



**BOSCH**  
Invented for life

## Expert Report

[www.bosch-industrial.com](http://www.bosch-industrial.com)

## Modern water treatment and water analysis

Dipl.-WirtschaftsIng. (FH), Dipl.-Informationswirt (FH) Markus Tuffner, Bosch Industriekessel GmbH  
Technischer Betriebswirt IHK, Christian Arnold, Bosch Industriekessel GmbH

In all applications in which water is brought to a higher temperature, difficulties can occur due to the water contents. The most frequent cause of damage in boiler operation is damage induced by inadequate water treatment, conditioning and analysis.

Corrosive components in feed water or in condensates can damage feed water tanks, boilers or the complete condensate system. These components are created mainly by oxygen or carbon dioxide corrosion. In addition, certain components in the water can cause unwanted deposits to form. The best known of these is the one caused by the water hardness. If the build-up of deposits is not noticed early enough, it will prevent the transmission of heat and cause the efficiency of the boiler to deteriorate. If the layers continue to increase in thickness, it can cause overheating of the heating surfaces and serious damage, which may even cause the boiler to explode. It can also cause problems in subsequent processes through

foaming and the entrainment of inadequately prepared boiler water. In addition to the deterioration in steam quality, this can have enormous effects on the working life of subsequent elements, fittings, pipes and the attached consumer units.

For this reason, legislators have approved a wide ranging set of regulations calling for compliance of precisely defined water qualities. DIN EN 12953-10 lays down requirements regarding the appearance, conductivity, pH value, overall hardness, acid capacity, iron, copper, silica, oil/grease, phosphate and oxygen concentration. In addition, water must be free from organic substances. Depending on the capacity

and size of the boiler system, various water treatment measures are applied. The raw water used is generally provided by municipal utility companies according to local drinking water ordinance (Germany: TrinkwV) and may be treated for use in boilers using the following methods.

## Softening or desalting

The methods most commonly used are softening using ion exchangers and desalting using reverse osmosis. With smaller systems or high condensate return flow rates, low-priced desalting is often used. In this process, the components that cause water to become hard (alkaline earths: Ca and Mg ions) are replaced with sodium (Na) ions. The salt content of the water remains more or less constant with this process. The ion exchangers are regenerated with a salt solution (NaCl).

Reverse osmosis is a more cost-intensive procedure and is therefore used mainly for systems with high make-up water rates or if boiler water with a low conductivity is needed for other reasons (e.g. steam quality). In this process, permeable membranes are used, which work like a filter in the molecular sector. If an aqueous solution is pressed through these membranes under high pressure (greater than the

osmotic pressure), most of the salts and other matter is left behind and pure water passes through the membrane.

Depending on the capacity, it may be necessary, with osmosis, that water softening is carried out before or afterwards. Presoftening is carried out as described and tends to be used for smaller capacities. If large quantities of water need to be desalted using osmosis, controlled quantities of chemicals are generally added before osmosis to prevent the osmosis from becoming blocked by the contents that produce hardness. Secondary softening is carried out after osmosis to remove any remaining alkaline earths (Ca and Mg ions).

Partial desalting is a process between softening and osmosis, also called decarbonization; it is used less and less frequently in comparison with the other two processes. The method is similar to softening using the ion exchange method. The calciumcarbon dioxide balance is shifted by the addition of hydrogen ( $H^+$ ) ions. Carbon dioxide which is bound in the carbonate compounds ( $HCO_3^-$ ) is released. The dissolved calcium and magnesium ions (non carbonate hardness) are then replaced with sodium in the subsequent ion exchange process. The ion exchangers are regenerated with hydrochloric acid or sodium chloride (NaCl).



Figure 1: A lack of water treatment caused the formation of a hard layer which can lead to boiler explosion in the extreme case.



Figure 2: Water treatment module WTM for softening the boiler feed water.

### Thermal deaeration (O<sub>2</sub> or CO<sub>2</sub> reduction)

Softening or desalting is followed by thermal deaeration. In this process, the chemical-physical law is used which states that the concentration of gases in liquids decreases as the temperature rises and is around zero when the liquid is boiling.

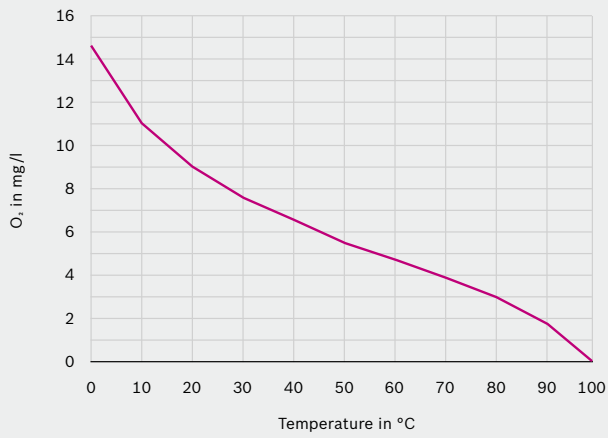
Because of the lower investment costs, an 'unpressurized' partial deaeration system is often used with smaller plants. Because of the low operating temperature between 85 and 90 °C, with partial deaeration no deaeration device and feed water tank have to be applied. The gases present in the water in dissolved form are removed by the heating and leave the system with what is called the vapour steam. Because of the working temperatures that have been set, this process is not complete. Minor concentrations of gases, especially oxygen and carbon dioxide, are still present. Chemical after-treatment is essential.

In general, a full deaeration system is the right choice in terms of the expected service life of the boiler

plant. Partial deaeration systems, which are applied in the low and unpressurized range are the better choice in case of discontinuous operation; especially in the low capacity range of up to 2,000 kg/h. In this case the recommendation is to carry out the feed water tank in stainless steel.

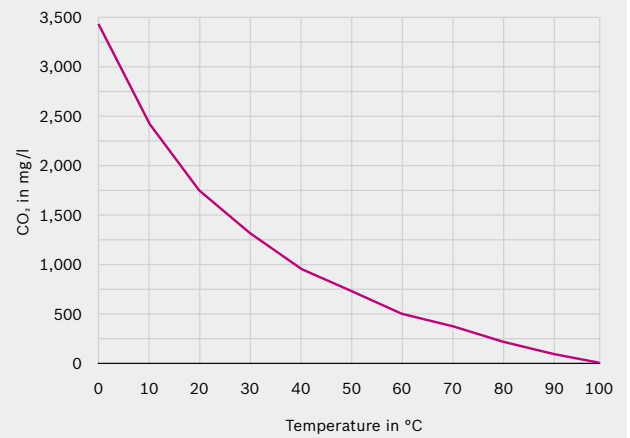
For larger systems or systems with a very low condensate return flow, full deaeration systems are therefore generally used. These work in a temperature range between 100 and 110 °C. A deaeration dome on the feed water tank or a spray deaeration device enlarges the surface of the make-up water or the returning condensate. By means of direct steam injection, the feed water in the feed water tank is heated to boiling temperature. The resultant steam heats up the incoming water and removes the gases. These escape via the vapour outlet of the deaeration device into the open air. Steam also flows constantly into the open, as the transport medium (vapour steam). The vapour pipe should be designed in such a way that all the

**Graphic 1: Solubility of oxygen as a function of temperature at 1 bar atmospheric pressure**



Source: WABAG Handbuch Wasser

**Graphic 2: Solubility of carbon dioxide as a function of temperature at 1 bar atmospheric pressure**



Source: TÜV Nord



Figure 3: Oxygen attack on a cut-out smoke tube

gases released are removed, even if the conditions are less than favourable. According to literature, the necessary vapour steam flow is up to 0.5 % of the steam capacity of the boiler. The residual quantities of oxygen and carbon dioxide are negligible after proper full deaeration. The addition of a small amount of chemicals is only recommendable for measurement or safety reasons.

### Chemical dosing (O<sub>2</sub> or CO<sub>2</sub> binding)

Depending on the various physical water treatment processes, residual hardness and residual oxygen binding must be carried out by chemical means. In addition, increasing the alkalinity (raising the pH) of the water is also required. Excessive quantities of chemicals are often added.

The reasons for this were generally lack of constant monitoring and an empirically determined dosage level. Regarding the residual oxygen content, the reason was the lack of a cost-effective measurement procedure for direct measurement. For this reason, the excess of dosed chemicals in the boiler, rather than the residual oxygen content, were determined in order to be able to guarantee complete removal of oxygen at least cyclically. In addition to the excessive price of the dosed chemicals, this also has a disadvantage in terms of energy use. An overdose of chemicals

often results in a rise of conductivity (salt content), or of precipitation of sludge, which has an influence on the energy losses through desalting and/or blowdown operations. In addition, problems can also be caused by the foaming of the boiler water. Faults in the form of lack of water or high water level switching off can result. Water entrainment causes a deterioration in steam quality, leading to water hammers and possible damage to subsequent consumer units.

### Measurement analysis

To ensure that the boiler water quality is suitable, the water parameters must be monitored continuously and/or periodically. The feed and boiler water in steam boilers and the circulating water in hot water systems must be tested to check the relevant parameters (pH, direct conductivity, acid capacity, hardness and oxygen content). The frequency of such inspections must be based on the requirements of the manufacturer, the operator and the relevant authorities. Normally, this is carried out manually to date (except for conductivity), which is both time-consuming and labour-intensive. The various water analyses should be carried out every day, or, if the system is equipped for operation without supervision, at least every 3 days and have to be recorded in the boiler logbook. Therefore, Bosch developed the water analyzer WA to support the boiler operator. The new WA allows the continuous measurements to be taken fully

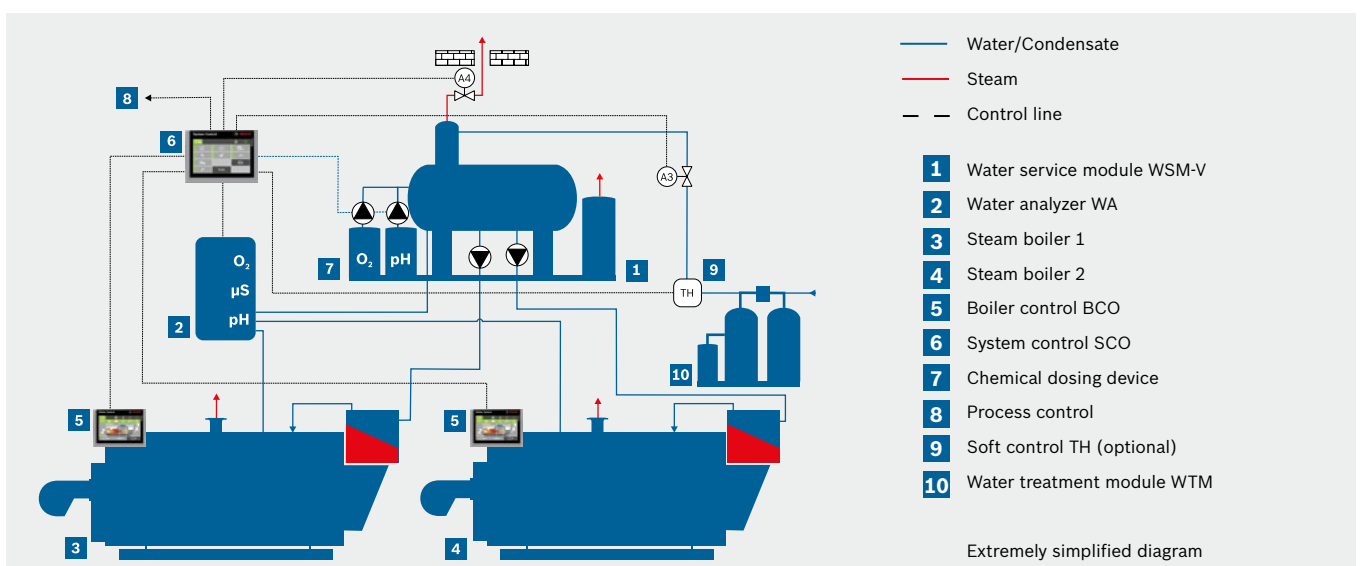


Figure 4: The modular integration of the water analyzer WA in a boiler plant overall system

automatically and digitally. All determined data is then saved and transmitted to the overall System Control SCO (Figure 4). Usually, a reduction of chemical use is the result due to the fact that the appropriate dosing of the used chemicals is carried out more precisely based on the determined values.

In order to allow measurements to be carried out, sample removal points should be provided at appropriate points in the system. Typical removal points are the boiler feed water tank, the desalting connection at the boiler and the makeup water after the water treatment system. These sample removal points must be fitted with suitable cooling devices (water sample coolers), which allow the water to be removed properly and safely.

The conductivity is determined continuously using a conductivity measurement electrode installed at the boiler water surface. The total hardness and the acid capacity (p value) have so far usually been determined by titration with dimensional solutions or photometrically with suitable measurement devices. With titration, reaction solutions are dripped into the sample water to be tested until the water changes colour. The quantity of reaction solutions allows conclusions to be drawn about the acid capacity or the total hardness. The photometric processes work on a similar basis, but the strength of the colour change after the addition of a defined quantity of reaction solution is measured. However, it has always only been possible to determine the oxygen content of the water using very expensive measurement analysis equipment.

All of the traditional measuring methods are very time consuming and susceptible to errors.

## Water analysis device WA

A newly developed water analysis device, known as water analyzer WA, deals with these problems and automatically carries out the continuous measurement and monitoring of:

- ▶ pH value of the feed water
- ▶ O<sub>2</sub> content of the feed water
- ▶ Softcontrol TH optionally
- ▶ pH value of the boiler water



Figure 5: The newly-developed water analyzer WA for fully automatic measurement and monitoring of the water quality.

### New measurement methods have been developed specially for this

A zero oxygen level is no longer confirmed by an excess of oxygen binders; instead, the O<sub>2</sub> content is measured at its actual level. The measurement electrode is a micro glass capillary filled with reaction liquid which generates a current flow due to the oxygen that is diffusing in. This current flow is measured, allowing the exact oxygen content to be determined within the measurement range relevant in boiler technology of 0.001 – 0.1 mg/l.

The pH value of the feed water and boiler water is determined with a pH reference measuring electrode which determines the positive hydrogen ions in the water. Once again, a small voltage is induced, which provides reliable statements about the pH value in the measurement range between 7 and 14.

All the electrodes are self-monitoring. At certain intervals, reference measurements are automatically carried out, either in comparison with raw water or with each other, to check that everything is working properly. The various measuring electrodes are subject to natural wear and tear. The costs of the replacement electrodes are roughly the same as the costs of the indicator solutions and test strips required for manual water analysis. All data are transmitted via a bus system to the higher level System Control SCO. Together with the boiler water conductivity and the conductivity or clouding of the condensate flows, all the relevant water parameters are then available in the SCO.

The water analyzer WA offers a range of advantages over conventional manual monitoring:

- ▶ Boiler and system damage is reduced by increasing operational reliability.
- ▶ In order to obtain correct measurement results, manual measurements must be carried out by well trained staff. Often, mistakes are made when taking the various water samples or when handling the reaction solutions, which distort the results dramatically.

- ▶ Analyses using the water analyzer WA, on the other hand, run completely automatically without any intervention, which means that the measurement results are correct and precise.
- ▶ If specified limit values for the water quality are exceeded, the boiler system protects itself. Depending on the way in which the values are exceeded, defined control tasks are carried out. If, for example, the hardness limits are exceeded, the make-up water valve is closed immediately.

### Fault alarm management

All the relevant parameters are transmitted to the fault alarm memory of the SCO if a limit value is exceeded (Figure 6). This makes it easier to analyze the failure causes.

### Logging

The data can also be continuously logged. The data (Figure 8) can then be transmitted at defined intervals either by Profibus to a higher level control point or via a defined interface directly to a local printer or screen writer. There is no need for manual measurements and the manual recording of the water values in a boiler operating logbook.

### Regulating and control tasks

The various dosing pumps are regulated on the basis of the water qualities measured. There is no need for excess dosing, since the water parameters are determined by direct methods. This means that enormous savings can be made on chemicals to be added and that desalting and blow-down losses are reduced. With conventional operation, the vapour steam flow is designed to be approx. 0.5 % of the nominal capacity

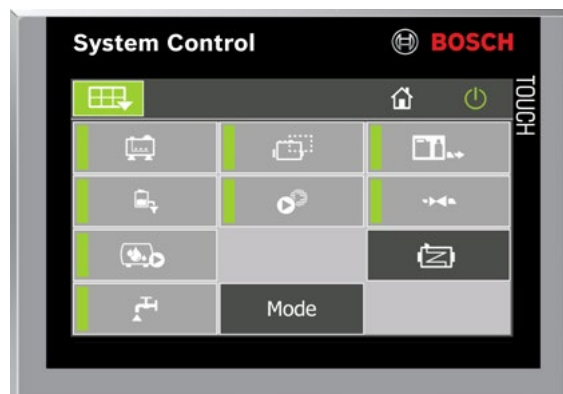


Figure 6: The higher-level System Control SCO collects and stores relevant water data and triggers protection, regulation and control tasks.

of the boiler. This results in a constant loss of energy through the rising vapour steam. Measuring the oxygen content with the water analyzer WA allows the vapour valve to be controlled specifically. The valve can be closed within the permitted limit values. Only if the required limit values are exceeded, i.e. when the deaeration function is really required, does the vapour valve open, so that the vapour steam containing oxygen and carbon dioxide can leave the system. This results in tremendous fuel savings.

### Savings potential

The potential for saving costs with the water analyzer WA is enormous. Depending on the size and equipment of the systems, fuel and water savings mean that they will pay for themselves in no time. This does not count the fact that operating safety is increased by the analytically correct measurement results and that system damage caused by inadequate water parameters is reduced.

### Measurement of residual hardness

The hardness is measured using a measurement electrode (Figure 7) which is based on an ion-selective polymer membrane. This membrane is only permeable to the ion hardness formers Ca and Mg. On the basis of the quantity of ions, a voltage is induced which allows the hardness grade of the water to be determined. In the measurement range between 0.0018 – 0.18 mmol/l (0.01 – 1 °dH) all deviations can be reliably determined.

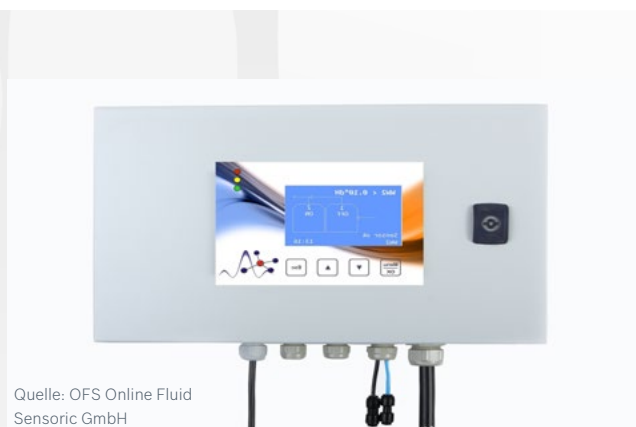


Figure 7: The measurement module Softcontrol for TH hardness measurement points out the hardness of the feed water regularly and independently and delivers the data to the SCO.

## Summary

The methods listed in the first section for the treatment of water by softening, desalting, deaeration or dosing describe very clearly how demanding and often how difficult it can be to ensure correct boiler water quality with the manual means used to date. Automatic water analysis using the water analyzer WA thus has the following advantages:

- ▶ Requirement-based dosing of chemicals depending on the pH value and O<sub>2</sub> level of the feed water – no expensive excess dosing with desalting and blow-down losses
- ▶ Automatic residual hardness monitoring of upstream softening systems on an ion exchange basis
- ▶ Control of a vapour valve depending on the oxygen content of the feed water, avoiding unnecessary energy losses
- ▶ Increased operating safety with analytically correct measurement results
- ▶ Time savings due to automatic measurement
- ▶ Reduction of damages caused by inadequate water parameters
- ▶ All data from the continuous, fully automatic water analysis can be forwarded by bus to a screen writer or printer, displayed, printed or saved – there is no need for a boiler logbook to be kept manually

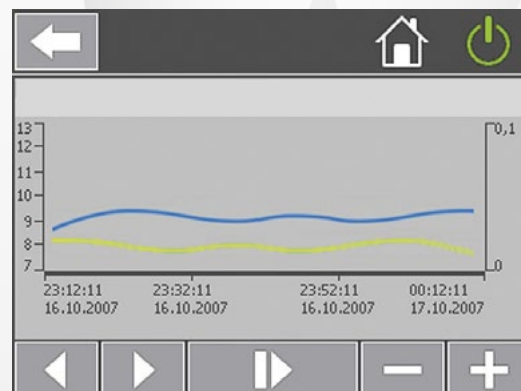


Figure 8: The water parameters saved in the SCO (System Control) can be clearly displayed as a graph.



## Requirements for feed water and boiler water quality

Raw water is water that is supplied to the water treatment plant. The connection is to the regional water system or company well. Make-up water is water that is supplied after the water treatment plant.

Independent of the quality of the feed water, the boiler systems can be operated with a high or low salt content. The quality of the feed water must be higher for salt-free operation.

Boiler design		Shell boilers				
Hydrochemical operation		Containing salt		Low salt	Salt-free	All areas
Area of application		≤ 20 bar	> 20 bar and all double flame-tube boilers	All boilers	All boilers	All systems with water analyzer WA
Column		1	2	3	4	5
General requirements <sup>8)</sup>	[-]	Colourless, clear, free of insoluble matter and foaming agents				
ph value at 25 °C <sup>1)</sup>	[-]	10.5–12.0	10.5–11.8	10.0–11.5	9.5–10.5	As column 1–4
K <sub>S,8,2</sub> (p value) <sup>7)</sup>	[mmol/l]	1–12	1–8	0.1–3	0.05–0.3	As column 1–4
Alkaline earths <sup>2) 8)</sup>	[mmol/l]	<0.01	<0.01	<0.01	<0.01	<0.01
(Total hardness) <sup>2) 8)</sup>	[°d]	<0.05	<0.05	<0.05	<0.05	<0.05
Phosphate (PO <sub>4</sub> <sup>-3</sup> ) <sup>3) 8)</sup>	[mg/l]	10–30	10–30	10–30	<6	>5
Sodium sulfite oxygen binder (Na <sub>2</sub> SO <sub>3</sub> ) <sup>4) 8)</sup>	[mg/l]	10–30	10–20	10–20	–	>2 <sup>4)</sup>
Direct electrical conductivity at 25 °C <sup>5) 7)</sup>	[µS/cm]	<6,000	<4,000	<2,000	<150	As column 1–4
KMnO <sub>4</sub> consumption <sup>7)</sup>	[mg/l]	<150	<100	<50	<30	As column 1–4
Salicylic acid (SiO <sub>2</sub> ) <sup>7)</sup>	[mg/l]	<150	<80	<40	<4	As column 1–4

Table 1: Requirements for the boiler water

		Shell boilers Working gauge pressure ≤ 20 bar and quick steam generators <sup>6)</sup> all pressure stages	Shell boilers Working gauge pressure > 20 bar
General requirements <sup>8)</sup>	[-]	Colourless, clear, free of insoluble matter and foaming agents	
ph value at 25 °C <sup>1)</sup>	[-]	from ... >9.2	
Direct electrical conductivity at 25 °C <sup>5)</sup>	[μS/cm]	≤ 5% of the boiler water threshold	
for quick steam generators		< 500 minimal salt	–
K <sub>S,8,2</sub> (p value) containing salt/low-salt	[mmol/l]	≤ 0.7	≤ 0.5
K <sub>S,8,2</sub> (p value) salt-free	[mmol/l]	≤ 0.1	
Alkaline earths <sup>2) 8)</sup>	[mmol/l]	< 0.01	
(Total hardness) <sup>2) 8)</sup>	[°d]	< 0.05	
Oxygen (O <sub>2</sub> ) <sup>4)</sup>	[mg/l]	< 0.05	< 0.02
Oxygen binding agent <sup>4) 8)</sup>	[mg/l]	see bullet points 4 and 8 of annotation	
for quick steam generators <sup>6) 8)</sup> (Na <sub>2</sub> SO <sub>3</sub> )		5–10	–
Total iron (Fe)	[mg/l]	< 0.3	< 0.1
Total copper (Cu)	[mg/l]	< 0.05	< 0.03
Oil, grease	[mg/l]	< 1	
KMnO <sub>4</sub> consumption	[mg/l]	< 10	
Salicylic acid (SiO <sub>2</sub> )	[mg/l]	≤ 5% of the boiler threshold	
for quick steam generators		–	–

Tabelle 2: Anforderungen an das Speisewasser

**Annotations to tables 1 and 2**

- 1)  
Setting of alkalinity (pH value or  $K_{S\ 8.2}$ ):
- ▶ With operation with salt with solid-matter alkalies (e.g. trisodium phosphate or tripotassium phosphate, sodium hydroxide), when the alkalinity does not adjust automatically. If necessary add volatile product.
  - ▶ With low-salt operation, mainly with trisodium phosphate or tripotassium phosphate, if necessary adding volatile products (ammonia). If, due to the level of steam purity required (food industry, sterilization, air humidification, etc.), the use of volatile chemicals is not possible, small quantities of soda lye can also be added to the phosphate.
  - ▶ With salt-free operation, only with trisodium phosphate or tripotassium phosphate, adding steam volatile products if necessary (e.g. ammonia).
- Note: When dosing ammonia, avoid the use of non-ferrous heavy metal resources in areas coming into contact with the media!
- 2)  
Both feed and boiler water should be practically hardness-free. Because the detection limit of current hardness tests is min. 0.01 mmol/l or 0.05 °d, the same limit values have been set for both waters irrespective of any thickening. Use of a dosing agent for binding or stabilization of residual hardness is recommended, e.g. a phosphate-based product. If the dosing agent used for hardness stabilization is one which produces negative results for hardness using the usual hardness test methods, then its excess concentration is to be tested with the test kit prescribed for that purpose according to supplier specifications, in place of the hardness measurement.
- 3)  
Stick to the limit values with phosphate dosing. With low-salt and salt-free operation, it is absolutely essential to add trisodium phosphate or tripotassium phosphate – see 1).  
With operation containing salt, phosphate-free agents may be used for earth alkaline compounds.  
Limit values for  $PO_4$  are not applicable in this case. The supplier is obliged to issue dosing instructions for the respective dosing agent and to make available appropriate analysis methods. The use of a dosing agent is to be agreed with the manufacturer. However, ultimate responsibility for the suitability and functioning of the dosing agent lies with the supplier.
- 4)  
The oxygen in the feed water must be reduced primarily using physical processes, e.g. thermal pressure deaeration, to the described limit values. Because in practical operation, partly through frequent down times, start-up and run-down processes etc. and with partial deaeration systems, compliance with the limit value is not guaranteed using deaeration alone, an oxygen binder should be added.  
Non-volatile sodium sulphite, for example, has proved effective – there are no hygienic/ toxicological restrictions. Addition to the feed water should be carried out in such a way that the limit values for the boiler water are maintained. The need for this and the choice of a suitable dosing agent must be decided in each individual case. For salt-free operation is not essential to dose an oxygen binder, even when an WA is used.  
Note: Film-forming amines are not oxygen binders!
- 5)  
In addition to the electrical conductivity, the silicon dioxide content ( $SiO_2$ ) and the pH (auxiliary parameter  $K_{S\ 8.2}$ ) are important parameters, and their maximum values must not be exceeded in the boiler. If one of these values is reached before the maximum conductivity value because of thickening in the boiler, this is then decisive for desalting. Because the desalting is regulated via a conductivity measurement, the corresponding conductivity value at which one of the named parameters reaches its permitted maximum value replaces the conductivity limit value shown in Table 1.  
The values given in Table 1 are the maximum permitted conductivity values. For plants in which the conductivity is incorporated into the safety chain, when these values are reached (at the latest), the firing is switched off and locked, i.e. the conductivity to be regulated is to be set with a sufficient distance from the limit value (min. 30 %).  
If unusually pure steam is needed, it may be, under some circumstances, that the maximum conductivity value in the boiler water needs to be lowered for this special case. The limit values for electrical conductivity, pH (auxiliary parameter  $K_{S\ 8.2}$ ) and silicon dioxide in the feed water are the result of the desalting rate (assumed at 5 %) and the limit value of the boiler water. Higher feed water conductivity,  $K_{S\ 8.2}$  value or silicon dioxide contents are permitted, whereby compliance with the boiler water values (Table 1) is binding.  
However, then desalting rates greater than 5 % will occur, and an examination of the boiler components (e.g. desalting valve, feed pump, burner, deaeration, etc.) is urgently required.
- 6)  
With quick steam generators, only the feed water needs to be examined. A test must be carried out for the oxygen binder in the separated residual moisture element (taken from the water separator which is attached directly to the quick steam generator, or the first pipe drainage in the steam line after the boiler).
- 7) For shell boilers with superheaters, the boiler water limit values must be halved for operation containing salt (direct electrical conductivity in the feed water at 25°C > 30  $\mu S/cm$ ) for  $K_{S\ 8.2}$  (p-value), direct electrical conductivity at 25 °C,  $KMnO_4$  consumption and silicon dioxide ( $SiO_2$ ).
- 8)  
Dosing agent on the basis of tannin and lignin compounds are used as oxygen-binding agent and for residual hardness stabilization and alkalization, among others. They cause brown discolouring of the boiler water and bind any residual hardness in the boiler water; however, this residual hardness remains measurable as such through the use of conventional residual hardness measuring instruments. Therefore, in the event that such substances are used, the respective supplier shall make sure through the operating instructions of the respective dosing chemical that the protection objective of the operating instructions B002 guideline on water characteristics for steam boilers is complied with, that deviating specifications (e.g. for visual appearance, for the perm. residual hardness, for excess of oxygen-binding agent, etc.) are explained and covered by alternative values and/or instructions in the documentation of the dosing chemical so that any occurring deviations are recognized immediately.

**Bosch Industriekessel GmbH**

Nuernberger Strasse 73  
91710 Gunzenhausen  
Germany  
Phone +49 9831 56253  
Fax +49 9831 5692253  
sales@bosch-industrial.com  
Service Hotline +49 180 5667468\*  
Spare Parts Hotline +49 180 5010540\*

**Bosch Industriekessel Austria GmbH**

Haldenweg 7  
5500 Bischofshofen  
Austria  
Phone +43 6462 2527300  
Fax +43 6462 252766300  
sales-at@bosch-industrial.com  
Service Hotline +43 810 810300\*\*  
Spare Parts Hotline +49 180 5010540\*

**info@bosch-industrial.com**  
**www.bosch-industrial.com**  
**www.bosch-industrial.com/YouTube**

\* EUR 0.14/min from German landline; maximum mobile phone price: 0.42 Euro/min  
\*\* max. EUR 0.10/min from Austrian landline  
Different charges may apply for calls from mobile networks and for international calls.

© Bosch Industriekessel GmbH | Images only exemplary |  
Subject to modifications 06/2018 | TT/MKT-CH\_en\_FB\_Wasseraufbereitung\_02