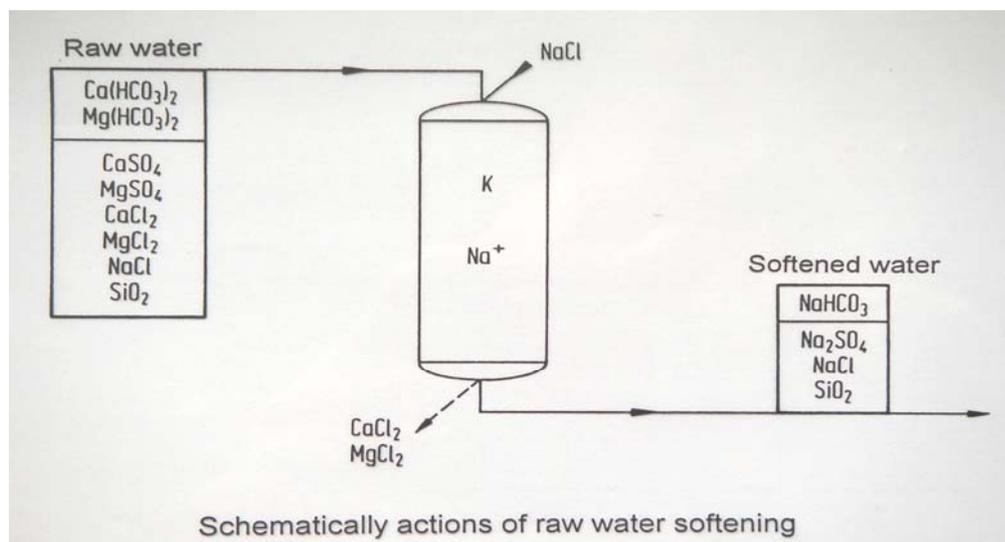


Fig. 13

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: 2 softener filter (made of coated steel or glass fibre reinforced polyester, filter internals and resin) for continuous supply of softened water, 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, if there are no further requirements to boiler operation and steam quality. Optimised quantity of condensate return is advantageous.

### 2.2.2 Decarbonisation

*Generals:* If the total alkalinity of the boiler feedwater exceeds about 2 meq/l, only softening of the raw water is not economical, because the blow down of the boiler becomes too much and leads to high loss of energy. For most shell boiler the composite alkalinity (p-value) of the boiler water is limited to 15 meq/l which results to a total alkalinity of approx. 18 meq/l. If the feedwater shows a total alkalinity of 2 meq/l, it can be concentrated only 18:2 = 9 times, that leads to a blow down rate of 100:9 = 11 % of the BFW flow. Economical are blow down rates < 5%! To reduce the total alkalinity of the BFW, either the condensate return must be increased or the make up water must be decarbonised. Decarbonisation reduces the total alkalinity of the raw water significantly, depending of the treatment process applied.

Common methods is "lime hydrate Decarbonisation" or "Decarbonisation with weak acidic cation exchangers".

*Lime hydrate Decarbonisation* is done with equivalent dosing of saturated lime hydrate solution to the raw water, optimal at elevated temperatures of 40-60 °C, see Fig. 14. In that case lime hydrate reacts with carbonate hardness and free carbonic acid to calcium and magnesium carbonate, that precipitates and must be removed in sand filters. Undissolved matter and some silica can be also removed. The reaction takes approx. 1-2 hours time and must be sufficient controlled by p- and m-value measurement, but is cheap, needs only unprotected steel or concrete tanks and is environment friendly. This treatment method leads to an weak alkaline water with p-value ca. 0.3-0.4 meq/l and m-value of approx. 0.6-0.8 meq/l. Heating of the process can be done indirectly with hot boiler water blow down which leads to heat recovery. The remaining hardness (residual carbonate hardness and non-carbonate hardness) must be

removed in a softener. Together with some condensate return it results to an excellent, already weak alkaline boiler feedwater for lower pressure boiler.

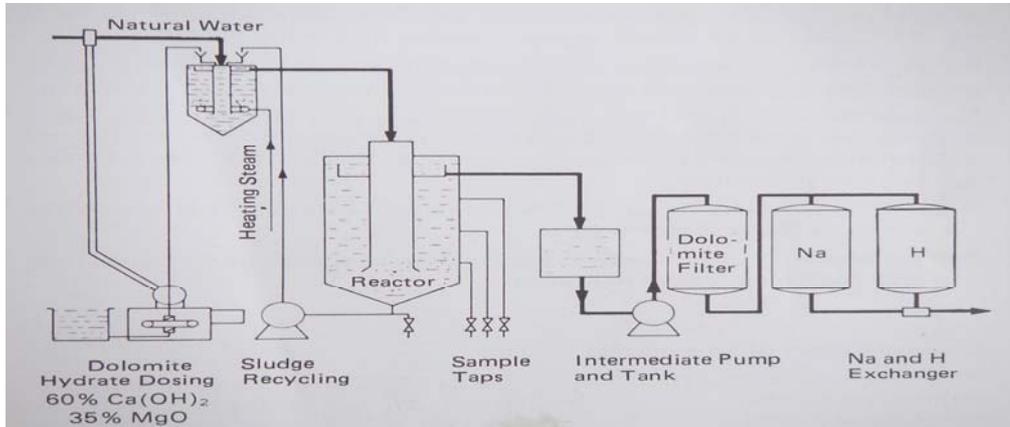


Fig. 14

Hot lime decarbonisation can be done with lime hydrate instead of dolomite hydrate dosing. In stead of dolomite filter quartz gravel filter can be used. H-exchanger is not necessary.

*Decarbonisation using weak acidic cation exchangers* in general is a more expensive method to reduce total alkalinity, but leads in average to a lower residual m-value of 0.2-0.3 meq/l and needs lesser control during operation. Disadvantage is handling and storage of hydrochloric acid (for regeneration of the weak acidic cation exchangers) and the weak acidic treated water. Downstream the Decarbonisation filter there is a softener necessary to remove residual carbonate hardness and non carbonate hardness, see Fig. 15. Both filters, the entire pipe work and valves must be corrosion resistant against hydrochloric acid respectively weak acidic decarbonised water. The filter vessel, pipe work and valves must be either glass fibre reinforced polyester, PE/PP, PVC or rubber lined carbon steel, for decarbonised water after softener stainless steel can be used too.

The Decarbonisation filter keeps most carbonate hardness on its resins and exchanges bicarbonate to free carbonic acid, which must be reduced to a minimum either in a corrosion resistant degassifier (CO<sub>2</sub> stripping) to < 10 mg/l or in a thermal deaerator made of stainless steel to < 2 mg/l. To get alkaline BFW dosing of alkaline chemical is necessary.

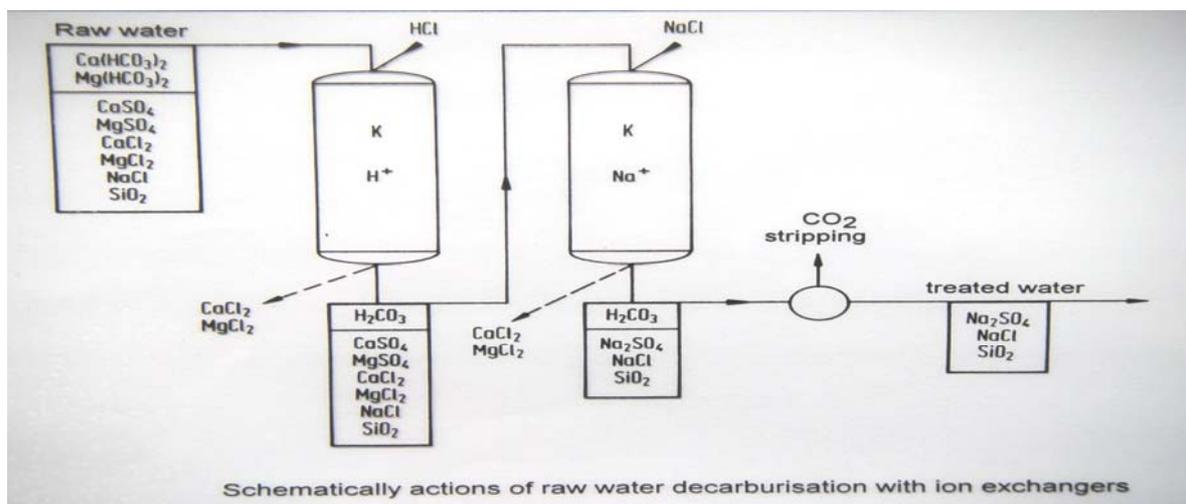


Fig. 15: Decarbonisation with K-H<sup>+</sup> Filter and subsequent Softening in a K-Na<sup>+</sup> Filter

### 2.2.3 Reverse Osmosis (RO, Desalination)

Reverse Osmosis is an excellent method to reduce the content of all dissolved solids of a raw water (e.g. total hardness and silica) to a minimum, that leads to a major reduction of its conductivity. For smaller demand (< 20-30 m<sup>3</sup>/day) upstream of a RO unit first softening of the raw water is recommended to avoid precipitation and blockage of the RO-membranes due to hardness and undissolved matter. Softened water downstream RO-units (also called permeate) is free of hardness, shows low conductivity and low silica! During thermal deaeration, residual sodium bicarbonate decomposes to alkaline sodium carbonate, increases the pH and leads to an excellent weak alkaline BFW for low pressure boiler. For pH-adjustment in the BW dosing of tri-sodium phosphate is essentially!

RO-units need less control, space fore installation, chemicals and are for a water demand < 20-30 m<sup>3</sup>/day much cheaper and easier to handle than weak acidic cation exchanger.

Permeate is recommended if higher steam quality is required, e. g. for food production, cosmetic or pharmacy industry.

#### 2.2.4 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**.

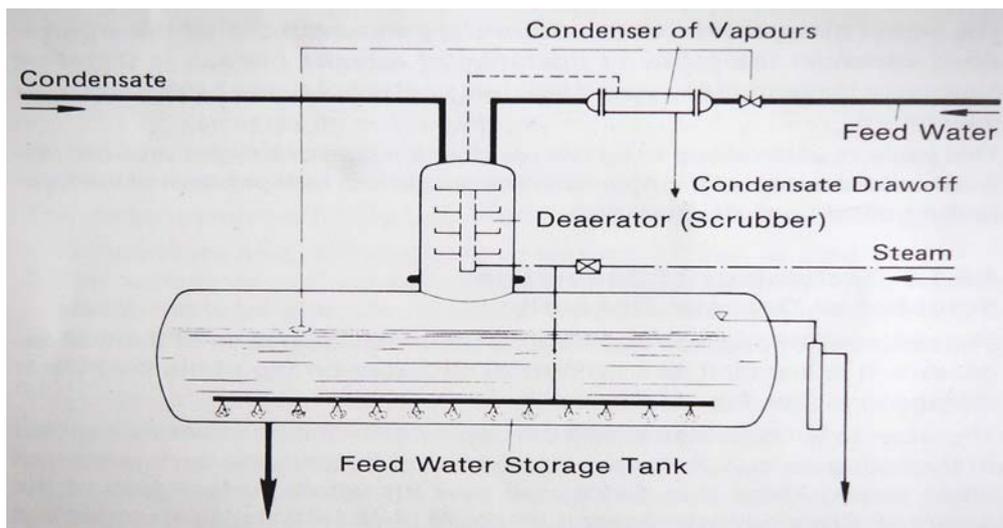


Fig. 16

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.

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. Remaining oxygen can be eliminated by dosing of an oxygen scavenger like sodium sulphite.

### 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 smoke tubes and flue gas within the tubes) and *water tube boiler* with boiler water within the tubes and flue gas around the tubes.

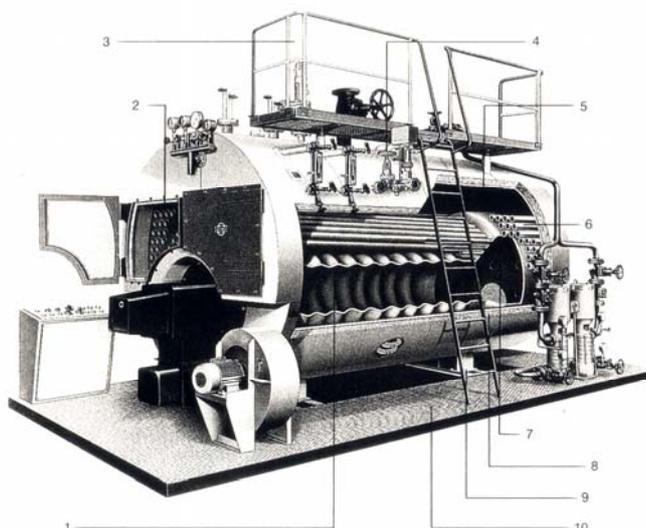
*Vertical Shell or Package Boiler* are mainly coal fired one-pass steam generator with fire box and some horizontal smoke tubes, operate at a pressure up to 12-15 bars and have steam capacity less than 2,000 kg/hr. Their specific steam production is regularly  $< 25 \text{ kg/m}^2 \cdot \text{hr}$ . 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.

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.

#### Fire-Tube Shell Boiler

- 1 Fire Tube with Front-Burner (First Pass)
- 2 Front Reverse Chambers (Change from 2<sup>nd</sup> to 3<sup>rd</sup> Pass)
- 3 Service Platform
- 4 Automatic Level Controller
- 5 Steam Space
- 6 Flue Gas Tubes
- 7 Wet Back (first) Reverse Chamber
- 8 Boiler Shell with Insulation
- 10 Installation Frame



**Fig.17:**

*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 domestic 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 ( $< 1 \text{ ppm CaCO}_3$  or  $< 0.01 \text{ mmol/l}$ ) 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 con-

ductivity 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 is free of hardness ( $< 1 \text{ ppm CaCO}_3$ ) and indicates at least a direct conductivity at  $25 \text{ °C} < 30 \text{ }\mu\text{S/cm}$  (mostly  $< 10 \text{ }\mu\text{S/cm}$ ) and silica content  $< 0.5 \text{ mg/l (ppm) SiO}_2$ .

*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.

*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 – 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 planned water treatment plant and the realistic feedwater quality - including condensate return.

*Steam Purity and Steam Requirements – 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.

#### 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 boiler are not included in international standards.

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

##### 3.3.2.1 Vertical Shell (Package) Boiler

With operation pressure  $> 0.5\text{-}10 \text{ bar(g)}$  and  $\leq 1,5 \text{ t/hr}$  steam production

*Preliminary Remarks:*

This water requirements refer to steam generators made of low-alloyed or carbon steel that are heated by combustion of manually fed solid fuel. The boilers must have low heat transfer (specific steam production  $< 25 \text{ kg/m}^2\text{-hr}$ ) and must be equipped with at least one sufficient blow-down drain.

For boiler with specific steam production  $\geq 25 \text{ kg/m}^2\text{-hr}$ , pressure  $>10 \text{ bar}$  and/or steam production  $> 1.5 \text{ t/hr}$  as well as for boiler being heated by combustion of liquid fuel or gas, the water requirements for "Horizontal 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, sufficient rinsing of show glasses and of 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 deposition and corrosion.

<u>Boiler Feedwater (BFW)</u>		<i>Softened</i>	<i>with IBWT</i>
* Total Hardness (Ca + Mg) <sup>a</sup>	ppm CaCO <sub>3</sub>	< 10	< 150
* pH value at 25 °C	—	8.5 - 9.5	7.0 - 9.5
* Composite Alkalinity (p-value)	ppm CaCO <sub>3</sub>	2.5 - 25	0 - 25
Oxygen <sup>b</sup>	mg/l	< 0.5	< 2

<u>Boiler Water (BW)</u>		<i>From softened BFW</i>	<i>with IBWT</i>
Undissolved matter <sup>c</sup>	—	—	< 5 ml / 100 ml
* pH value at 25 °C	—	11 - 12.3	11 - 12.0
* Composite Alkalinity (p-value)	ppm CaCO <sub>3</sub>	100 - 1000	100 - 500 ppm CaCO <sub>3</sub>
* Total Hardness (Ca + Mg) <sup>a</sup>	ppm CaCO <sub>3</sub>	< 10	< 50
* Direct Conductivity at 25 °C	µS/cm	< 5000	< 3000
* Phosphate (PO <sub>4</sub> ) <sup>a</sup>	mg/l	10 - 20	10 - 40

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

*Notes*

<sup>a</sup> Water samples must be clear filtered to get correct values!

<sup>b</sup> 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.

<sup>c</sup> 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

With operation pressure > 0.5-30 bar(g)

#### *Preliminary Remarks:*

This water requirements refer to shell boiler (steam generator & hot water boiler > 110 °C) made of low-alloyed or carbon steel that are heated by combustion of one or more 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. Further chemical dosing may be necessary to adjust pH in BFW and BW as well as to bind oxygen.

#### Requirements:

This document sets out safety related minimum requirements for the boiler feedwater, boiler water or circulating hot water to reduce the risk of corrosion, sludge formation or deposition within 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) <sup>a</sup>	ppm CaCO <sub>3</sub>	< 3	< 1
* pH value at 25 °C	—	(7.5) 8 - 9.5	8.5 - 9.5
* Oxygen <sup>b</sup>	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 <sup>c</sup>	µS/cm	< 4 000	< 2 000
* pH value at 25 °C	—	10.5 - 12.0	10.5 - 11.8
* Composite Alkalinity (p-value) <sup>c</sup>	ppm CaCO <sub>3</sub>	100 - 900	100 - 600
* Total Hardness (Ca + Mg) <sup>a</sup>	ppm CaCO <sub>3</sub>	< 10	< 3
* Phosphate (PO <sub>4</sub> ) <sup>a, d</sup>	mg/l	10 - 30	10 - 30
* Silica (SiO <sub>2</sub> )	mg/l	< 120	< 100



<b>A 2.2 Boiler Water (BW)</b>		Using BFW with direct Conductivity $\leq 30 \mu\text{S/cm}$	
Boiler with operation pressure	bar(g)	> 0.5 - 15	> 15 - 30
* Direct Conductivity at 25 °C	$\mu\text{S/cm}$	< 2 000	< 1 000
* pH value at 25 °C	—	10.5 - 11.5	10.5 - 11.3
* Composite Alkalinity (p-value)	ppm $\text{CaCO}_3$	25 - 250	10 - 100
* Total Hardness (Ca + Mg) <sup>a</sup>	ppm $\text{CaCO}_3$	< 3	< 1
* Phosphate ( $\text{PO}_4$ ) <sup>a, d</sup>	mg/l	10 - 30	10 - 20
* Silica ( $\text{SiO}_2$ )	mg/l	< 100	< 80

**B Hot Water Boiler**

**B 1 Feedwater and Make-up Water**

* Total Hardness (Ca + Mg) <sup>a</sup>	ppm $\text{CaCO}_3$	< 5
* pH value at 25 °C	—	> 7.0

**B 2 Circulating Hot Water with temperature >110 °C**

* Direct Conductivity at 25 °C	$\mu\text{S/cm}$	< 1 000
* Total Hardness (Ca + Mg) <sup>a</sup>	ppm $\text{CaCO}_3$	< 5
* pH value at 25 °C	—	9.5 -11.5
* Composite Alkalinity (p-value)	ppm $\text{CaCO}_3$	25 – 250

Notes: \* most important values; mg/l is equal to ppm in water.

<sup>a</sup> Not really clear water samples must be filtered clear to get correct values!

<sup>b</sup> 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. In that case an excess of 10-30 mg/l sodium sulphite in the BW is recommended.

<sup>c</sup> With super-heater operation consider 50 % of the noted upper value as maximum value.

<sup>d</sup> Tri-sodium phosphate dosing *must* be applied if BFW with direct conductivity  $\leq 30 \mu\text{S/cm}$  is used, but it is also recommended for BFW > 30  $\mu\text{S/cm}$ !

**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 Conditioning, pH-adjustment, Oxygen Scavengers, „Anti-Scalants“**

As far as the necessary alkaline pH in the BFW is not created by the water treatment procedure, the pH must be adjusted by continuous (flow proportional) dosing of tri-sodium phosphate or - if allowed with caustic soda into the feedwater storage tank.

Oxygen scavenger like sodium sulphite should be dosed in the same way than alkalisating reagent into the BFW storage tank at elevated temperatures, even together.

“Anti Scalants” should be applied in shell and drum boilers to reduce scaling. Organic anti-scalants can be dosed also as preventive measure to clean a boiler from some 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 remain mostly in suspension and avoids widely scale of limestone, gypsum and aluminium-silicate.

*Organic anti-scalants*, mostly poly-carbonic (poly-acrylic) acids or amides, as well as organo-phosphonates show a weak complex forming behaviour and keep Ca- /Mg- compounds in solution but are not too aggressive to the protective iron oxide than 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.

Attention: Organics may influence the steam quality.

The limited values in BW can be kept by adapted dosing e. g. of phosphate and sulphite, the limit for composite alkalinity (p-value), conductivity and silica by adapted blow down.

## 5 Preservation

Preservation means basically any method to avoid corrosion - mostly oxygen corrosion - on the waterside of boiler, 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 or decarburised water or permeate is used, the time without preservation is restricted to approx. 1 week.

Exceeding times require 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 alkaline water 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 either:

- Application of inert gas (nitrogen) with partly filled or empty but wet boiler,
- Excess of oxygen scavenger and elevated pH with completely filled boiler (full up to vent!),
- Keeping steam pressure from top (steam blanket) leads to condensate formation in the drum, lowers the BW pH in the drum and needs drainage to keep the BW level.

Dry preservation is recommended for longer downtime by either:

- Using of re-circulating dryer or
- Desiccants e. g. silica gel (avoid direct contact to steel!)

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

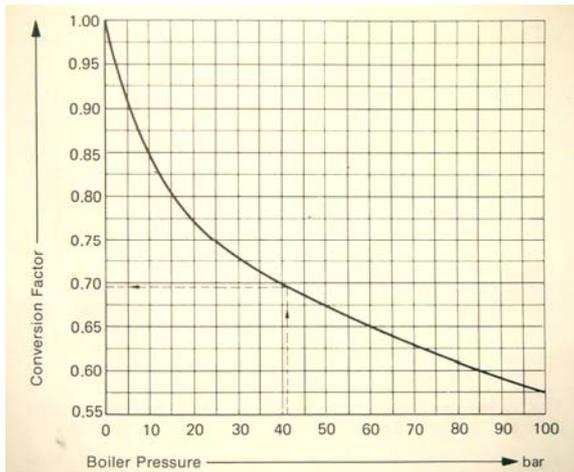
Presupposition for any preservation methods mentioned is a real protective oxide layer!

## 6 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 1.5 mm or 12 x 2 mm.

Hot samples - at least BW – should be cooled down to ca. 25 -30 °C with a flow of ca. 25 l/hr using a cooler coil that should be made from stainless steel. BW samples taken without cooling must be corrected by factors taken from **Fig. 18**.

All sampling devices should have a straight blow out line before entering the cooler or the measuring equipment.



**Fig. 18:**

Conversion factor for non volatile BW compounds like alkalinity, conductivity, phosphate, silica, sulphite etc.

Example: Results from BW sample taken without cooling from a boiler with 42 bar must be corrected by 0.69 to get values existing in reality within the boiler.

For a 10 bar boiler the correction factor is 0.85, e.g. a p-value of 100 in the sample corresponds to a p-value of 85 in the BW!

## 6.1 Sampling of Water

No special design necessary, but a representative average (bulk) sample must be available.

Sampling points are recommended after any treatment step and chemical dosing point, which leads to a possible change of the water quality, for instance:

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

## 6.2 Chemical Control of Plant Circuits

Manuel controlled should be at least Boiler Feedwater (BFW) and Boiler Water (BW) for the following safety related parameters in clear samples (if not clear – filtrate!)

- |              |  |
|--------------|--|
| 1 x per day  | Total and composite alkalinity (P- an M-value) or pH |
| 1 x per day  | Total hardness                                       |
| 1 x per day  | Conductivity / Gravity                               |
| 2 x per week | Phosphate / Anti-scalants - if dosed                 |
| 2x per week  | Silica   |

On-Line controlled should be conductivity of BW because it can be used as signal for automatic blow down.

Additional checked should be make-up water and condensate return.

## 7 Boiler Pre-Treatment and Chemical Cleaning of Boilers

## 7.1 Procedures for Boiler Cleaning

### 7.1.1 Alkaline boil out

Before alkaline boil out, boilers must be mechanically cleaned and rinsed with BFW or softened water 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 from manufacturing as well loose oxides and dust. Commonly applied is tri-sodium phosphate, in special cases caustic soda in 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.

For boiler with *heated* crevices e. g. between tubes and tube-sheet, like shell boiler smoke tubes the exclusively use of caustic soda is prohibited (may initiate caustic 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 solution.

### 7.1.2 Chemical Cleaning during shutdown

#### *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/m<sup>2</sup>. 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!

Inhibitors for acid cleaning are organic compounds that reduce corrosion to metallic surfaces drastically in specific media. 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/m<sup>2</sup> during application.

The cleaning process must be controlled by measuring at least acid and metal concentration. Cleaned boiler shall go into operation as soon as possible

### 7.1.3 Chemical Cleaning during operation

Cleaning during operation (see also chapter 4) 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.

Recently biological degradable organic anti-scalants and dispersants have been developed with sufficient forming strength, 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.

## 7.2 Application of Cleaning Procedures

### 7.2.1 New Boiler

New boiler may be very dirty and rusty - but it must not be! Do not accept rusty vessels, a new boiler shall not show more than approximately 5-10 % rusty surface! Insist in quality management during manufacturing and erection to keep boiler components and auxiliary equipment as clean as economically possible aiming to avoid chemical cleaning!

Accept only surfaces with thin mill scale without significant rust!

Practice quality control during erection:

Control clean erection, cover holes and bores from welding slag, grinding dust, remains of electrodes etc. Preserve parts of the boiler during erection.

New boiler in good condition must not be cleaned with acid, alkaline boil out (see 7.1.1) is mainly sufficient, exceptions see chapter 7.1.1.

### 7.2.2 Used Boiler

Industrial boiler and boiler with scale/deposits of water constituents and corrosion products should be cleaned every 5 to 10 years during shut-down, depending on their surface conditions particularly at areas with the highest heat flux. Thermal stressed boiler and boiler with high heat transfer should be preventively cleaned every 3 to 5 years.

Preventive cleaning during operation using organic anti-scalants and dispersants (see 7.1.3) may extend the need for acid cleaning as far as this is done e.g. every year for about 1 month time to remove possible deposits.