

VGB-Standard

Feed Water, Boiler Water and Steam Quality for Power Plants / Industrial Plants

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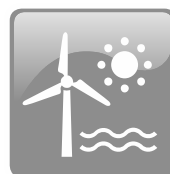
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Preface to the 2011 edition

VGB PowerTech hereby presents a revised version of the European VGB-Standard for Feed Water, Boiler Water and Steam Quality for Power Plants/Industrial Plants. This new VGB-Standard replaces the former "Guideline for Feed Water, Boiler Water and Steam Quality for Power Plants/Industrial Plants", edition 2004.

The present VGB-Standard summarises the experiences gained within water-steam chemistry and is the work of a project group under the VGB Technical Committee Chemistry. The following co-workers were involved in the revision of the VGB-Standard:

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They and everybody else who has actively taken part in the revision of the VGB-Standard are thanked sincerely for their effort. The VGB office will be happy to receive comments, further information and proposals for improvement for the next version of this VGB-Standard.

This VGB-Standard covers all pressure ranges applied to boilers generating heat, steam and/or electricity. In general the VGB-Standard covers steady state/full load operation of those boilers as well as start up operation mode by using action levels. This concept allows a quite flexible approach to combine requirements of the materials used throughout the water-steam cycle with economical needs of the plant operator.

The VGB-Standard does not deliver absolute limiting values of chemical parameters but demonstrates permissible operation ranges to achieve minimal corrosion within the water-steam cycle and to reach an optimised lifetime of the plant.

Essen, December 2011

VGB PowerTech e.V.

Preface to the 2004 edition

EPPSA, FDBR and VGB PowerTech hereby present a European **Guideline for Feed Water, Boiler Water and Steam Quality for Power Plants / Industrial Plants**. This new guideline replaces the former "VGB Guideline for Boiler Feed Water, Boiler Water and of Steam Generators with a Permissible Operating Pressure > 68 bar, October 1988 Edition".

The present Guideline is the work of a joint European Technical Committee with representatives of EPPSA, FDBR and VGB from most EU countries. The Technical Committees of these organisations have discussed and agreed this guideline.

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The reader should be aware, that this guideline covers all pressure ranges applied to boilers generating heat, steam and/or electricity. In general the guideline covers steady state/full load operation of those boilers as well as start up operation mode by using **action levels** for the first time. This concept allows a quite flexible approach to combine requirements of the materials used throughout the water-steam cycle with economical needs of the plant operator.

It should be pointed out that this guideline does not deliver absolute limiting values of chemical parameters but prefers to demonstrate reasonable areas of permissible operation ranges in respect to a minimal corrosion within the water-steam cycle to reach an optimised lifetime of the plant. Plant specific agreements on various parameters may supplement these guidelines.

Use it ***cum grano salis*** and as well ***respice finem!***

Essen, December 2004

VGB PowerTech e.V.

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1 Scope

This VGB-Standard supports the operator of water-steam cycles in power plants and related branches in selecting and judging suitable water regimes with respect to a safe and economically sound operation of the power plant for a long period of time. Of course the shown parameter values are no absolute commandments or limits – they are recommendations and represent the bandwidth of water regimes in use. Deviations are always possible if the plant design is specific and/or good operating experience has been made during a long time.

Additional flexibility has been introduced by applying the “action level” philosophy. This is true for continuous operation and especially for start up periods. The same rule applies here: the user has to take into account the specific design of his plant and modify the parameter limits according to the specific needs.

To clarify the difference between this VGB-Standard and the EN 12952-12: the EN 12952-12 describes minimal requirements for feed water and boiler water to operate a boiler in a **safe** way. This standard supersedes various national requirements, e. g. the German TRD 611.

This VGB-Standard (S-010-T-00;2011-12.EN), gives recommendations for the complete water-steam cycle that go further: not only a safe operation is looked upon, but it aims at an **economically sound and safe** mode of operation for a long period of time.

The VGB-Standard describes requirements for feed water, boiler water and steam of water-steam cycles in once-through and drum boilers and all pressure ranges. It is valid for salt free and salt containing feed water.

Examples of the grave consequences experienced by not following the recommendations of the VGB-Standard are mentioned in the relevant chapters.

2 Definitions

For the purpose of this VGB-Standard the following definitions apply:

conductivity	Directly measured (specific) conductivity of water
acid conductivity	Conductivity of water measured downstream of a strongly acidic sampling cation exchanger.
all volatile treatment (AVT)	Conditioning concept where only volatile alkalizing agents are used, mainly ammonia.
oxygenated treatment (OT)	Conditioning concept where alkalizing agents and oxygen are added.
caustic treatment (CT)	Under this treatment boiler water pH is maintained with sodium hydroxide.
phosphate treatment (PT)	Under this treatment boiler water pH is maintained with tri-sodium phosphate.
make-up water	Water which compensates for losses of water and steam from the system.
feed water	Mixture of returned condensate and/or make-up water supplied to the boiler inlet.
boiler water	Water within a natural or assisted circulation boiler.
attenuator spray water	Water for injection to control steam temperature.
drum boiler	Water tube boiler in which the water to be evaporated circulates due to the differences in density (natural circulation) or by means of pumps (forced or assisted circulation).
once-through boiler	Water tube boiler in which the water flow is forced by the feed pump. In such a boiler the water is evaporated completely or in a major portion during one single stage.
shell boiler	In this type of boiler the boiler water flows around the tubes, and hot flue gas or process gas flows through the tubes.
steam turbine feed water pump (German: SPAT)	Feed water pump driven by steam from an exhaust of the main turbine.
air preheater (German: LUVÖ)	Heat exchanger in which air for the combustion in the boiler is preheated, usually by means of steam. Condenser in which steam from the exit of the turbine flow through tubes and condenses in indirect heat.

air condenser (German: LUKO)	Exchange with the surrounding air.
district heater (German: HEIKO)	Heat exchanger in which heat is transferred to a district heating net, i. e. the district heating water is heated up primarily by the condensation heat.
reserve condensate tank (German: KAKO)	Buffer tank for storage of condensate that is fed to or withdrawn from the water-steam cycle in case of start-up or shut-down situations or load changes.
FAC	Flow accelerated corrosion, i. e. corrosion near edges of the material induced or accelerated by water films under influence of the flowing steam.
softening of water	Removal of calcium and magnesium ions in the water by means of a strongly acidic cation exchanger in the sodium form.
decarbonisation	Reduction of alkalinity by means of lime treatment, addition of acid, or ion exchange.
demineralized water	Water that fulfils the quality criteria (according to VGB-M 407 G): Conductivity 25 °C $\leq 0.08 \mu\text{S}/\text{cm}$; $\text{SiO}_2 \leq 0.010 \text{ mg}/\text{L}$; $\text{Na} \leq 0.005 \text{ mg}/\text{L}$.
key parameter	Quality indicator for the purity of feed water, steam, or condensates that is typically monitored continuously by means of an appropriate sampling system (according to VGB-S-006-T-00;2012-00.EN).
diagnostic parameter	Quality indicator for the purity of feed water, steam, or condensates that usually is analysed only in the case of passage of the AL1 threshold to clarify the cause of the excursion.
combined cycle	Power plant in which the generator is driven both by a gas and a steam turbine.
HRSG	Heat recovery steam generator. Compact steam generator typically used in the gas turbine exhaust duct of combined cycle power plant.
protective layer	A protective layer on a metal surface is a substance that reduces the corrosion of the metal.

3 Water-steam cycle system

The present VGB-Standard specifies the quality of feed water, boiler water and steam.

Process diagrams of typical water-steam cycle systems are shown in Figure 1 and Figure 2.

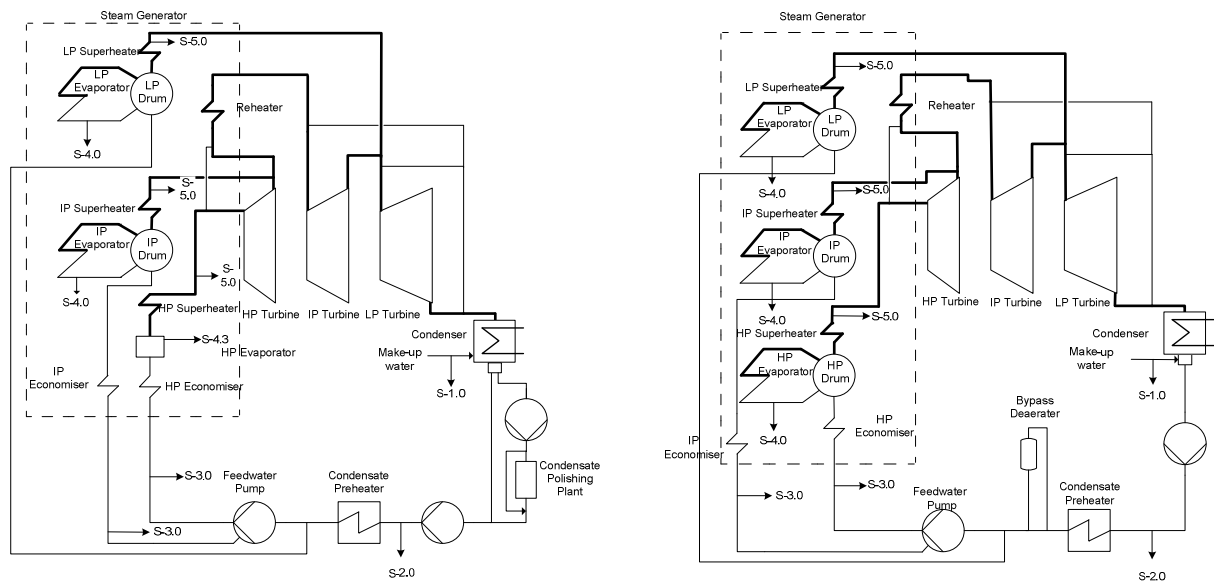


Figure 1: Examples of process diagrams of water-steam cycle systems; Left: HRSG with once-through HP-stage and with steam reheater; Right: 3-stage drum HRSG with steam reheater.

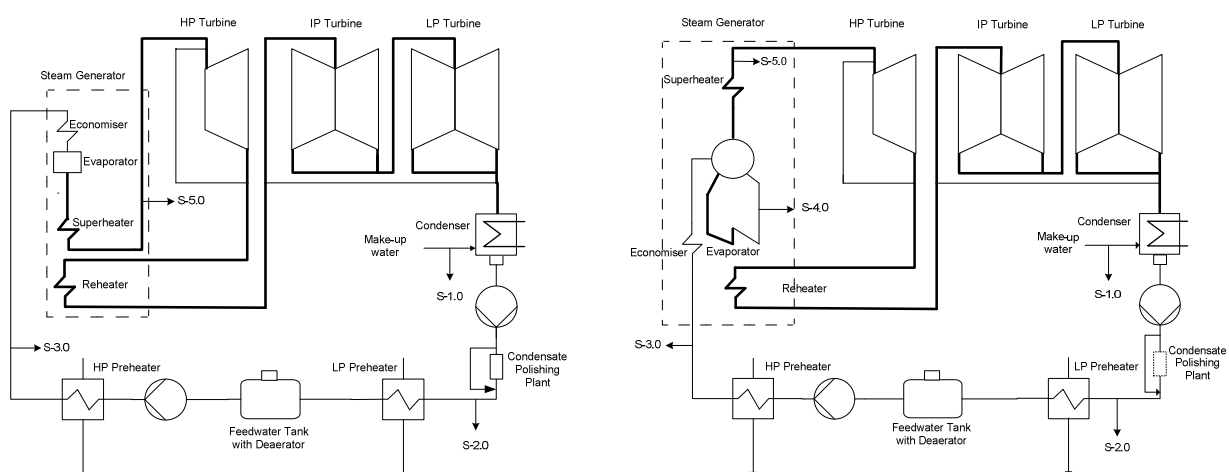


Figure 2: Examples of process diagrams of water-steam cycle systems; Left: Once-through boiler with steam reheater; Right: Drum boiler with steam reheater.

Fundamentally, the regimes for conditioning of water-steam circuits are divided in two major groups:

- I. All volatile treatment, AVT
 - Ia. OT (oxygenated treatment with dosing of oxygen)
 - Ib. AVT-O (without oxygen scavenger)
 - Ic. AVT-R (with oxygen scavenger)
 - Id. Conditioning only with oxidizing agents (German: Neutrale Fahrweise) represents a special case and is only used when dosing of alkalising agents is not possible or appropriate (e. g. food industry)
- II. Alkalising with solids (drum boilers only)
 - Ila. CT, caustic treatment with dosing of NaOH
 - Ilb. PT, phosphate treatment with dosing of Na_3PO_4
 - Ilc. Other solid alkalising agents (e. g. LiOH, Na_2HPO_4 , ...)

3.1 Feed water/feed water system

The basic demand on feed-water quality is maintenance of sufficient water purity to limit corrosion of feed train materials and to minimise the transport of corrosion products and corrosive contaminants to the boiler. In general the only addition of conditioning agents to the feed water system are volatile chemicals applied to the condensate.

For drum boiler circuits, although further control measures may be applied in the evaporator, it remains good practice for modern power units to have the same target for feed water as for steam quality.

Traditionally the chemical systems for conditioning of feed water fall into two subgroups:

- The oxidising treatment (OT), which distinguishes itself relative to AVT-O by the active dosing of oxygen to the condensate. Between AVT-O and OT a continuum exists in which the oxygen concentration may be increased and the ammonia concentration decreased – on condition of very low anion concentrations (low acid conductivity) however. By OT the protection of steel is based on low solubility of iron oxides at elevated redox potential.
- The all volatile treatment (AVT), where the protection of steel is based on low solubility of iron oxides at elevated pH.

The AVT-O (only ammonia is dosed) is the recommended AVT-method, and this mode has during the past 20 years superseded the AVT-R worldwide for copper-free water steam cycles. With AVT-O even periodic dosing of oxygen scavenger (e. g. under start-up, shut-down, or lay-up) is strongly dissuaded.

AVT-R (dosing of ammonia together with a volatile oxygen scavenger) should only be utilised in exceptional cases. This mode may be suitable for water-steam circuits with preheaters or other heat exchangers (including process steam installations) of copper alloy materials to minimise the corrosion rate of these materials. In multistage HRSG's the oxygen scavenger may accumulate in the low pressure evaporator, and the use of these chemicals is definitely not recommended.

Although individual national and company guidelines generally specify limited concentration ranges, overall experience indicates that these two protection mechanisms act simultaneously and there are no distinguished border lines between these types of conditioning. On the contrary, there seems to be a continuum of suitable operating conditions in a broad range with high pH and low oxygen concentration at one end, and low pH and high oxygen concentration at the other. Achievable purity of feed water determines the degree of freedom available to operators within this range (high oxygen concentrations are incompatible with chloride and sulphate contamination) /1/.

Choice of the optimal chemical conditions within this broad range will be influenced by the boiler type, operational conditions, design and materials of construction.

General corrosion rarely threatens the integrity of properly conditioned feed water systems. However, local disturbances stemming from the materials used, the flow conditions, or the conditioning may occur as further explained in Chapter 4.3.

3.2 Steam generator/boiler water system

Boilers are generally classified in these types:

- **Once-through boilers** in which water is evaporated to high steam content. These are intolerant of non-volatile dosing chemicals
- **Drum boilers** in which steam separation takes place in an unheated vessel. Boiling occurs in tubes through which water from the drum is re-circulated, preventing dry-out at the boiling surfaces. Such boilers may be tolerant of addition of low levels of solid alkalis to prevent any risk of acidic corrosion.
- **Shell boilers:** These systems are often designed as cylinders through which the gas tubes pass in the longitudinal direction. Typical examples and a more detailed description may be found in the EN 12953 /2/.

The major objectives of boiler water treatment are to minimise deposition and corrosion of the boiler and to ensure steam of the appropriate quality. From the very first start of the operation and all the way through the lifetime, the boiler steel reacts with the water and steam to produce a protective film of iron oxides. The rate of reaction decreases with time as the thickness of the protective oxide film increases. The rate of transport of iron oxides through the system is at its peak during the initial period of operation.

Boiler water-side integrity can be harmed by a number of corrosion mechanisms or by overheating due to an excessive thickness of the oxide layer. The protective properties of the oxide layer are dependent on the chemical conditions of the surrounding water as well as the chemical conditions during its build up. The optimal chemical conditions are characterised by minimum solubility of the oxide. Generally, the highest possible purity, a slightly alkaline pH, and an appropriate redox potential are the basic parameters for integrity of the protective oxide layer.

Non-volatile impurities concentrate in boilers and may increase the risk of corrosion. A number of factors influence this. The build up of porous oxides by deposition of transported oxides onto the heat transfer surfaces is particularly detrimental. Other important factors include details of design, construction and operating regime.

The optimum boiler water condition is alkaline. Deviation either to acidic or to highly alkaline conditions carries a risk of damage.

- Acid forming species (particularly chlorides, but also sulphates and organic anions) if present and able to concentrate at boiler tube surfaces can result in very rapid rates of general corrosion. This type of corrosion is often accompanied by hydrogen damage in mild steels, which can lead to immediate tube cracks. Acids can be generated from neutral salts particularly under oxidising conditions, and so it is particularly important to minimise ingress of chlorides and sulphates when using oxidising treatments and during oxygen transients at start-up (combination of salts and oxygen from the air intruding during the lay-up period).
- If strong alkalis concentrate at surfaces or in crevices, corrosion at unacceptable rates may also occur. This type of attack does not normally cause hydrogen damage, but some alloys are vulnerable to stress corrosion cracking and attacks of welding seams.

The required benign boiler water, which is mildly alkaline at operating temperatures and pressures, is achieved using either AVT- or solid alkali treatment. The choice of regime may be limited both by heat flux considerations and the level of soluble salts in the water, since this has a strong effect on concentration of non-volatile materials at boiling surfaces. Furthermore all substances that are added to control boiler water corrosion will inevitably impact upon steam quality (e. g. increase the volatility of certain components or increase carry-over, see Chapter 4.3).

Ideally the aim is to have a zero concentration of impurities, but this is impossible, and realistic targets are needed that are economically sound and still optimize operation with respect to purity and conditioning.

3.3 Turbine/steam system

Normally, direct conditioning of steam is not applied, and hence the chemical quality of steam derives from the measures applied to control feed water and boiler water. Thus, one of the objectives of feed water and boiler water conditioning is to avoid deposition and corrosion in the steam path, e. g. on pipes, valves and turbine parts.

Steam purity must be high and actual quality is determined by:

- Vaporous carry-over (volatility) of boiler water constituents. The volatility is a function of pressure, temperature and secondary influences of other chemical components.
- Mechanical carry-over of droplets of boiler water.
- Injection of feed water into steam for attemperation.
- Transport of solid particles (e. g. from disintegrating protective oxide layers).

The interaction of steam impurities with turbine materials is basically determined by deposition and by condensation of these impurities. Deposition can take place when the solubility limit has decreased – with steam expansion – below the actual impurity concentration. Condensation can take place when steam expansion forms water droplets or water films, in which the impurities can partition in relation to their distribution coefficients. Due to the rapid expansion of steam in the turbine, these processes may however be too slow to reach equilibrium conditions.

The early condensation zone of the turbine is particularly sensitive to low volatility contaminants. These impurities can concentrate on surfaces and in the very first droplets of condensate to form an aggressive environment. Enrichment of impurities can also occur when wet steam is locally dried up on turbine components.

Enrichment of acidic impurities leads to a decrease in local pH on turbine components, which in turn enhances corrosion fatigue and stress corrosion cracking.

Sodium hydroxide and chlorides at certain concentrations present a particular stress corrosion cracking risk to steels with non-heat treated welds or with austenitic structures.

Organic impurities may due to the formation of acidic decomposition products be implicated in turbine damage.

Silica is the most soluble of the common boiler water contaminants in high pressure steam and has a high volatility. It can become supersaturated during expansion in the turbine. This results in deposition on the blades causing loss of turbine efficiency and in severe cases in damage.

Salts deposited in steam pipe-work on-load can result in the development of concentrated solutions off-load following introduction of moist air or condensation of residual steam. This effect is particularly significant for re-heaters, turbines and some types of feed heaters. In the turbine, it may cause pitting. Besides causing mechanical degradation, pits may also initiate other forms of corrosion like stress corrosion cracking during the following turbine operation.

3.3.1 Backpressure Turbines

If the steam at the turbine exhaust is sufficiently overheated, neither condensation nor salt deposition will take place in the turbine. Some of the steam purity

requirements for condensing turbines may therefore be exceeded in backpressure turbines. However, this is only permitted if the composition of the steam is known and in accordance with the steam data at the turbine exhaust. These values must be defined plant-specifically.

3.4 Condensate/Condensing system

Because condenser leakage is the major source of impurities in circuits, monitoring of condensate is particularly important as an early indicator of the need for action. As station circuits vary, consideration for each plant on an individual basis is necessary to ensure that contaminated condensate is not fed to vulnerable components (such as attemperator sprays, etc.).

The operation of a condensate polishing plant (CPP) is an efficient means to handle this problem.

3.4.1 Secondary condensates

The increasing use of the heat from the water/steam cycle for heat exchange to peripheral systems of the power plant demands a careful consideration of the condensates lead back to the cycle, for instance starting from turbine extracts, steam-driven feed water pumps, (district) heater drains, leak steam condensers, reserve condensate tanks and other water tanks.

3.4.2 Process condensate return

Process condensates are returned when part of the steam is utilised for other industrial purposes than power and heat production. Contamination of the process condensates occurs frequently, and the nature of the contamination always reflects the process media of the steam consumer. Due to this, the quality of the return condensates must be monitored (separately) prior to the re-entrance into the water-steam circuit.

The positions of the sampling points should be chosen such that it is possible to monitor the contamination level continuously with short lag time in order to take the appropriate actions when needed. This may demand a decentralised and stream-specific arrangement of the sampling points.

The parameters to monitor are chosen according to the contaminants likely to occur in the given industrial process; however, the continuous monitoring of acidic conductivity is always recommended.

Contamination with organic substances is to be expected from petrochemical, chemical, or food industries and such compounds should be targeted in the design of the monitoring system. In practice this is often achieved by means of instruments that continuously monitor either total organic carbon (TOC) or dissolved organic carbon (DOC).

4 Boiler types, materials and water chemistry

This chapter describes the interaction between plant design, materials and water chemistry. Damages caused by corrosion during operation and lay-up may be avoided by choosing the most appropriate chemical conditioning and the applied conservation methods under consideration of the given plant design and the materials present. In relation to this, the chemical surveillance has the task to identify conditions that degrade the life length expectancy of the components in proper time to counteract them.

4.1 Boiler types

The following subchapters 4.1 to 4.3 go through the common plant designs, the materials most often applied, and the physicochemical processes that occur in the water-steam circuit. Finally, the subchapter 4.4 focuses on the effects of these processes on the specific components.

4.1.1 Water-tube boiler

In water-tube boilers the water/steam flows through the boiler tubes which partly form the boiler walls.

The major part of the boiler tubes is hanging inside the boiler, and the flue gas flows by on both sides. In principle water-tube boilers consist of these major parts:

- Economizer: where the feed water is preheated to a temperature near the boiling point.
- Steam generator/evaporator: where the partial or complete evaporation of the feed water takes place.
- Superheater, reheater: the saturated steam from the steam generator is heated further in the superheater to high pressure steam; the partly expanded steam from the turbine is heated again in the reheater. The temperature control of the steam through injection of feed water (spray-water) in the attemperators takes place here. Operation of the attemperators with contaminated spray-water leads to deposition of solids which in turn will have a serious corrosion risk as a consequence (see Chapter 4.3.1).

4.1.1.1 Once-through boilers

Once-through boilers are steam generators where the feed water evaporates completely within the tubes and the non-volatile rest of contaminants will be deposited on the tube walls. Therefore once-through boilers need demineralised feed water that must be conditioned with volatile agents (AVT/OT) only.

4.1.1.2 Drum boiler

Drum boilers are steam generators with natural or assisted circulation of the boiler water. The partial evaporation of the feed water takes place in the boiler tubes, and the separation of water and steam takes place in the drum. The standard procedure of boiler water conditioning is the application of solid alkalizing agents (see Chapter 4.3.1). The dosing point of the solid alkalizing agent must be situated down-stream of the point where spray water for attemperators is drawn off, since this water must not contain any solids.

4.1.1.3 Heat recovery steam generator

Combined cycle power plants use the energy of a gas turbine exhaust for steam production in an adjacent heat recovery steam generator (HRSG) for operation of a steam turbine. Heat recovery steam generators are made both as drum and as once-through boilers or even as combination thereof with several pressure levels. These combinations demand careful consideration of the chemical conditioning of the separate pressure levels (see Chapter 5.3).

4.1.2 Fire tube boiler (auxiliary steam boiler)

Fire tube boilers are usually characterised by operating pressures < 3 MPa.

The boiler consists of a cylindrical pressure tank. One or two tubes with burners are situated in the lower third and make the flame tubes and the first pass, whereas the second and third pass consist of flue gas tubes above. Both flame and flue gas tubes are surrounded by the boiler water. Softened water or demineralised water may be used as feed water, and the boiler water is usually conditioned with phosphate or with AVT.

In case of gaps or weld voids, e. g. dissolved solids of a “boiling out” solution or boiler water may be concentrated within the heated gaps and may cause corrosion. To avoid caustic stress corrosion cracking in particular, tri-sodium phosphate should be used for conditioning instead of caustic (see Chapter 5.3).

4.1.3 Waste Heat Boiler, Process Gas Cooler, and steam generators from solar thermal plants

Most process gas coolers and steam generators in the chemical industry as well as in solar thermal plants show both high heat transfer rate (local max. heat flux up to 700 kW/m^2) and high operational pressure (up to 13 MPa). The design is characterised by numerous gaps and spatially tightly ordered tubes. The heating medium flows ordinarily inside the tubes, and the steam is generated outside. Due to the special design they require demineralised boiler feed water and conditioning with volatile alkalising agents (AVT).

4.2 Materials

Typical materials used in the water-steam cycle are carbon steel, cast iron and stainless steel. For condensate respectively feed systems copper or copper alloys are occasionally still applied because of their good thermal conductivity.

Copper is very sensitive to complex forming agents like ammonia and is subject to increasing corrosion rates and risk of stress corrosion cracking in presence of ammonia or ammonium ions, particularly in presence of oxygen. Therefore the pH value has to be considered carefully in the presence of copper or copper alloys in the water/steam cycle.

The following sections summarize the basic corrosion risks associated with the materials and the components of power plants.

4.2.1 Steel materials

Un- or low-alloyed steel materials are used extensively for the tubes of the steam generator and superheaters as well as for the numerous connecting tubes of the water/steam circuit and auxiliary systems like extract and drain systems. Low-alloyed steel is sensitive to flow-induced corrosion (erosion corrosion) when the critical flow rate under the given conditions is exceeded.

Low-alloyed steel materials that are welded and not sufficiently well heat treated afterwards are susceptible to alkaline stress corrosion cracking when the conditioning agent or contaminating salts are concentrated at the surface.

Cast iron is, for instance, used for the support of low pressure turbine blades and for the rotor turbine blades themselves, whereas alloyed cast materials may be used for the housing. Both types of materials are sensitive to flow induced corrosion like the carbon steel.

9 to 12 % Cr-steel are used for the steam generator tubing, the high pressure steam tubes, turbine blades and turbine housing, valves *etc.* Cr-steels with relatively low Chromium concentration are susceptible to corrosion through concentration of chlorides in gaps and to chloride induced stress corrosion cracking with outset in crevices.

Austenitic stainless NiCr-steels are with the increasing temperature of the high pressure steam used more extensively for superheater tubing as well as for heat exchange tubes in preheaters, condensers, process gas coolers, and partly for turbine blades. These materials may at high tensile stress be attacked by chloride- or caustic-induced stress corrosion cracking.

4.2.2 Non-ferrous metals

In addition to the classical iron-based materials also non-ferrous metals are used – as listed in the following chapters.

4.2.2.1 Copper alloys

Copper alloys were earlier in widespread use in main condensers, condensers of steam-driven feed water pumps, and leak steam condensers as well as low pressure and high pressure preheaters. Today, these materials are frequently used for sea water evaporators and machine coolers.

The use of copper alloys limits the flexibility of the chemical regime available for operation. A conditioning that is optimal for all materials of the water-steam cycle cannot be achieved in presence of these materials.

Besides the specific sensitivity to ammonia-related corrosion, the Cu-alloys tend to exfoliate to some extent, and the corrosion products may initiate corrosion attacks further downstream in several ways.

4.2.2.2 Aluminium alloys

Aluminium alloys may be present and cover large areas in air-cooled condensers or intermediate coolers. Aluminium is amphoteric and is only stable in a very narrow pH interval. A stable protective layer may form on Al-alloys as an oxide layer with some iron oxide included when oxygen is present in sufficiently high concentrations in the steam or condensate. However, the release from aluminium ions to the water-steam cycle is unavoidable. The operation of a full-flow condensate polishing plant may remove the major part of the aluminium from the condensate. The remaining part may accumulate in the boiler water of a drum boiler and is as volatile as copper. Silica and solid alkalis agents may promote the solubility and thus enhance the volatility of aluminium further. Copper- and aluminium-containing deposits on the turbine may occur and influence the turbine efficiency quickly and considerably.

4.2.2.3 Titanium

Titanium is in some cases used for the last row of low-pressure turbine blades, and is in common use as material of condensers and intermediate coolers. Titanium is very stable towards corrosion. Negative effects on the water-steam cycle have so far not been reported.

4.2.2.4 Special alloys

Special alloys may also behave specially with respect to corrosion attacks. This should be considered when the conditioning is decided. Soldering alloys (e. g. in machine coolers) may for instance be susceptible to corrosion attacks due to the presence of ammonia.

Protective layers, e. g. in fittings, and several nickel-based alloys are sensitive to corrosion in presence of molten salts or caustic and in case of tensile stress.

4.3 Physicochemical processes

The word corrosion stems from the Latin word „corrodere“ (to gnaw or to fret) and describes the reaction between a material and its environment that leads to a measurable change of the material and may cause a corrosion damage. If no measurable change of the material occurs, it is regarded as stable under the prevailing conditions.

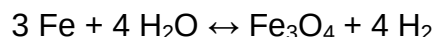
4.3.1 Basics of material protection

The control of corrosion (securing the durability of the applied materials towards corrosion) to avoid damages is of considerable economic and ecological importance because:

- Corrosion destroys the materials and wastes the energy used during the production process
- Corrosion influences the economical basis of operation modes and products
- Safety and environment may be endangered through corrosion and its consequences
- Corrosion may hinder the implementation of new, promising technologies.

The corrosive attack of water or steam on steel leading to the formation of iron oxides is limited naturally if a protective layer, i. e. a dense and uniform oxide layer, forms on the surface of the steel. The only iron oxide, which can exist in direct contact with the metal, is magnetite, on which oxides of trivalent iron can grow, depending on the redox conditions. Such protective layers restrict the transport of corrosion products to pore diffusion and reduce the area available for reaction between steel and water or steam, thereby minimizing the material loss rate (surface layer passivity).

The basic chemical reaction between iron (steel) and water involves iron dissolution through several reaction stages – a redox stage $\text{Fe(II)} \rightarrow \text{Fe(III)}$ and condensation stages (Schikorr reaction) – to the thermodynamically stable end product, magnetite. The kinetics of the Schikorr reaction show marked temperature dependency which is characterized by inhibition of the redox stage. Oxidation of the divalent iron by water needs particular configurations and conditions, which only occur in exceptional cases at low temperatures (Chapter 5.3). On the other hand, magnetite is spontaneously formed at temperatures, when condensation of iron(II) hydroxide is possible. The steel is covered by a protective layer.



Based on these interactions, water/steam cycles in power plants can be divided into two areas:

- the temperature range up to around 200°C, where an inhibited Schikorr reaction assures that the steel surface in contact with water remains active in respect of iron dissolution and

- the hot water area from around 200°C, where the magnetite protective layer forms spontaneously.

Iron dissolution is at maximum at around 150°C.

In the condensate/feed water line, i. e. near the LP pre-heaters at low and medium water temperatures, the iron dissolution in pure water is normally diffusion controlled. It may change into erosion-corrosion under unfavourable local flow conditions. Conditioning is needed to reduce corrosion and corrosion product pick-up by the feed water.

4.3.2 Deposition

Depositions may take place both – from the water as well as from the steam.

4.3.2.1 Deposition from water

The water may contain dissolved and undissolved compounds.

For the dissolved compounds, the term “solubility” refers to the maximum amount that at a given temperature may be absorbed by the solvent (water), i. e. the compound is in solution as long as the solution is not saturated. If the solubility is reached, the compound is likely to precipitate. The solubility of many substances in water decreases with increasing temperature. This is of importance for heat exchangers or other apparatuses in which heat is transferred to water. Precipitation (scaling) of dissolved substances is likely to occur as the temperature increases because the solubility limit is crossed.

The undissolved compound, however, represents a second phase (solids in water). Due to their particle size and density, the undissolved substances are dispersed and transported with the flowing water. The tendency to separate from the dispersion – and thus for the solid phase to settle – increases with decreasing water flow.

In both cases deposits of solids in tubes or other apparatuses are formed. Underneath the deposits other electrochemical conditions prevail than at the uncovered surface of the material. Through this difference in surface conditions a difference in electrochemical potential (Nernstian concentration cell) is likely to occur, which may lead to dissolution of the metal under the deposit.

Iron(II) hydroxide, the dissolved corrosion product of iron whose solubility decreases as the temperature increases, tends to form supersaturated solutions above 200°C. At points of high turbulence, e. g. around boiler control devices, or on heating faces subjected to high heat fluxes, magnetite precipitates from such solutions in crystalline form. This leads to reductions in cross-section or hampers the heat transfer in steam generation tubes and may cause damage to materials due to overheating.

Undissolved, suspended corrosion products, which are carried with the feed water into the boiler or are produced in the boiler itself, may form deposits, especially on thermally stressed tube walls and these normally have a detrimental effect. On the

one hand, such deposits can affect the heat transfer which causes the tube wall temperature to rise, leading to overheating and rupture of the tubes due to hydrogen damage from enhanced reaction between iron and water. On the other hand, electrolytes dissolved in the water can concentrate under deposits, thereby initiating a chemical attack on the tube material or protective layer. The concentration of electrolytes depends on the heat flux (evaporation intensity) and the electrolyte concentration in the bulk water.

4.3.2.2 Deposition from steam

Impurities in steam can deposit on super-heaters, control devices and turbine blades and lead to corrosion and a decrease of the turbine efficiency.

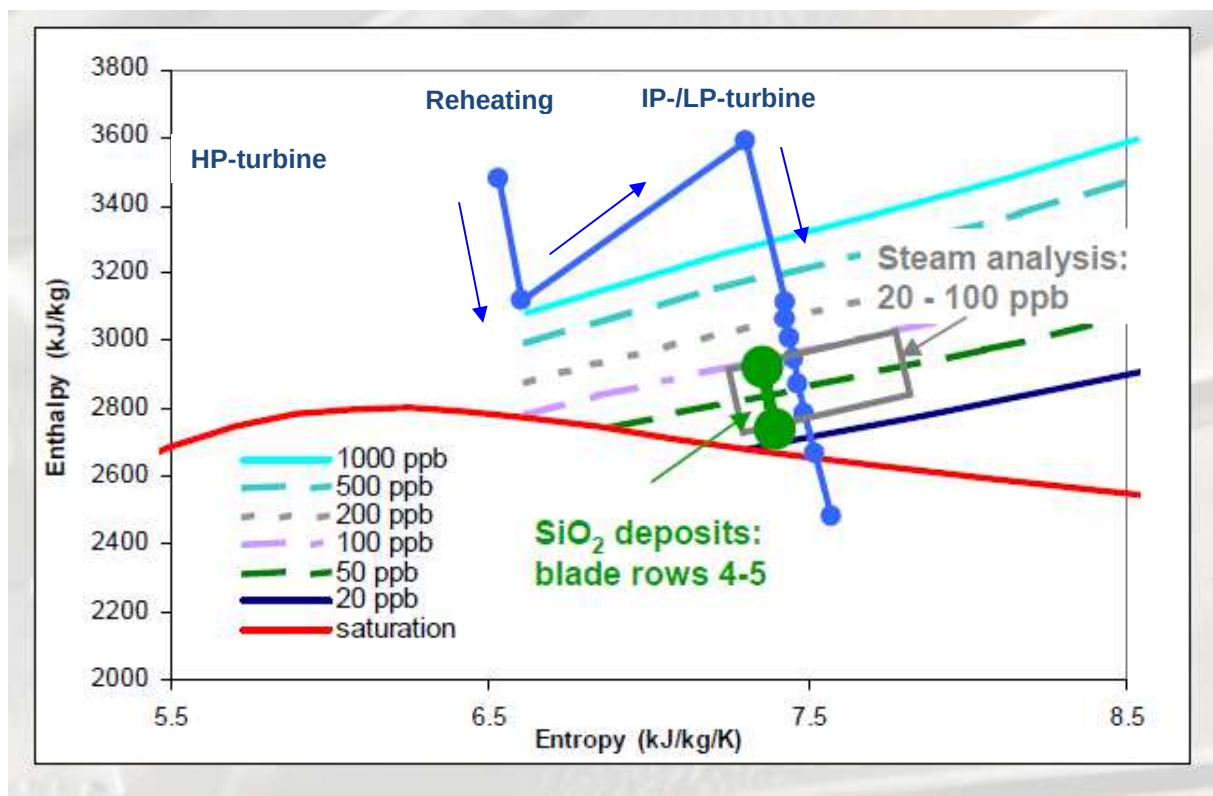


Figure 3: The process of a steam turbine in a Mollier diagram with solubility curves for different concentrations of silica.

Dissolved solids enter the steam by physical or chemical carry-over. The physical carry-over of boiler water droplets is typical for drum boilers only. Satisfactory water/steam separation in the drum should be ensured by appropriate design measures. However, operational conditions have significant effect on mechanical carry-over: Disturbance of the control of boiler water level in the drum, foaming due to contamination of boiler water, and sudden change in pressure or load are typical disturbances that may lead to enhanced contamination.

The chemical carry-over is due to the solubility of water-soluble solids in steam. The solubility in steam is primarily dependent on density of steam. The density of steam rises with pressure and falls with temperature, and the solubility will follow the same pattern (Figure 3). The highest solubility at a given pressure is in saturated steam. Dissolved solids in steam can therefore precipitate in super-heaters because of the decrease in density as the temperature rises and on turbine blades because of the decrease in density as the pressure drops (Figure 4). The deposits – where electrolytes are involved – cause corrosion in the presence of water or as a molten material (Figure 5). The commonly observed corrosion at the last turbine rows is connected to the enrichment of contaminants decreasing the pH in the early condensate zone. Non-electrolytic deposits (i. e. silica) may change the roughness of turbine blades resulting in decrease of turbine efficiency (Figure 6).

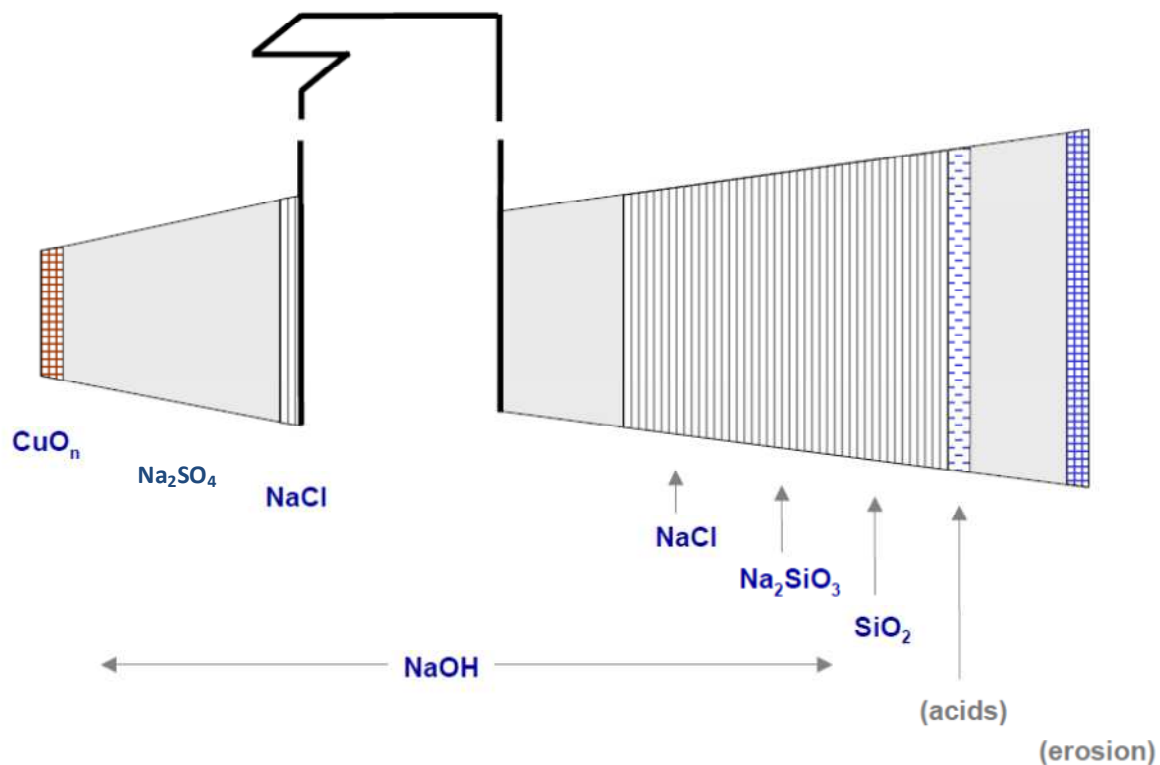


Figure 4: Typical composition of the deposits on a HP-, IP-, and LP-turbine.



Figure 5: Corroded turbine after salt intrusion and insufficient conservation.

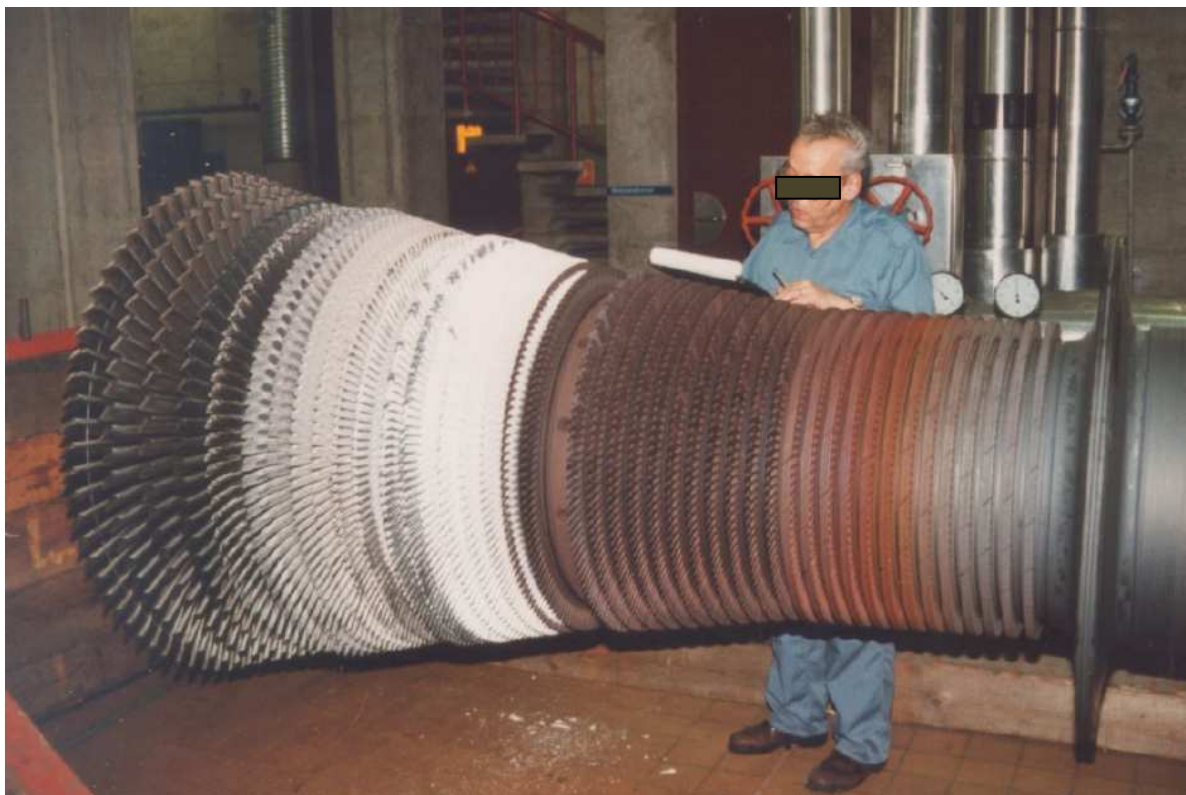


Figure 6: Deposits of silica on an industrial turbine.

4.3.3 Corrosion in the water-steam cycle

pH has a considerable influence on the corrosion of the non- or low-alloyed steels that are ordinarily applied in power plants. The pH value required may be achieved by dosing (condition) the boiler water with non-volatile alkalising agents (e. g. caustic or sodium phosphate) or by dosing the condensate or feed water with volatile alkalising agents (e. g. ammonia). As far as possible, the conditioning agents should be dosed continuously.

The pH value of the water-steam cycle must be controlled to secure the optimal protection of the materials and to avoid other undesirable reactions to take place (e. g. foaming of boiler water).

The increasing solubility of the protective layers of iron oxides with increasing acidity demands that the pH value in the water-steam circuit be controlled in the neutral to alkaline region. However, pH is also limited upwards, since magnetite begins to dissolve at very basic conditions (Figure 7).

Increasing conductivity enhances the corrosion processes, in particular in the presence of oxygen.

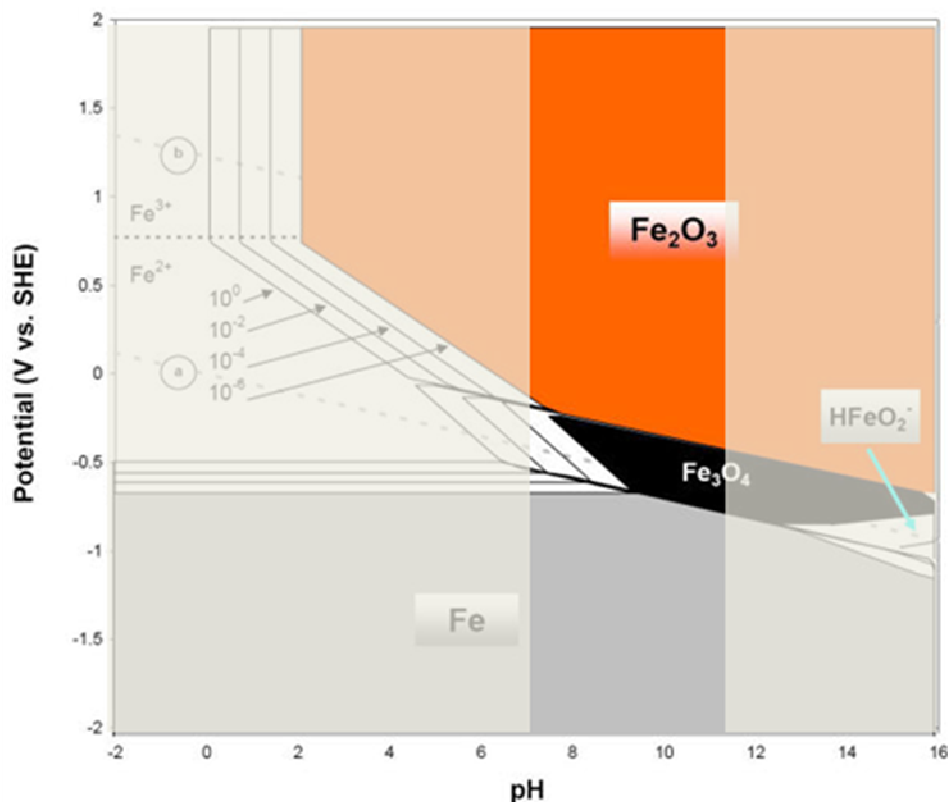


Figure 7: Pourbaix diagram for iron and iron oxides [3/].

4.4 Physicochemical processes at the components

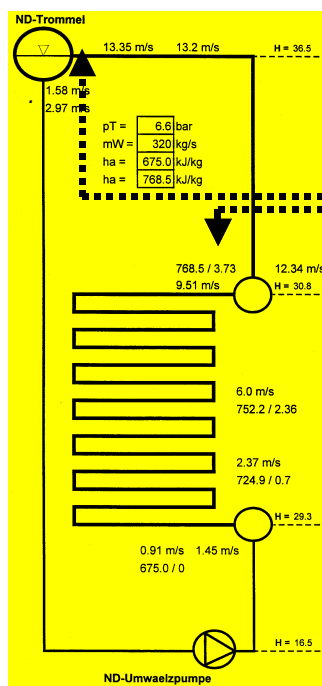
The following chapters describe the physicochemical processes at the components of the water-steam cycle.

4.4.1 Steam generator

The physicochemical processes in the steam generator can be of various nature.

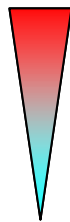
4.4.1.1 Erosion corrosion/stress corrosion cracking in exit ends of boiler tubes

In the evaporation zone of drum boilers, especially by horizontal arrangement of the boiler evaporator tubes, e. g. in an HRSG, erosion corrosion and stress corrosion cracking may occur. The fraction of fluid remaining as water is continuously decreasing through the tubes due to the evaporation taking place. Critical flow rates or critical concentrations of caustic may be reached when flow rates of boiler water and flue gas are not sufficiently well balanced /5/.



Example of increase of flow rates of the two-phase flow through the evaporator of a drum boiler.

The design of the connecting pipes (narrow bends) at the exit of the tubes, where acceleration takes place, is critical for the risk of flow accelerated corrosion.



Schematic outline of the increase in volumetric flow rate in relation to the heat uptake.

Figure 8: Sketch of the evaporator of a drum boiler.

4.4.1.2 Hide-out/negative hide-out

Hide-out is the phenomenon of dissolved species unevenly distributed in the water phase due to temperature gradients. The protective oxide layer of a heated surface is porous, and the pores are water-filled. Due to the higher temperature underneath the layer, species less volatile than water are concentrated in the pores. If the heat flux is decreased, a re-dissolution of the concentrated species takes place – hide-out return.

This is in particular observed with phosphate conditioning when changes of boiler load may be followed by considerable fluctuations of the boiler water pH.

The opposite phenomenon (negative hide-out) is seen for species which are more volatile than water. Their concentration in the protective layer of heated surfaces will be lower than in the exterior free-flowing water. This is, for instance, the case for oxygen and ammonia.

Due to the concentration of less-volatile species under the protective layer and/or the lower pH and the depletion of oxygen, the risk of corrosion of the water-side of heat tube walls is enhanced.

4.4.1.3 Volatile alkalisating agents/distribution equilibrium

The dissolved species in the water distribute accordingly to their volatility when water and steam are separated. The non- or less-volatile species (salts and silica) stay mainly in the water phase whereas the volatile compounds follow the steam. The non-volatile species concentrate in the boiler water through this mechanism, whereas the volatile compounds are depleted. This makes it possible to remove the concentrated non-volatile contaminants from the boiler water by blow-down from the drum (drum type boilers) or the flask (once-through boilers operating at low load).

On the other hand, the depletion of the volatile compounds in the boiler water raises particular demands on the alkalisating. This is in particular problematic at low pressures due to the pressure dependence of the ammonia distribution equilibrium. Adequate corrosion protection may either be achieved by raising the ammonia concentration or by using solid alkalisating agents additionally.

4.4.1.4 Water separation for drum boilers

Drum boilers are usually equipped with water/steam separators and demisters at the steam exit (Figure 9).

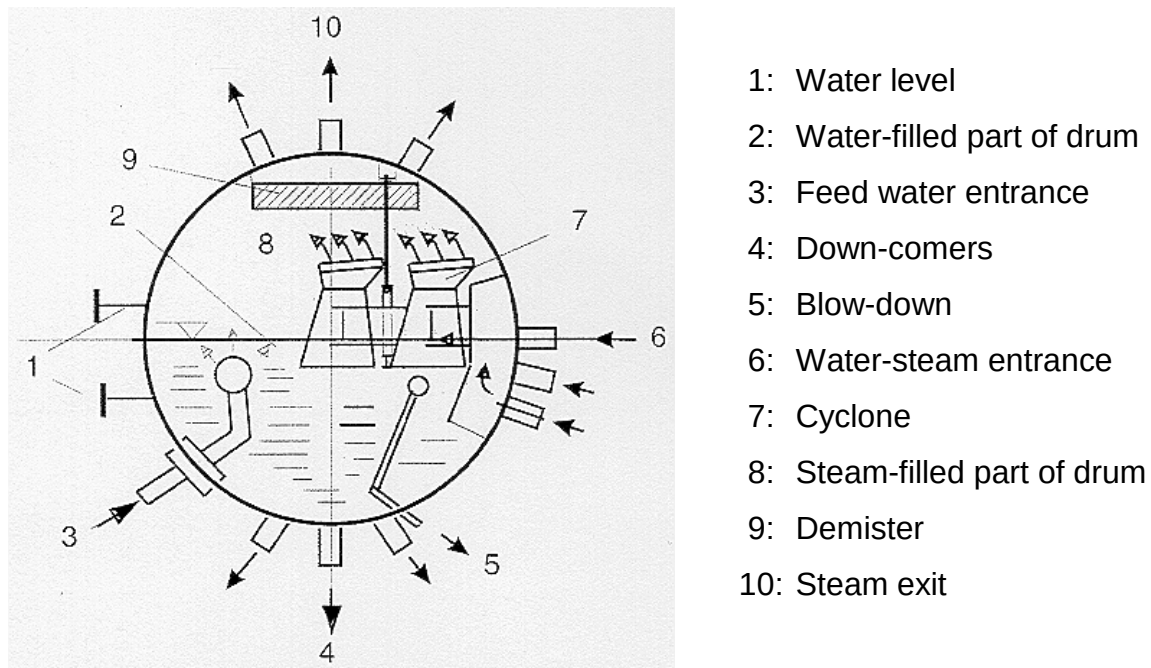


Figure 9: Schematic outline of the drum and its components /8/.

These devices must ensure that only a minute fraction of water (carry-over) is transported with the steam as tiny droplets. The droplets carried this way contain a relatively high concentration of contaminants and thus influence the quality of the saturated steam. In the case of solid alkalisizing agents (caustic or phosphate) and operation with overloaded separation devices, boiler water rich in contaminants and alkalisizing agent may reach the entrance of the superheaters. For the determination of carry-over see reference /6/.

For drum boilers conditioned with solid alkalisizing agents the sodium concentration in the saturated steam ordinarily fulfils the AL1 limit for acceptable operation according to Table 10 when the concentration of caustic or phosphate is held within the specifications in Table 7 and Table 8. If this is not the case, an unfavourable separation of water and steam in the drum and carry-over of boiler water droplets are strongly indicated.

The contaminants carried with the steam are partly deposited in the superheater due to the subsequent evaporation of the water droplets. The steam-soluble parts of the contaminants may cause deposits on the turbine blades because the solubility limit is reached during the expansion of the steam in the turbine. Corrosion caused by molten salts, stress corrosion cracking and corrosion during lay-up may be initiated by this mechanism both in the superheaters and in the turbine.

4.4.1.5 Spray-water for temperature control

Water containing dissolved salts must not be used as spray-water for temperature control because the complete evaporation of the water takes place at the surfaces of the subsequent superheaters. Due to the temperature regime of the superheaters,

corrosion initiated by molten salts and stress corrosion cracking as well as corrosion during standstill are likely to occur, if the spray water contains salts.

High amounts of spray-water for temperature control may promote growth of the oxide layer down-stream of the attemperators and to enhanced exfoliation due to the temperature gradients. Increased erosion from solids and formation of deposits on the components further down-steam (e. g. by-pass valves, turbine inlet valves, and on the turbine itself) may be experienced under such circumstances. Such phenomenon cannot be influenced through changes in the feed water chemistry.

4.4.1.6 Superheaters

The attention is in particular focussed on hanging superheaters. Condensate formed from remaining steam during the cooling phase of the boiler may accumulate in these. Salts deposited on superheater surfaces during the previous operation phase may be partly dissolved by the condensing steam and gather in the bottom of the hanging superheater. In this way highly concentrated and very corrosive salt solutions may form.

This type of superheaters is not always equipped with devices for draining, and the conservation of these parts is thus of particular importance. The amount of condensate formed during the cooling phase may be big enough that the water acts as a siphon trap and prevents proper dry-conservation of the boiler (see VGB R116 (8)).

4.4.2 Steam turbine

According to DIN 4304 [3] the following terms are applied:

- Steam turbine: It is the machine with the rotating part, i. e. the turbine blades mounted on a shaft. The steam passing by the turbine blades creates the rotation and thereby converts part of the enthalpy to mechanical energy. The energy transfer leads to a decrease of pressure and temperature of the steam.
- Steam turbo set: It is the steam turbine and the connected working machine (generator, feed water pump) – and in some cases the gear in between.
- Steam turbine island: It is the complete unit with steam turbine, working machine, condenser and the attached pipe-work.

Furthermore, these additional terms are commonly used:

- Axial and radial turbine, according to the flow direction.
- Action turbine (steam enthalpy decreases at the rotor blades as the kinetic energy decreases) or reaction turbine (steam enthalpy decreases both at rotor and stator blades as both kinetic energy and pressure drops) according to the working principle.

- Superheated steam turbine, saturated steam turbine, high pressure turbine, intermediate pressure turbine, or low pressure turbine according to the properties of the steam
- Live steam turbine, waste steam turbine, and steam accumulator turbine according to the steam supply
- Condensing turbine, exhaust condensing turbine, and back-pressure turbine according to the steam condition at the exit.

4.4.2.1 Turbine inlet valves

Turbine inlet valves are in particular exposed for flow-induced wear (erosion) that may be caused by the flowing steam only. However, increased erosion is usually observed when solid particles are carried with the steam into turbine. Magnetite plays the main role in relation to this because this iron oxide is very hard, is formed on every steel surface as the oxide layer, and inevitably reaches the steam through partial exfoliation (e. g. by start-up, shut-down, or fast load changes). The uptake of magnetite by the steam increases with time because the mechanical tension between steel and magnetite caused by the difference in thermal expansion coefficients increases with the thickness of the oxide layer.

4.4.2.2 Control stage

The erosion caused by solid particles in the steam also represents the major cause of strain for the control stage. Deposits formed from other contaminants dissolved in the steam are usually not observed at the control stage.

4.4.2.3 Turbine rotor blades in the first condensate zone

The turbine blades in the region of the first condensate experience particular strain. There is a risk of erosion damage from the condensate droplets on the leading edges of the blades. Especially the region from approximately 1/3 of the blade height is exposed, because the droplets are driven in outward direction by centrifugal forces.

Depending on the prevailing quality of steam deposits may form on these blades. The upper 2/3 of the blades remains free from deposits because they are always wetted by the condensate and contaminations are thus washed away. This is not the case at the lower part of the blade, and deposits may build up that usually contain corrosive substances (e. g. chloride and sulphate). By load changes, start-up, and shut-down the lower part of the blades is also wetted (displacement of the Wilson-line, increased saturation of the steam). Through this strong electrolytes are formed that lead to corrosion of the blades particularly during standstill.

The transition zone between the blades and the support is at particular risk regarding pitting corrosion. The pitting corrosion may subsequently promote stress-corrosion cracking starting out in the pits. This means that the purity of steam (formation of

deposits), the shut-down process (saturated steam at the last rows of turbine blades), and the conservation during standstill (corrosion prevention) are of special importance for turbines.

4.4.2.4 Basis of rotor blades in low pressure turbines

Depending on the construction of the last rows of the LP-turbine a minute amount of steam may flow through the crevices between the rotor blade and the basis/shaft. Deposits may form in the crevices if promoted by the steam quality. These sites are usually dry so that the deposits are not washed away by condensate. By standstill and higher moisture content at the turbine exit the deposits are wetted and form strong electrolytes that may lead to corrosion at the rotor foot and in the crevices, in particular during standstill. Because these sites experience high tensile stress, even small corrosion pits may lead to stress-corrosion cracks (see also 4.4.2.3).

4.4.2.5 Basis of stator blades in low pressure turbines

The basis of the stator blades is particularly in the first condensate zone vulnerable to flow accelerated corrosion (FAC). Besides measures taken in the design and choice of FAC-resistant materials flow accelerated corrosion may be avoided or minimised by means of appropriate water chemistry – usually an increase in pH helps out. Organic contaminants of the water-steam cycle call for particular attention here. Organic substances are usually degraded by passage of the boiler and may form organic acids that decrease the pH of the first condensate significantly /9/, /10/.

4.4.2.6 Steam lines for exhaust steam

The same processes that take place in the turbine during the decrease in pressure and temperature are active in the exhaust steam pipes and at the connected steam consumers. Thus, formation of deposits at these places is to be expected. Such deposits present a corrosion risk for the turbine when steam or condensate of lesser quality flow backwards into the turbine due to not tight or missing countermeasures (valves etc.). This may in particular occur during start-up and shut-down processes due to the occurring shift in pressure levels between the exhaust steam pipes and the connected consumers /11/.

4.4.3 Turbine condensers

Turbine condensers are classified as either surface condensers or air condensers.

4.4.3.1 Surface condensers (steam side tubing)

Turbine or surface condensers belong to the major sources of contamination of the water-steam circuit.

The shell and support devices (baffles) are usually made from carbon steel. Under the prevailing conditions practically no stable oxide layer forms on these materials, which makes the condenser the major source of iron oxides in the water-steam cycle.

If the condenser is equipped with tubes made from copper alloys, it will also be the major source of copper in the circuit.

Cooling water may intrude into the steam-filled part and thus contaminate the condensate through leaky connections between tubes and tube sheet (tubes only rolled into the tube sheet or cracks in welding seams between tubes and tube sheet). In this relation chloride (pitting and stress corrosion cracking), carbonates (deposits and soda cleavage), and organic matter (foaming of boiling water) are of particular concern.

Air and thus carbon dioxide and oxygen may intrude into the steam-filled part through leaks in the shell. The oxygen increases the oxygen content of the condensate and the carbon dioxide the acid conductivity (see also VGB R130e (13)).

4.4.3.2 Air condensers

Air-cooled condensers made of steel are the major source of iron carried into the water-steam cycle. Due to the very large surface areas the amount of iron transported is distinctly higher than seen for water-cooled condensers. This makes a mechanical condensate polishing plant necessary for removal of the suspended matter.

Oxygen and carbon dioxide may intrude into the water-steam circuit through air-leaks in the vacuum region. Due to the construction these gases cannot be removed from the system by ejection as efficiently as for surface condensers, and this fact explains the higher content of oxygen and acid conductivity (through CO₂) in the condensate compared to condensate from surface condensers (see also VGB R131e (2)).

To protect the air-cooled condenser and to minimise the amount of iron oxides carried into the water-steam circuit the pH of the steam should be ≥ 9.5 . Even higher pH values should be aimed for, if possible from other technical concerns, to minimise the risk of erosion corrosion further /11/.

4.4.4 Condensate polishing plant

Condensate polishing based on ion exchange is an efficient means to maintain the purity of the water-steam circuit and is in many cases indispensable (see Chapter 5.1.2). Although the advantages of the CPP clearly dominate, it may also be a source of contamination of the water-steam circuit. The release of sodium ions to the water-steam circuit due to problems with regeneration is well-known (insufficient flushing of resins, incomplete regeneration, incomplete separation of resins, etc., see also VGB-M 413 (9)). Furthermore, the ion exchange resins may release degradation products (leachables) that are further degraded to e. g. carbon dioxide, organic acids, and inorganic acids on the heated surfaces of the boiler. The cation exchanger contains

sulphonic acids as the active sites and so do the break-down products that are slowly released during the lifetime of the resin. In the boiler the sulphonic acid groups are converted to sulphuric acid and subsequently neutralised by the alkalising agent. The sulphate salts are carried further on, either as tiny particles suspended in the steam or as solutes of the (supercritical) steam. The particles may deposit on dry surfaces in contact with the steam. The soluble salts are deposited on surfaces of components where steam density decreases and saturation is reached. This mechanism is a major source of the sulphate salts found at various places of the water-steam circuit (e. g. evaporators of once-through boilers, superheaters, steam side of heaters, re-heaters, turbines, and connecting steam lines). The anion exchanger contains quaternary or tertiary amines that are correspondingly converted to nitrate salt and subsequently deposited.

When the CPP is operated below a limiting temperature (usually 60 °C)¹ the release of leachables is hardly noticeable, and the acid conductivities of the feed water and steam may be well below the AL1 action level (e. g. < 0.08 µS/cm). Nonetheless, the release and degradation of the leachables is continuously taking place, and over long periods of operation considerable amounts of especially sodium sulphate may accumulate on dry surfaces of various components [11/, /14/]. Thus, it is recommended from time to time to pass through the region of saturated steam as part of the shut-down procedure in order to wash these deposits away prior to the standstill (see Chapter 5.1.3.3). Subsequently, the plant should even by short standstill be conserved to avoid corrosion during this period (see VGB R116 (8)).

4.4.5 Steam side of low and high pressure pre-heaters

During periods of high load major parts of the tubes of the heaters are in contact with slightly superheated steam and are thus dry. In this situation salts carried with the steam may deposit on the surfaces. When the load is reduced, the surfaces are wetted to a larger extend, and the salts dissolve in the condensate. If the contaminated condensate is returned to the cycle without further polishing, the contamination spreads to the condensate and feed water. The situation may be handled by monitoring the acid conductivity of the drains and diverting them to condensate polishing when a threshold is passed (e. g. 0.15 µS/cm).

The deposited salts present a corrosion risk during standstill that may be avoided by a previous wash of the heaters (see Chapter 5.1.3.3).

4.4.6 Feedwater tank

The feed water tank serves as the reservoir of the feed water pumps and often also as buffer tank for the retrieved condensate, the make-up water, or a mixture of both.

¹ The limiting temperature is dependent on resin type and should be specified by the supplier.

This is often also the place for thermal degassing and possibly additional conditioning of the feed water.

If the thermal degassing takes place below 135 °C, the complete removal of carbon dioxide is not possible. The higher pH of the feed water, the more carbon dioxide remains in the feed water chemically bound.

At temperatures below 100 °C and normal air pressure only a partial degassing is achievable according to the solubility of the gases.

The thermal degassing in the feed water tank may among other things be disturbed by irregular spraying of condensate and insufficient gas extraction/ejection, which lead to increased oxygen content of the feed water.

5 Treatment of water-steam cycles

To avoid corrosion damage a treatment of the water-steam cycle must take place.

5.1 Purification

The main purification steps are the make-up water treatment, the condensate treatment and the removal of salts.

5.1.1 Make-up water treatment

The necessary type of make-up water treatment for the water-steam circuit depends on:

- Raw water quality (e. g. hardness, alkalinity, conductivity, silica content, turbidity);
- Amount and quality of condensate return to the boiler feed water;
- Specifications of the boiler feed water and boiler water (depending on boiler type, boiler pressure, max. heat transfer);
- Specifications of the steam produced (e. g. super-heater/turbine operation, high quality steam for production processes, corrosion in the steam and condensate system);
- Economic and ecologic requirements (e. g. blow down rate, effluent requirements).

Make-up water treatment is a demineralization process most commonly done in ion exchanger units of different design or in case of surface water with reverse osmosis combined with a polishing filter like e. g. mixed bed filter, electro deionisation (EDI) etc. (see VGB-M 404G (10), VGB-M 405G (11), and VGB-M 407G (3)).

5.1.2 Condensate treatment

The necessary type of condensate treatment for the water-steam circuit depends on:

- Condensate quality (e. g. conductivity, corrosion products, hardness, silica content, hydrocarbons, pollutants due to ingresses of product);
- Amount and quality of condensate return in the boiler feed water;
- Specifications of the feed water and boiler water (depending e. g. on boiler type, boiler pressure, max. heat transfer);
- Specifications of the steam produced (e. g. super-heater/turbine operation, high quality steam for production processes);
- Economic and ecologic requirements (e. g. blow down rate, effluent requirements);

- Demands from the operation mode (e. g. frequent start-up or shut-down);
- Design of and materials used for the components (e. g. low-pressure heaters in low-alloyed steel).

An overview of methods and recommendations for condensate polishing are detailed in VGB guideline M 412 L (5).

5.1.3 Removal of salts

Even with use of the best purification technology for make-up water and condensate polishing some impurities will enter the water/steam cycle. These contaminants will accumulate at certain places, where the physical-chemical conditions cause deposition due to solubility relations. This paragraph describes possible methods to eliminate the concentrated contaminants from time to time.

5.1.3.1 Blow down from drum and shell boilers

Blow down is a well-known and generally used method to divert low volatility contaminants accumulated in the boiler water. By commissioning and start-up continuous blow down is necessary to reach the specified purity of the boiler water as soon as possible. During the operation many units change to periodic blow down depending on the concentration of contaminants in the boiler water. The common parameters used as blow down criteria are silica and acid conductivity.

5.1.3.2 Blow down from once-through boilers

Strictly speaking blow down is applicable on drum boilers only. However, most of the once-through boilers have a separation vessel, which is acting at low load operation similarly to a drum. Diversion of the “boiler water” from the separation vessel at the right time is a useful method to eliminate the contamination accumulated in the evaporator during high load operation. The separation vessel is dry during high load operation. The main part of the ionic contamination accumulated in the evaporator will enter the separation vessel with the very first water at the transition to low load. It is recommended to divert this water out of the cycle and start the recirculation when the water from the separation vessel reaches appropriate purity.

5.1.3.3 Heaters

Steam is often used for heating purposes both internally (feed water heaters, air heaters) or externally (district heating, industrial heating). Drain from indirect heat exchangers of this type is usually returned into the cycle, often without any polishing. If the steam is superheated, deposition of contaminants appears on the dry parts, where desuperheating occurs. When wetting the dry surfaces during start-up and shut-down as well as during low-load operation the deposits dissolve and may purposely be diverted out of the circuit.

The procedure starts with diversion of the drain expected to pick up the deposited contamination to the condensate polishing plant. The closing of the steam supply of the heater for 5 to 10 minutes results in a cooling of the heat exchange surfaces to the temperature of the cooling medium. At the re-opening of the steam supply the deposits dissolve in condensate appearing on the dry surface. When the contamination is washed out, the recycling of the drain can be re-established. Periodical washing of the deposits is recommended, particularly up to a standstill period. The removal of the ionic deposits improves the conservation during the outage.

5.2 Deaeration and oxygen scavenging

Deaeration is a key word for proper reliable chemistry management. Its action is applicable for condensates, make-up and feed water.

5.2.1 Deaeration

In condensates and feed water, gas may exist at different concentrations in dissolved form (f. e. through open funnel ends, leakages of gas and vacuum tightness, open condensate-/deionate reservoir)

The condenser and the deaerator/feed water tank are the specific items of the plant where deaeration takes place.

The presence of non reactive gases in liquids is governed by their solubility, which is a function of the temperature and partial pressure of the gas in the vapour-phase. The deaeration principle is therefore based on the closest contact between the liquid-phase and vapour-phase of which the gas concentration is lowered down to its reachable minimum. Deaeration key parameters are:

- Pressure and the relevant partial pressures
- Temperature
- The surface to volume ratio
- Contact time

The lowest concentration of the gas in the vapour-phase is achieved by air extraction and/or steam ventilation.

5.2.2 Oxygen scavenging

With the measures for deaeration mentioned above it is possible to reach the conditions for AVT-conditioning. When a reducing medium (AVT-R) is chosen, it may worthwhile injecting an additional conditioning chemical to implement the oxygen removal and ensure a reducing medium. The most commonly used scavenger has been hydrazine whose properties match all the high pressure chemistry requirements, since it does not decompose into troublesome by-products. Safety

precautions must be taken since it is classed as carcinogen in the European Union (see EU-executive order 1907/2006) /1/.

Other oxygen scavengers have proven to be effective but add carbon dioxide and acid decomposition products to the fluid which lead to increased acid conductivity.

For low pressure specific shell boilers, sodium sulphite may be used when the specifications for conductivity and pH value of the boiler water and steam are fulfilled.

5.3 Conditioning

Corrosion of plant components in contact with water and steam in a water-steam cycle can be minimized by chemical measures.

Low-alloyed steels make up the major part of the materials applied in the water-steam cycle. The dissolution of iron in pure, virtually oxygen-free water involves a hydrogen reaction, i. e. the formation of iron(II) hydroxide and hydrogen. The oxidation of Fe(II) to Fe(III) and the subsequent condensation to oxides which can form a protective layer are not possible with water as the oxidizing agent at temperatures of $< 180^{\circ}\text{C}$. Condensate and feed water always contain traces of oxygen, which promote these reactions at the phase boundary, thereby facilitating layer formation, albeit slowly, if the low oxygen level is matched by correspondingly low concentrations of iron(II) hydroxide. This condition can be satisfied by raising the pH above the saturation pH of $\text{Fe}(\text{OH})_2$ ($\text{pH} = 9.25$ at 25°C) in order to suppress the solubility of the iron(II) hydroxide and thus the iron dissolution itself (conditioning with alkalizing agents, see section 5.3.1 and 5.3.2).

Oxidation of Fe(II) to Fe(III), the limiting stage of the Schikorr reaction with water as the oxidizing agent, can be brought about by addition of oxygen. This is the underlying principle of conditioning with oxidizing agents.

5.3.1 Feed water conditioning

The feed water conditioning can be achieved in different ways, which is explained in the following chapters.

5.3.1.1 Feed water conditioning with alkalizing agents (AVT)

Ammonia is the most common volatile alkalising agent. In demineralised water at low temperature pH around 9.5 is necessary to achieve the minimum solubility of iron, and thus minimise corrosion product take-up (Figure 10).

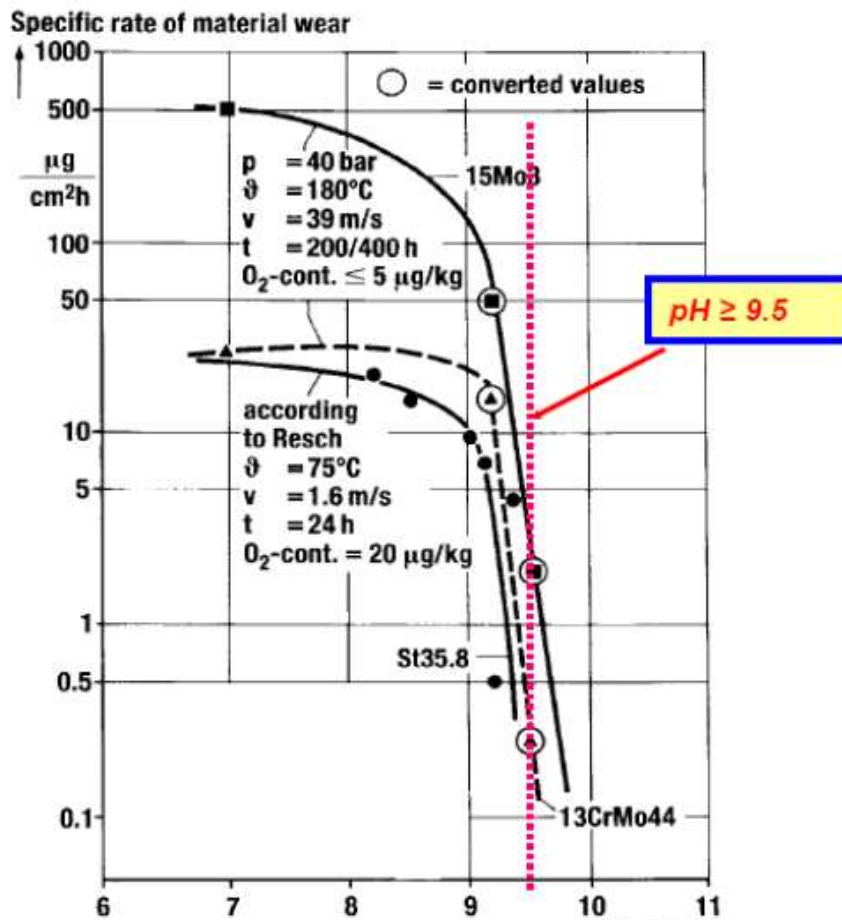


Figure 10: Corrosion rate of different low-alloyed steels in dependence of pH [12/.

If copper materials are present in the water/steam cycle the upper limit must be set according to the design characteristics and the materials of the condenser and is generally kept below 9.4. The upper limit to ammonia concentrations with tubing made from steel, chromium-nickel steel or titanium is given by limits on condensate polishing plant load if any available.

The optimum pH level for the whole plant must be established in the condensate/feed water train upstream of the low pressure heaters to ensure maximum corrosion protection for these heaters. Where a condensate polishing plant is installed, ammonia must therefore be dosed just downstream of that. In cycles without a condensate polishing plant the ammonia only escapes from the water-steam cycle via vent in condenser and deaerator.

5.3.1.2 Feed water conditioning only with oxidizing agents

Iron take-up by the feed water is reduced by dosing with gaseous oxygen, if the purity of feed water is high. This makes it possible to dispense with alkalinizing agents in the condensate and feed water zone, if an ammonia-free steam is desired, or if ammonia must not be present in the water/steam cycle for any reason. The solubility of iron is greatly reduced by oxidizing the primary corrosion product, iron (II)

hydroxide, which creates the conditions necessary for protective oxide layer formation.

A successful application of this special conditioning is based on very sharp control of feed water purity. Generally it requires condensate polishing plant to ensure the purity. Due to the absence of alkalizing agents for buffering, intrusion of even minute amounts of contaminants leads to drastic excursions in pH.

5.3.1.3 Feed water conditioning with alkalising and oxidising agents (OT)

The concentration of iron in the feed water is reduced by adding both gaseous oxygen and ammonia. The alkalising agent promotes the oxidation process of Fe (II) to Fe (III) in water containing oxygen and also offers a certain amount of protection against the harmful effect of anions on the protective layer in the event of salt penetrations.

The oxygenated treatment demands high purity of the condensate and feed water as illustrated in Figure 11 (see also Chapter 7.3). This may necessitate the operation of a condensate polishing plant.

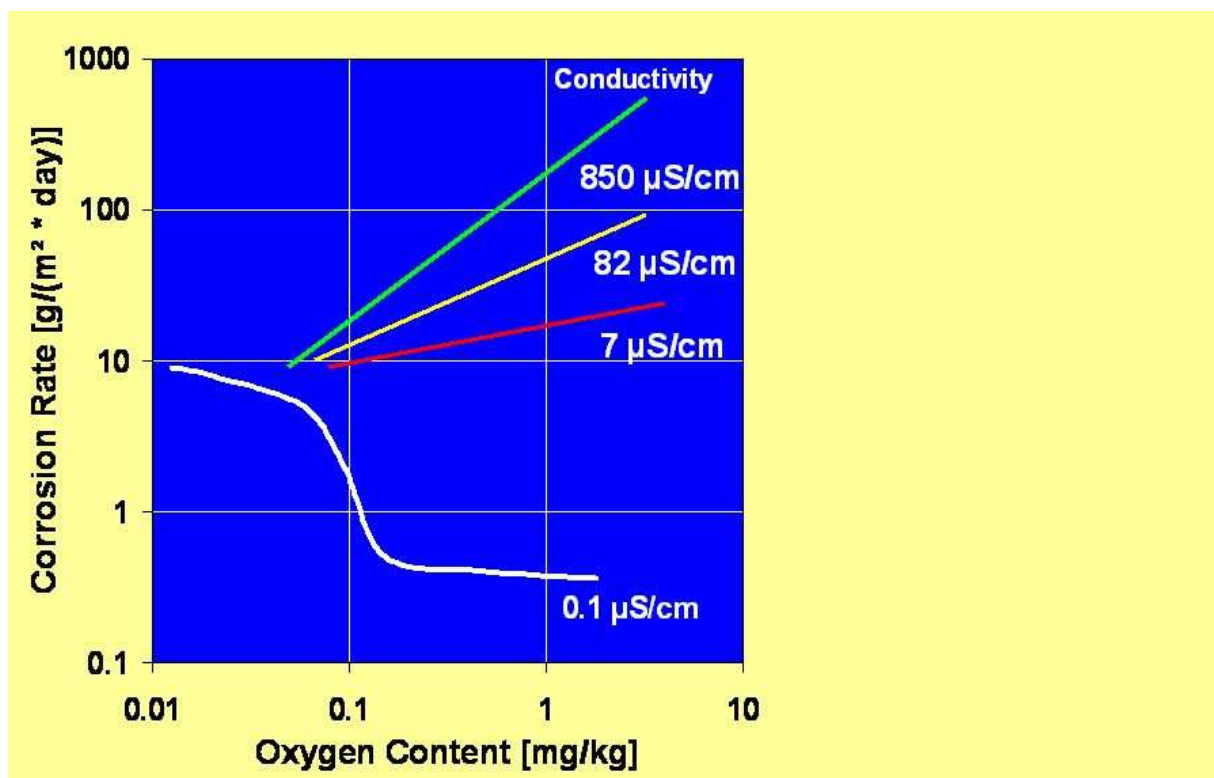


Figure 11: Dependence of corrosion rate of low-alloyed steel of the conductivity of feed water/condensate and oxygen concentration [13/, /2/.

Ammonia and molecular oxygen must be fed separately into the condensate upstream of the low pressure heaters in concentrations, which ensure that the conditions stipulated in Table 3 to 6 are fulfilled in the feed water upstream of the boiler inlet.

5.3.2 Boiler water conditioning

Drum boilers may be operated by means of volatile alkalis agents (AVT) only, with phosphate (PT), or with caustic (CT) treatment. For once-through boilers the oxygenated treatment (OT) is recommended; alternatively, the AVT may be applied.

The AVT is applicable for low-pressure drum boilers only with a correspondingly high pH in the boiler water or with high quality materials (highly alloyed) in the evaporator that are resistant to erosion corrosion. Erosion corrosion is the main cause for evaporator tube damages in low-pressure boilers because the temperature during operation matches the region in which the erosion corrosion is most likely to occur (Figure 12 and Figure 13).

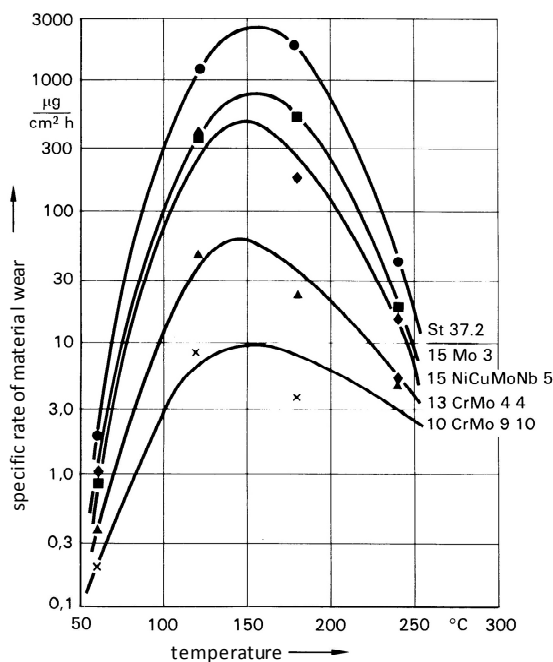


Figure 12: Temperature dependence of erosion corrosion.

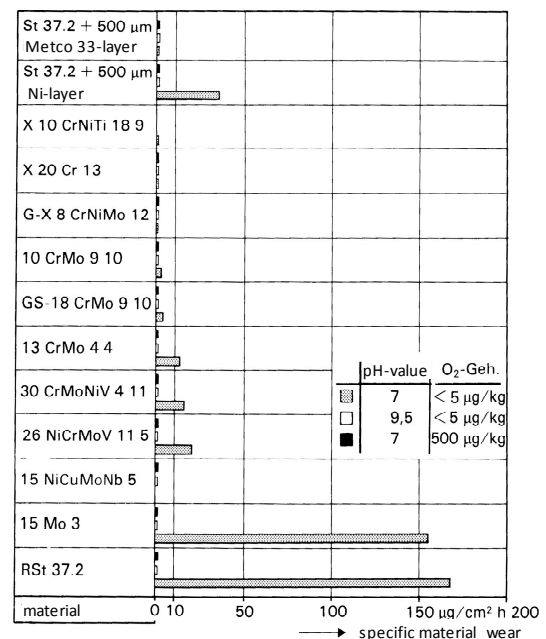


Figure 13: Rate of erosion corrosion for various materials depending on pH and oxygen content of the flowing medium.

The required high pH of the feed water to avoid erosion corrosion may not be applicable, e.g from a limitation posed by the supply of process steam for industrial processes. If a upgrade of the sensitive materials is not an option, conditioning of the low-pressure boiler water is necessary.

High-pressure evaporators conditioned with phosphate or caustic are susceptible to corrosion underneath deposits (acid and caustic corrosion, hydrogen embrittlement).

The operation of shell type steam generators with additional flame tube firing in combination with phosphate or caustic treatment is connected with risk. The flame tube firing results quite often in at least temporary dry-out of the evaporator tubes locally that leads to concentration of the solid alkalis agent on the surfaces and subsequently to corrosion attack.

Besides demands of efficient and flexible operation with daily or weekly stops and short start-up time, most HRSG-plants are faced with claims for low operational costs. Frequent start/stop and phosphate or caustic treatment demands a qualified chemical supervision system (see VGB-S-006-T-00;2012-00.EN (4)). When this cannot be guaranteed, the conditioning must be reviewed with respect to the operational concept of the plant. In this relation the simplest possible conditioning is with a volatile alkalising agent only.

HRSG-plants are also operated in combined-heat-and-power mode in which steam is supplied for industrial purposes. This makes an increased consumption of make-up water and chemical excursions caused by process return condensates likely. Particular attention in the supervision should be given to the process return condensates since they are very likely to be contaminated with products of the process (see VGB-S-006-T-00;2012-00.EN (4) and VGB-R 412 (5)).

In drum-type boilers operating at the pressures above 1 MPa, the temperatures in the boiler water circulating system are such that a protective layer is produced by spontaneous magnetite formation. The solubility of magnetite depends on the pH, with a minimum at around pH 10 (measured at 25°C, Figure 14) /7/. At much lower pH values, the magnetite solubility increases considerably, likewise in the highly alkaline range (Figure 7).

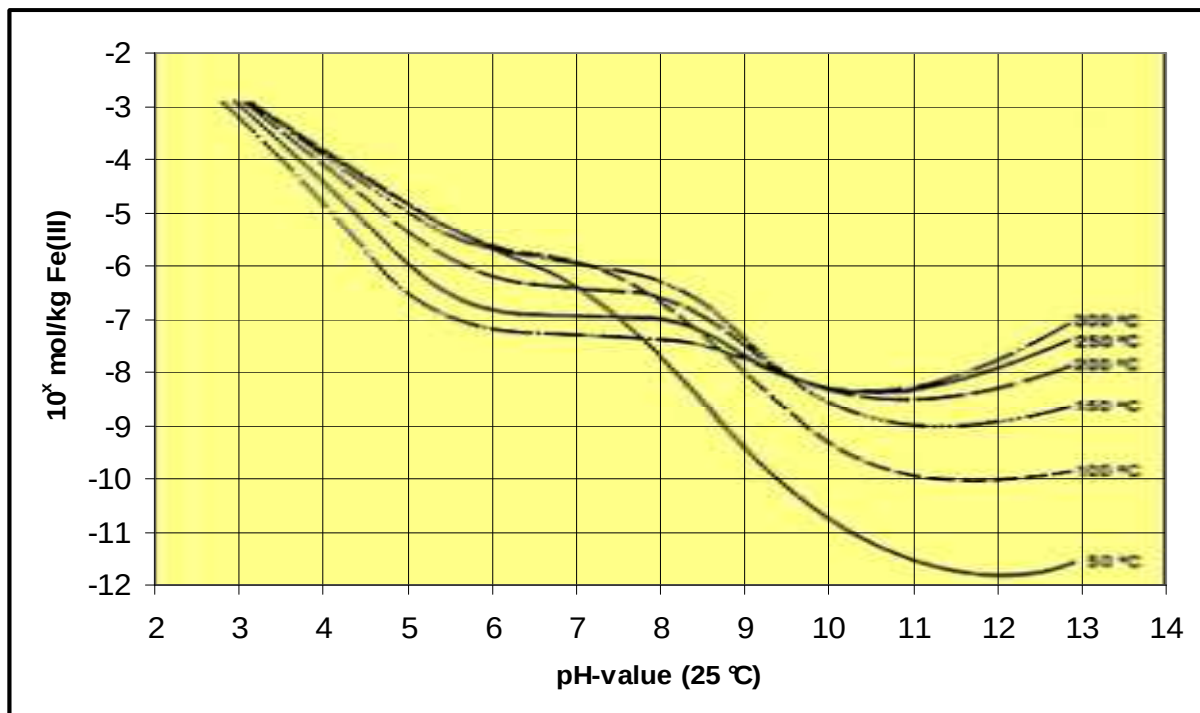


Figure 14: Solubility of magnetite as function of pH.

In principle, a solubility equilibrium is established in the circulating system, which, however, is disturbed by the evaporation process. This results in supersaturation that may lead to carry-over of corrosion products and the depositing of corrosion products on the heated side of the evaporator tubes.

5.3.2.1 Caustic or phosphate treatment (solid alkalising)

When contamination of the feed water is likely to occur, the pH of the boiler water must be maintained within a specific range. This is not always achievable by use of volatile alkalising agents. The high pH minimises the solubility of the magnetite and counteracts the effect of contaminants concentrated in the boiler water that reduce the pH. The recommended standard procedure for drum-type boilers operating at less than 16 MPa is the application of volatile and solid alkalising agents. The aim of the volatile alkalising agents is to maintain a pH above 9 in the condensate/feed water area whereas the solid alkalising agents aim to achieve satisfactory boiler water alkalinity and pH. In order to ensure thorough mixing, the solid alkalising agent must be added to the feed water downstream of the spray water tapping point. Alternatively, the solid alkalising agents can be dosed into downcomers or to the boiler drum, if the dosing points are designed to ensure good distribution and avoid local overdosing.

5.3.2.2 All volatile treatment

Volatile alkalising agents may be used solely in the water-steam cycle of drum-type boilers on condition that demineralised feed water is applied and that ingress of trace contaminants can be virtually eliminated. This means that the conductivity of the boiler water must be maintained at a very low level (Table 8).

The distribution of the alkalising agent between boiler water and saturated steam in a drum boiler determines the alkalisation achievable for the evaporator, in which non-volatile contaminants are accumulated during operation. The most volatile alkalising agent, ammonia, has a distribution in favour of the steam, whereas others may distribute more evenly between the two phases. In practice the concentration of the alkalising agent in the feed water is controlled, and nearly the same concentration is experienced in the steam. The concentration in the boiler water adjusts accordingly, such that the distribution equilibrium between water and steam at the drum temperature and pressure is fulfilled.

The distribution of ammonia is of particular importance for two- or three-stage HRSG-plants because the volatility (ammonia in the saturated steam) increases as the drum temperature and pressure decreases. That means that the low pressure evaporator is alkalised to the lowest degree. Furthermore, the operating temperature combined with poor alkalisation makes the typical materials of the low pressure evaporators sensitive to erosion corrosion. Thus, the common feed water of all stages must be conditioned with respect to sufficient alkalisation of the low pressure evaporator. The distinct dependence of the distribution coefficient with temperature and pressure is depicted in Figure 15, and the relationships between pH, specific conductivity, and ammonia concentration are shown in Figure 16.

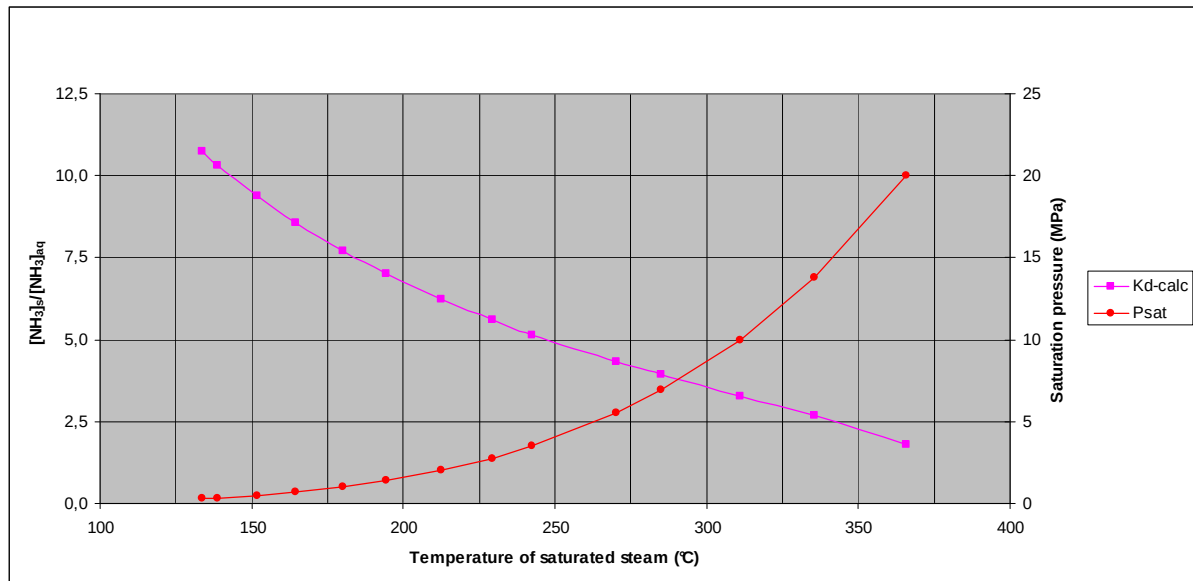


Figure 15: Distribution coefficient of ammonia and saturation pressure in relation to temperature.

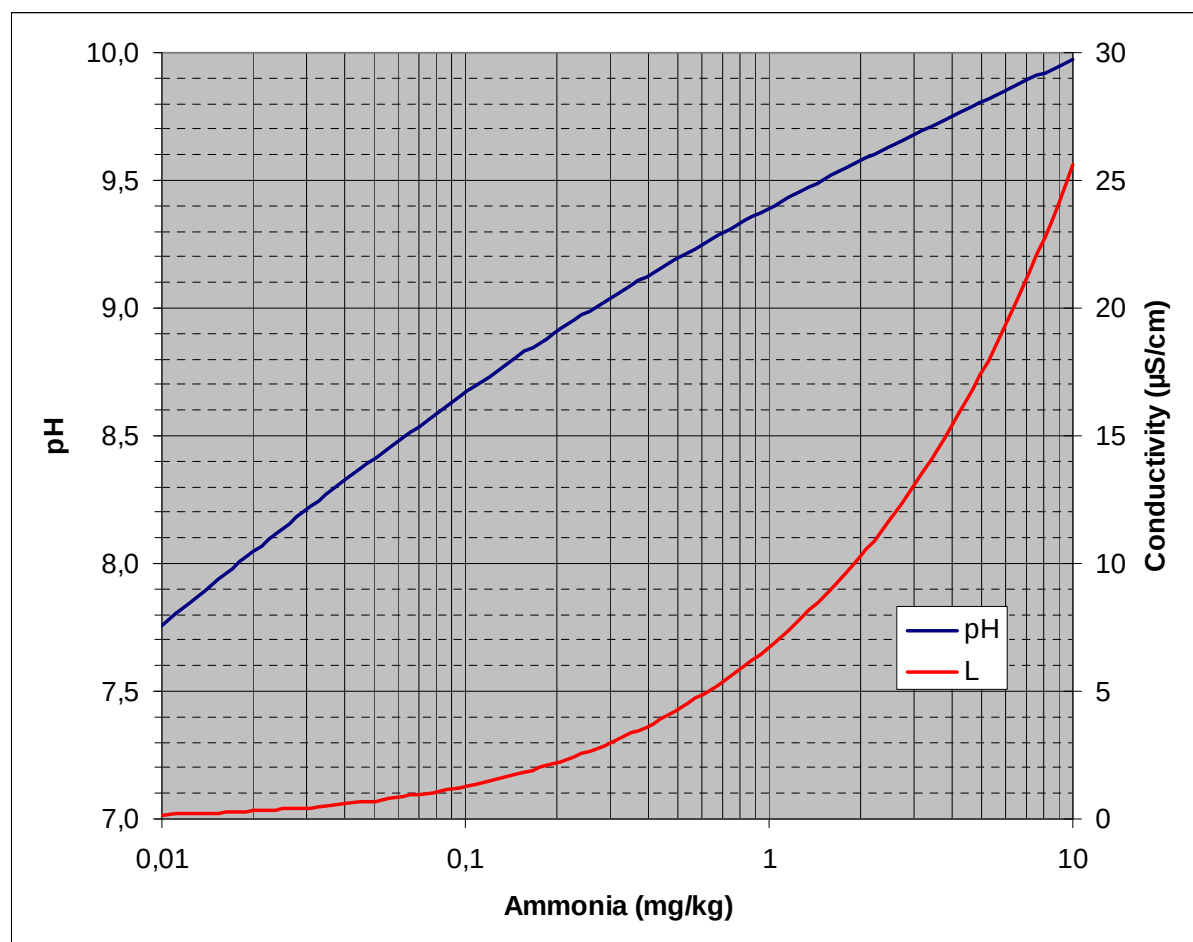


Figure 16: pH and specific conductivity in relation to ammonia concentration.

Due to the pH- and temperature dependent equilibrium between dissolved ammonia (NH_3) and ammonium ions (NH_4^+) the required ammonia concentration in feed water

cannot be read directly from the two figures. This is possible in Figure 17 that displays the total ammonia concentration in the feed water to achieve a given pH of the boiler water depending on the temperature (and pressure) of the boiler water.

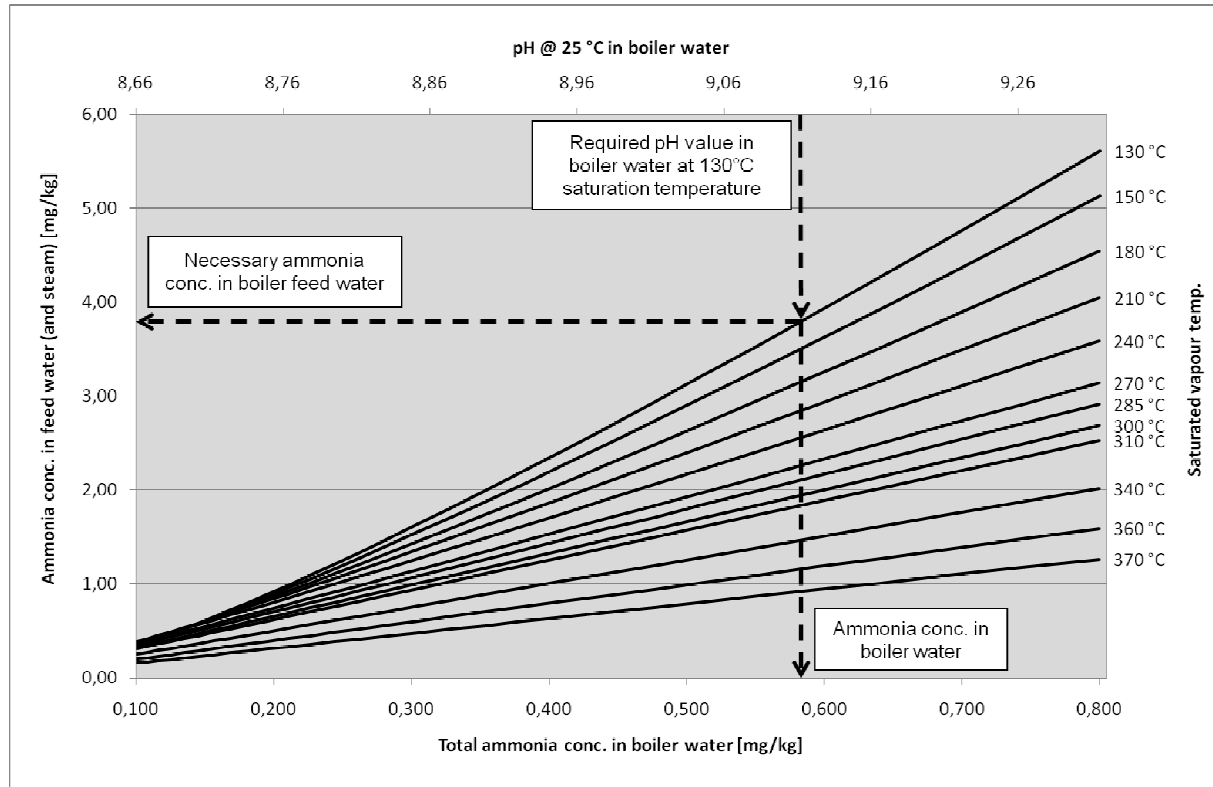


Figure 17: Distribution between total concentration of ammonia in feed water and steam in relation to the boiling temperature.

5.3.3 Organic conditioning agents

The treatment chemicals described in chapter 5.3.1 and 5.3.2 are typical for power plants and also for industrial plants. Besides those “basic” chemicals numerous organic treatment chemicals are offered and in use, mainly in industrial plants. The use of such chemicals should be well considered because nearly all of these chemicals are subject to thermal degradation under boiler operating conditions, resulting in formation of organic acids and/or carbon dioxide. The break-down products increase the acid conductivity in the entire steam water cycle. Furthermore, they tend to mask the possible ingress of contaminants from other sources because the agent itself or the break-down products are not as easily removed as ammonia from the sample steam by means of a cation filter ahead of the cationic conductivity measurements (see VGB M 418e (6)).

The concentration of break-down products in the first condensate of a condensation turbine may lead to corrosion attack.

Acid break-down products lower the pH of the boiler water und call for the use of solid alkalising agents.

The chemicals can be classified as follows:

- Neutralising/alkalising amines
- Film-forming amines
- Oxygen scavengers
- Dispersants

Plants using organic treatment chemicals should thoroughly reconsider the actual chemical regime and investigate, if the applied chemicals are really indispensable or if a reduction in the number of chemicals is feasible. Single substances should be preferred, rather than proprietary chemical blends.

A redesign of systems may be a worthwhile challenge to reduce the number and dosing concentrations of organic treatment chemicals or even enable a chemical treatment according to Chapter 5.3.1 and 5.3.2 and thus save operating costs.

Plants with long-term good operational experience without any damages or upsets related to the use of organic treatment chemicals may continue with the proven chemical regime, but take the above mentioned into account.

The design of new plants should enable a chemical treatment according to chapter 5.3.1 and 5.3.2.

The application of alternative treatment chemicals requires the agreement of the boiler and steam turbine manufacturer.

6 Chemical specification

In this chapter chemical influencing variables are specified and assessed.

6.1 Action level control system

It is the aim of the action level control system to avoid the shut-down requirement as long as there is any realistic chance to eliminate the source of trouble. This should be managed by plant specific measures, but possible actions are mentioned in Chapters 4 and 5.

The chemical control is based on specifications of normal operating values and 3 action levels for concentrations of chemical species. The most significant parameters are defined as key parameters and stringent control of them is required, if possible by continuous monitoring. These parameters are marked by yellow background in the tables 2 to 13.

If continuous monitoring of the key parameters is not available or possible, these parameters should be followed intensively by means of laboratory analysis. In that case an analysis frequency of several times per week is recommended as long as the normal values are observed.

Other chemical measurements according to tables 2 to 13 will frequently provide valuable diagnostic data. Laboratory support is required for periodical analysis (routine analysis) and check of monitors. If a key parameter deviates from the normal values, it is recommended to intensify the laboratory analyses (extended analysis, see Chapter 8).

The action levels AL1 to AL3 are defined as common limits, and the adherence to those generally secures a safe operation of the plants. By operating within these thresholds and acting as recommended when they are crossed, the risk of disturbance or failure of the power plant components is reduced on long term (action level N to AL1), intermediate term (AL1 to AL3) and short term (outside AL3).

The operating range below AL1 is divided into the N-range with optimal conditions and a range between N and AL1 with acceptable conditions. The N-range will vary from plant to plant depending on the plant age and state, possibilities to clean the water-steam circuit (e. g. condensate polishing) and operating conditions (base- or peak load). The N-range limits valid for a specific water-steam cycle have to be evaluated from historic data from a period of operation without major disturbances. A statistically based procedure for this is given in chapter 8. The N-range limits are estimated such that a known fraction (80 to 90 %) of the values falls within the range during normal operation.

If the N-range is adhered to, only supervision of the chemistry by means of the key parameters and the routine extent of laboratory analyses is necessary. When an N-range limit is crossed, the scope of laboratory analysis should be extended to identify

the cause of the deviation and bring the system back to optimal operation. The extended analysis allows the operator to decide, if the deviation of one of the measured values has been caused by incident (random variation) only or by a real change in the process. The use of the N-range method serves the purpose to maximise the life length of the components, to minimise the risk of failure, and on the long term to achieve an operation free of disturbances.

The limits of action levels for boiler water are defined as a function of pressure. This is a simplified approach; there are other parameters which affect the "true" limits (e. g. heat flux). Nevertheless, pressure has been chosen as the most convenient parameter for operators. Boilers with extraordinary high heat flux (some designs of oil fired boilers) may require more stringent limits.

The action levels are defined so that they allow the operator to use the same set of limits for continuous operation and for start-up. The detailed definitions of action levels are specified separately for these situations in Table 1. Action levels are time related and the combination of concentration and time are set to minimise damage to feed, boiler and turbine components from corrosion and deposition processes.

Remark: During a start-up process, the values of the action level are only applicable when the sample lines, cation filters, and instruments have been flushed adequately and thus give measurements representing the process stream.

Table 1: Definition and characteristics of action levels.

Action level or range	Characteristics	Action during operation	Action during start-up
<i>N</i>	<i>Plant-specific normal operating value</i>	<i>Supervision of key parameters</i>	
<i>N to AL 1</i>	<i>Acceptable range</i>	<i>The supervision should be extended to diagnostic parameters in order to identify possibilities to go back to the N-range</i>	
AL 1			
<i>AL 1 to AL 2</i>	<i>Operation in this range possibly increases the long term risk of failure</i>	<i>Measures should be taken to identify and rectify the cause of the excursion within a week. Further actions to minimise possible damage to the plant should be taken</i>	<i>The action level 1 should be reached for key parameters in 2 to 8 hours for warm and cold starts, respectively.</i>
AL 2			
<i>AL 2 to AL 3</i>	<i>Basically, operation within this range increases the risk of failure.</i>	<i>Measures should be taken to identify and rectify the cause of the excursion within a day. Further actions to minimise possible damage to the plant should be taken</i>	<i>Fire the boiler up. Check the steam quality. At least action level 2 for all key parameters in steam should be reached before the turbine is brought into service.</i>
AL 3			
<i>Outside AL 3</i>	<i>Chemistry is out of control; operation is connected with immediate risk of damage.</i>	<i>The unit should be shut down as soon as possible using the normal shut-down procedure, if one of the key parameters is outside AL 3. For diagnostic parameters see AL 2 to AL 3.</i>	<i>The cause of excursion above AL3 must be identified and counter-measures taken before the start-up process is resumed.</i>

6.2 Operation with demineralised feed water

Most of the steam generators can be operated with demineralised feed water.

6.2.1 Requirements on feed water for once-through boilers

Table 2: Once-through boilers with a copper free condensate/feed water system³⁾

FEED WATER and Attemperator Spray Water						
Boiler Type	Once-through; copper free condensate / feed water system					
Feed Water Treatment			AVT (Alkaline)		OT	
pH		N	*)		*)	
		AL 1	9.2		8.4	
		AL 2	8.8		8.2	
		AL 3	7.8		7.8	
Acid Conductivity	µS/cm	N	*)		*)	
		AL 1	0.20		0.15	
		AL 2	0.30		0.20 ¹⁾	
		AL 3	1 ²⁾		1 ²⁾	
Conductivity (only valid for ammonia dosing)	µS/cm	N	*)		*)	
		AL 1	4.3		0.7	
		AL 2	1.7		0.4	
		AL 3	0.25		0.25	
Oxygen (O ₂)	µg/kg	N	*)		*)	
		AL 1	100		250	
		AL 2	250		500	
		AL 3	—		—	
Silica (SiO ₂)	µg/kg	N	*)		*)	
		AL 1	20		20	
		AL 2	50		50	
		AL 3	—		—	
Iron (Fe), total	µg/kg	N	*)		*)	
		AL 1	10		10	
		AL 2	20		20	
		AL 3	—		—	
Sodium (Na)	µg/kg	N	*)		*)	
		AL 1	5		5	
		AL 2	20		20	
		AL 3	—		—	
Organics	see chapter 7.10					

*) Must be evaluated plant-specifically, see Chapter 8

N: Normal Level

AL 1 (2, 3): Action Level

¹⁾ Once AL 2 is reached, stop oxygen dosing and change to AVT. The higher the acid conductivity is, the lower must the oxygen content of the feed water be in order to minimise the corrosion risk.

²⁾ Acid conductivity > AL3 causes damage on superheaters due to contaminated spray-water

³⁾ By components of aluminium in the water-steam circuit the values cited are not directly applicable.

Table 3: Once-through boilers with copper in condensate/feed water system.

FEED WATER and Attemperator Spray Water						
Boiler Type		Once-through; copper alloy in the condensate / feed water system				
Feed Water Treatment			AVT (Alkaline)		OT	
pH		N	*)		*)	
		AL 1	8.8	9.3	8.4	8.8
		AL 2	8.5	9.4	8.2	9.0
		AL 3	7.8	-	7.8	-
Acid Conductivity	µS/cm	N	*)		*)	
		AL 1	0.20		0.15	
		AL 2	0.30		0.20 ¹⁾	
		AL 3	1 ²⁾		1 ²⁾	
Conductivity (only valid for ammonia dosing)	µS/cm	N	*)		*)	
		AL 1	1.9	5.5	0.7	1.8
		AL 2	0.9	7.0	0.4	2.7
		AL 3	0.25	—	0.25	—
Oxygen (O ₂)	µg/kg	N	*)		*)	
		AL 1	20		250	
		AL 2	50		500	
		AL 3	—		—	
Silica (SiO ₂)	µg/kg	N	*)		*)	
		AL 1	20		20	
		AL 2	50		50	
		AL 3	—		—	
Iron (Fe), total	µg/kg	N	*)		*)	
		AL 1	10		10	
		AL 2	20		20	
		AL 3	—		—	
Copper (Cu), total	µg/kg	N	*)		*)	
		AL 1	3		3	
		AL 2	5		5	
		AL 3	—		—	
Sodium (Na)	µg/kg	N	*)		*)	
		AL 1	5		5	
		AL 2	20		20	
		AL 3	—		—	
Organics	see chapter 7.10					

*) Must be evaluated plant-specifically, see Chapter 8

N: Normal Level

AL 1 (2, 3): Action Level

⁽¹⁾ Once AL 2 is reached, stop oxygen dosing and change to AVT. The higher the acid conductivity is, the lower must the oxygen content of the feed water be in order to minimise the corrosion risk.⁽²⁾ Acid conductivity > AL3 causes damage on superheaters due to contaminated spray-water⁽³⁾ By components of aluminium in the water-steam circuit the values cited are not directly applicable.

6.2.2 Requirements on feed water for drum boilers

Table 4: Drum Boilers with a copper free condensate/feed water system.

FEED WATER and Attemperator Spray Water					
Boiler Type	Drum; copper free condensate/feed water system				
Feed Water Treatment	AVT (Alkaline)			OT	
pH ⁽¹⁾		N	2) ^{*)}		2) ^{*)}
		AL 1	9.2		8.6
		AL 2	9.0		8.4
		AL 3	8.6		8.2
Conductivity (only valid for ammonia dosing)	µS/cm	N	^{*)}		^{*)}
		AL 1	4.3		1.1
		AL 2	2.7		0.7
		AL 3	1.1		0.4
Acid Conductivity	µS/cm	N	^{*)}		^{*)}
		AL 1	0.20 ³⁾		0.15
		AL 2	0.50		0.20 ¹⁾
		AL 3	1		0.50
Oxygen (O ₂)	µg/kg	N	^{*)}		^{*)}
		AL 1	100		100
		AL 2	250		250
		AL 3	-		—
Silica (SiO ₂)	µg/kg	N	^{*)}		^{*)}
		AL 1	20		20
		AL 2	50		50
		AL 3	—		—
Iron (Fe), total	µg/kg	N	^{*)}		^{*)}
		AL 1	20		20
		AL 2	30		30
		AL 3	—		—
Sodium (Na)	µg/kg	N	^{*)}		^{*)}
		AL 1	5		5
		AL 2	20		20
		AL 3	—		—
Organics	see chapter 7.10				

^{*)} Must be evaluated plant-specifically, see Chapter 8

N: Normal Level

AL 1 (2, 3): Action Level

⁽¹⁾ Once AL 2 is reached, stop oxygen dosing and change to AVT. The higher the acid conductivity is, the lower must the oxygen content of the feed water be in order to minimise the corrosion risk.

⁽²⁾ The pH value of the feed water must be controlled such that the pH value according to Table 9 is achieved for the boiler water of the lowest pressure stage.
To estimate the pH value of the feed water see Chapter 5.3.1.4

⁽³⁾ A higher value up to AL 2 may be acceptable if the increase of acid conductivity can be attributed to carbon dioxide

Table 5: Drum Boilers with copper in condensate/feed water system.

FEED WATER and Attemperator Spray Water						
Boiler Type		Drum; copper alloy in the condensate / feed water system ¹⁾				
Feed Water Treatment			AVT (Alkaline)		OT	
pH ⁽¹⁾		N	3) *)		3) *)	
		AL 1	8.8	9.3	8.6	9.3
		AL 2	8.5	9.5 ⁵⁾	8.4	9.5 ⁵⁾
		AL 3	8.2	9.8	8.2	9.8
Conductivity (only valid for ammonia dosing)	µS/cm	N	*)		*)	
		AL 1	1.7	5.5	1.1	5.5
		AL 2	0.9	7.2	0.7	7.2
		AL 3	0.4	18	0.4	18
Acid Conductivity	µS/cm	N	*)		*)	
		AL 1	0.20 ⁴⁾		0.15	
		AL 2	0.50		0.20 ²⁾	
		AL 3	1		0.50	
Oxygen (O ₂)	µg/kg	N	*)		*)	
		AL 1	100		100	
		AL 2	250		250	
		AL 3	-		-	
Silica (SiO ₂)	µg/kg	N	*)		*)	
		AL 1	20		20	
		AL 2	50		50	
		AL 3	—		—	
Iron (Fe), total	µg/kg	N	*)		*)	
		AL 1	20		20	
		AL 2	30		30	
		AL 3	—		—	
Sodium (Na)	µg/kg	N	*)		*)	
		AL 1	3		3	
		AL 2	5		5	
		AL 3	-		-	
Organics	see chapter 7.10					

*) Must be evaluated plant-specifically, see Chapter 8

N: Normal Level

AL 1 (2, 3): Action Level

¹⁾ This mode of conditioning is only recommended at drum pressures > 5 MPa²⁾ Once AL 2 is reached, stop oxygen dosing and change to AVT. The higher the acid conductivity is, the lower must the oxygen content of the feed water be in order to minimise the corrosion risk.³⁾ The pH value of the feed water must be controlled such that the pH value according to Table 9 is achieved for the boiler water of the lowest pressure stage.
To estimate the pH value of the feed water see Chapter 5.3.1.4⁴⁾ A higher value up to AL 2 may be acceptable if the increase of acid conductivity can be attributed to carbon dioxide⁵⁾ The pH value of the feed water must within very short time be brought back below AL2

6.2.3 Requirements on boiler water for drum boilers

Table 6: Drum Boilers with Caustic Treatment (CT) ¹⁾.

BOILER WATER								
Boiler Type		Drum						
Boiler Water Treatment			Caustic Treatment					
Steam Pressure (MPa)			< 4		4 to 10		> 10	
pH		N	*)		*)		*)	
		AL 1	9.5	10.5	9.4	10.2	9.3	9.7
		AL 2	9.0	10.7	9.1	10.3	9.1	9.9
		AL 3	8.5	-	8.7	-	8.8	-
Conductivity	µS/cm	N	*)		*)		*)	
		AL 1	8	80	6	40	5	12
		AL 2	2.5	125	3.0	50	3.5	20
		AL 3	2.2		2.5		3.0	
Acid Conductivity	µS/cm	N	*)		*)		*)	
		AL 1	50		50		30	
		AL 2	100		100		50	
		AL 3	250		250		100	
Silica (SiO ₂)	mg/kg	N	*)					
		AL 1	according to Figure 19					
		AL 2	2 x AL 1					
		AL 3	—					
Organics	see chapter 7.10							

*) Must be evaluated plant-specifically, see Chapter 8

N: Normal Level

AL 1 (2, 3): Action Level

¹⁾ If other alkali metal hydroxides (e. g. LiOH, KOH) are used, this table serves as orientation

²⁾ In order to control or measure the pH value by caustic treatment see Figure 18 to Figure 23

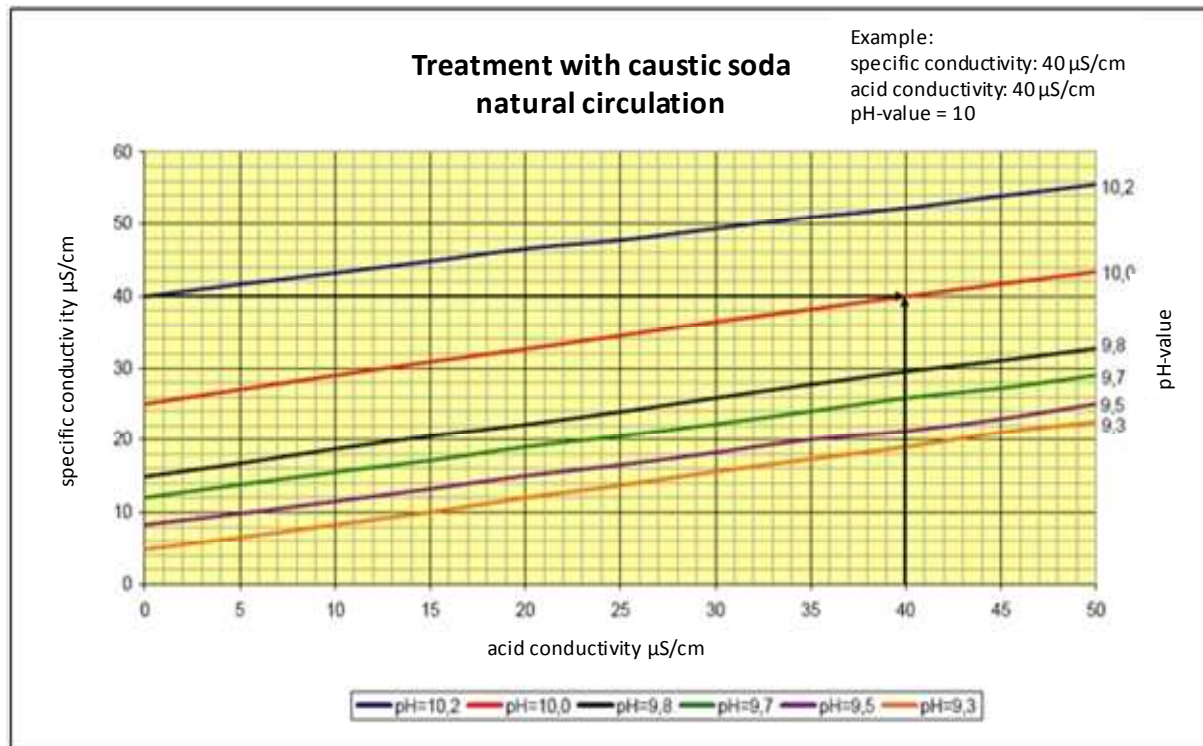


Figure 18: Relationship between pH value, specific conductivity, and acid conductivity for caustic treatment of boiler water.

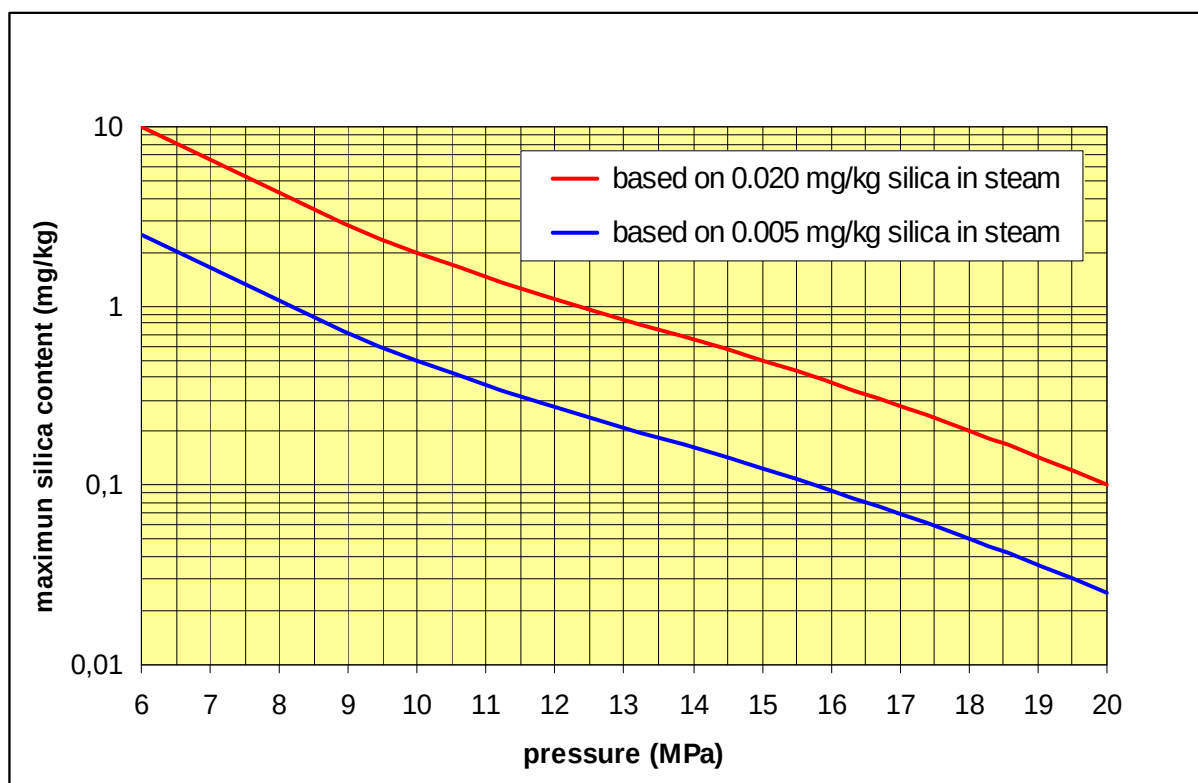


Figure 19: Drum boiler water (feed water demineralised), silica content versus pressure to achieve less than 20 $\mu\text{g/kg}$ or 5 $\mu\text{g/kg}$, respectively, in the steam.

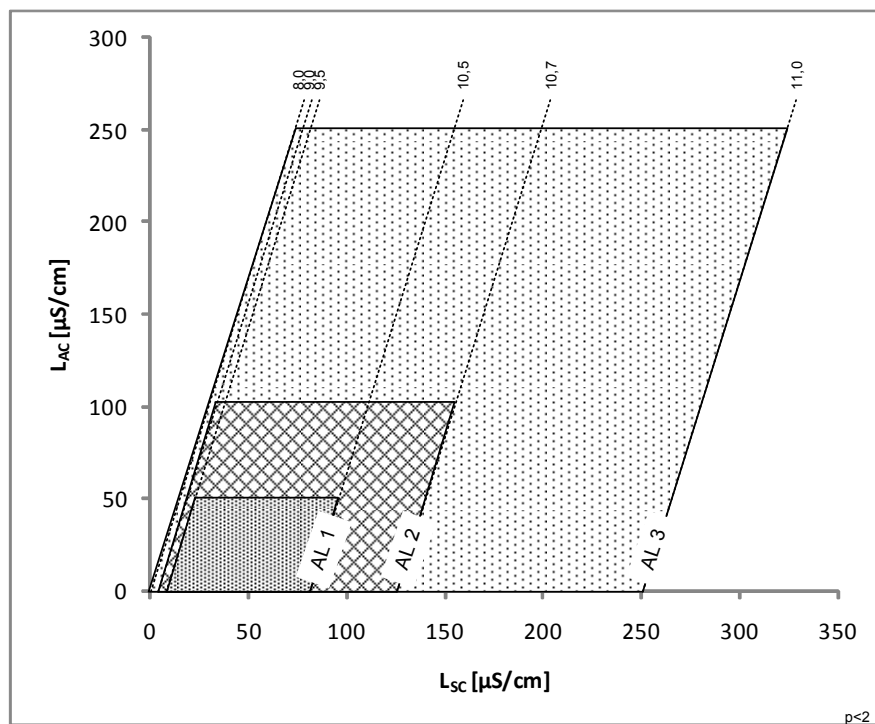


Figure 20: Relationship between specific conductivity (L_{SC}) and acid conductivity (L_{AC}) in boiler water with caustic treatment for pressures < 4 MPa.

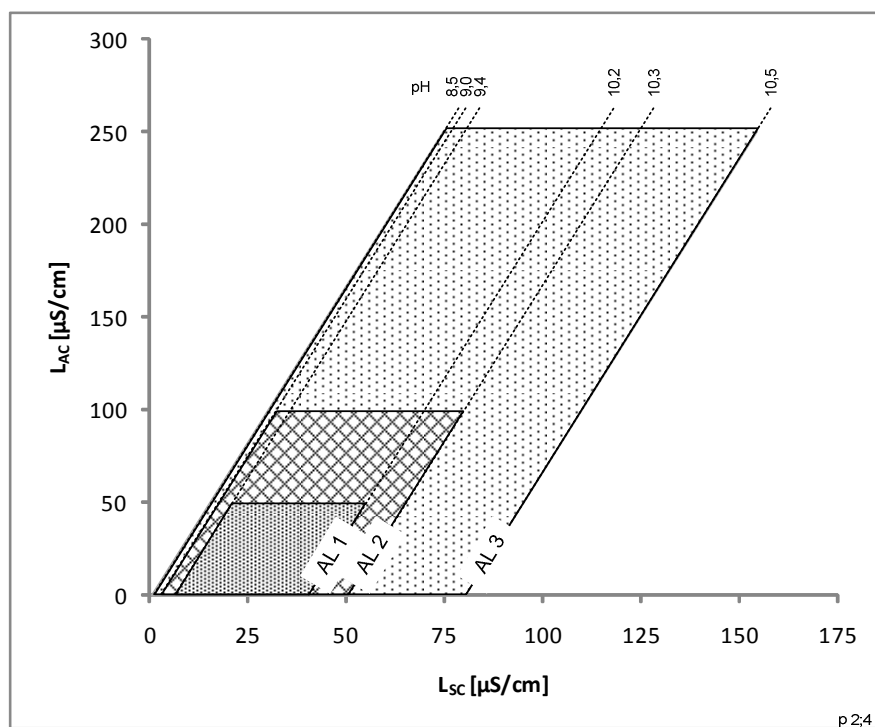


Figure 21: Relationship between specific conductivity (L_{SC}) and acid conductivity (L_{AC}) in boiler water with caustic treatment for pressures 4 MPa < x < 10 MPa.

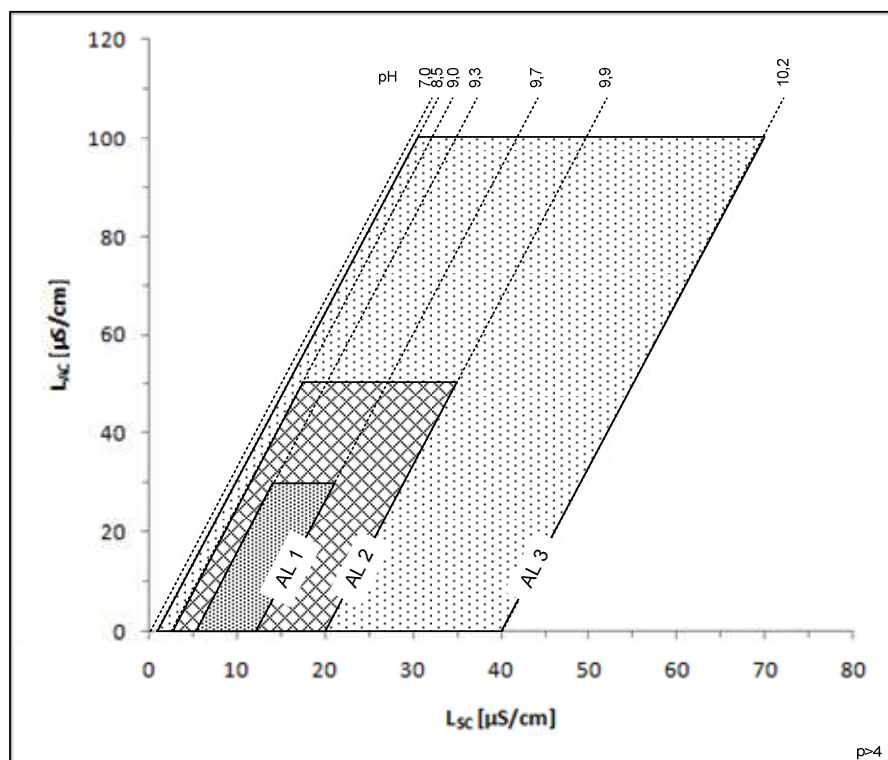


Figure 22: Relationship between specific conductivity (L_{SC}) and acid conductivity (L_{AC}) in boiler water with caustic treatment for pressures > 10 MPa.

Table 7: Drum Boilers with Phosphate Treatment.

BOILER WATER								
Boiler Type		Drum						
Boiler Water Treatment			Phosphate Treatment ¹⁾					
Steam Pressure (MPa)			< 4		4 to 10		> 10	
pH		N	*)		*)		*)	
		AL 1	9.5	10.5	9.4	10.2	9.3	9.7
		AL 2	9.0	10.7	9.0	10.3	9.0	9.9
		AL 3	8.5	-	8.5	-	8.5	-
Conductivity ³⁾	μS/cm	N	*)		*)		*)	
		AL 1	100		50		30	
		AL 2	250		100		50	
		AL 3	500		200		100	
Phosphate (PO ₄)	mg/kg	N	*)		*)		*)	
		AL!	15		6		3	
Silica (SiO ₂)	mg/kg	N	0.25 x AL 1					
		AL 1	according to Figure 19					
		AL 2	2 x AL 1					
		AL 3	—					
Organics	see chapter 7.10							

*) Must be evaluated plant-specifically, see Chapter 8

N: Normal Level

AL 1 (2, 3): Action Level

¹⁾ If other phosphates (e. g. Na₂HPO₄) are used, this table serves for orientation.

²⁾ In order to control or measure the pH value by phosphate treatment see Figure 23

³⁾ With phosphate treatment there is no direct relationship between pH and conductivity as for caustic treatment. Thus, the pH value must be measured directly

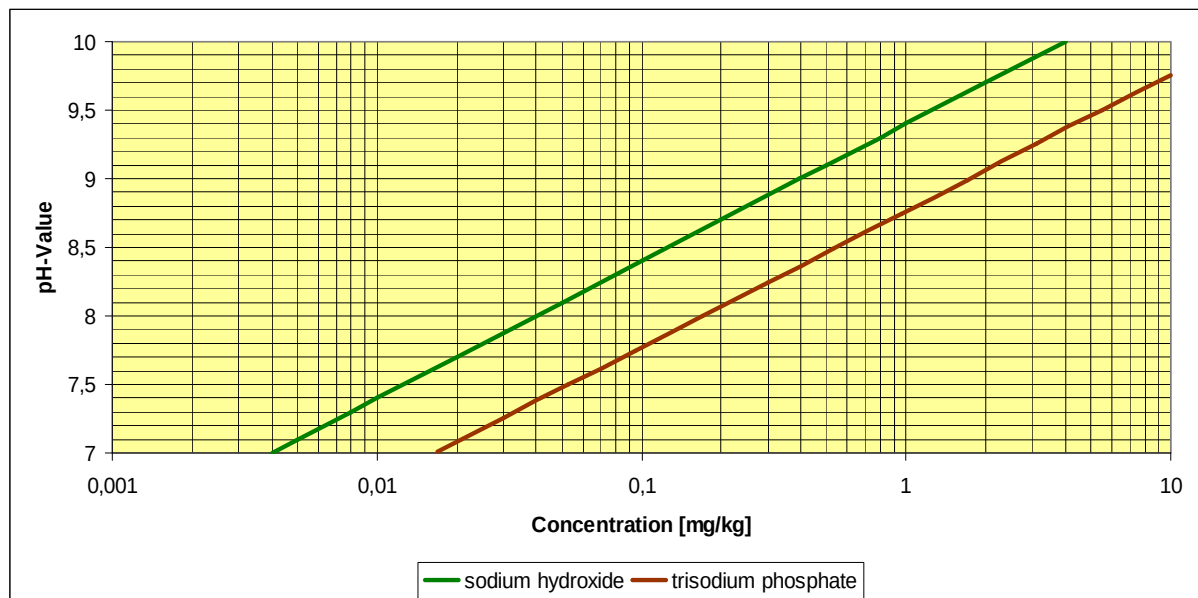


Figure 23: Relationship between pH at 25 °C and concentration of sodium hydroxide (NaOH) and trisodium phosphate (Na₃PO₄), respectively, in pure water.

Table 8: Drum Boilers with AVT.

BOILER WATER					
Boiler Type		Drum			
Boiler Water Treatment			AVT and OT		
Steam Pressure (MPa)			< 8	8 to 16	> 16
pH		N	pH ≥ 9.2 is recommended ^{*)}		
		AL 1	9.1		
		AL 2	8.6		
		AL 3			
Acid Conductivity	μS/cm	N	^{*)}	^{*)}	^{*)}
		AL 1	5	3	1
		AL 2	10	6	2.5
		AL 3	20	12	5
Silica (SiO ₂)	mg/kg	N	0.25 x AL 1		
		AL 1	according to Figure 19		
		AL 2	2 x AL 1		
		AL 3	—		
Organics	see chapter 7.10				

^{*)} Must be evaluated plant-specifically, see Chapter 8

N: Normal Level

AL 1 (2, 3): Action Level

6.2.4 Requirements on steam for condensing turbines

Table 9: Steam.

STEAM for steam turbines				
Acid Conductivity	μS/cm		Without additional measurement of degassed, acid conductivity	With additional measurement of degassed, acid conductivity
		N	^{*)}	^{*)}
		AL 1	0.20	0.5
		AL 2	0.50	0.8
		AL 3	1	1.3
Degassed, acid conductivity	μS/cm	N	—	^{*)}
		AL 1	—	0.20
		AL 2	—	0.50
		AL 3	—	1
Silica (SiO ₂)	μg/kg	N	^{*)}	
		AL 1	20	
		AL 2	50	
		AL 3	—	
Sodium (Na)	μg/kg	N	^{*)}	
		AL 1	5	
		AL 2	10	
		AL 3	20	
Iron (Fe), total	μg/kg	N	^{*)}	
		AL 1	20	
		AL 2	—	
		AL 3	—	
Copper (Cu), total	μg/kg	N	^{*)}	
		AL 1	3	
		AL 2	—	
		AL 3	—	

^{*)} Must be evaluated plant-specifically, see Chapter 8

N: Normal Level

AL 1 (2, 3): Action Level

⁽¹⁾

The higher action limits (column “With additional measurement of degassed, acid conductivity”) may be applied when the increase in acid conductivity is associated with carbon dioxide, and organic degradation products are excluded as the cause.

6.3 Operation with non-demineralised feed water

Saline water is water that contains even dissolved solids such as decarbonized or softened water.

6.3.1 General

For economical reasons, non-demineralised water may be used in some specific cases (industry, low pressure boiler). The application of low-salinity water (specific conductivity $< 30 \mu\text{S/cm}$) as well as high-salinity water (specific conductivity $> 30 \mu\text{S/cm}$) is limited to boilers operating below 6 MPa.

Non-demineralised water is a water which still contains dissolved solids such as decarbonised water or/and softened water.

The feasibility of this kind of make-up is directly linked to the raw water characteristics, water treatment, ratio of make-up/condensates and main design/characteristics of the steam generator. Each case must be specifically studied to estimate its feasibility and compliance with these recommendations. None of these water qualities are suitable for attemperator spray water because of salt deposition in the superheaters.

6.3.2 Raw water/treated water parameters

Considering non-demineralised water make-up, several parameters have to be checked since the water treatment removes them partly or not at all. These parameters are mainly silica, chlorides and salinity. Total alkalinity and hardness are a key parameters for decarbonised and softened water, respectively. The limiting values can be found in the subsequent tables.

6.3.3 Condensate percentage return

Condensate returns have a significant influence on the feed water quality. To assess the feed water quality, it is necessary to know both amount and quality of the condensate return.

The mineral species are concentrated in the boiler water. Alkalinity is decomposed in the boiler to give caustic. Since a maximum concentration is given in the boiler water, blow-down is necessary to keep the water within the limits. This is particularly true for steam quality, silica, hardness, alkalinity and strong acid salts.

Table 10: Non-demineralised feed water for drum boilers.

FEED WATER ²⁾								
Boiler Type		Drum						
Steam Pressure (MPa)			< 2		2 to 4		4 to 6	
pH ¹⁾		N	*)		*)		*)	
		AL 1	9.2 ¹⁾	9.5	9.2 ¹⁾	9.5	9.2 ¹⁾	9.5
		AL 2	8.8 ¹⁾	10.0	8.8 ¹⁾	10.0	8.8 ¹⁾	10.0
		AL 3						
Conductivity	µS/cm		not specified – consider boiler water					
Total Hardness (Ca + Mg)	mmol/kg	N	*)		*)		*)	
		AL 1	0.02		0.01		0.005	
		AL 2	0.05		0.02		0.01	
		AL 3						
Silica (SiO ₂)	µg/kg		not specified – consider boiler water					
Iron (Fe), total	µg/kg	N	*)		*)		*)	
		AL 1	50		30		20	
		AL 2	200		100		50	
		AL 3	—		—		—	
Copper (Cu), total	µg/kg	N	*)		*)		*)	
		AL 1	20		10		3	
		AL 2	50		25		10	
		AL 3	—		—		—	
Oxygen (O ₂)	µg/kg	N	*)		*)		*)	
		AL 1	20		20		20	
		AL 2	50		50		50	
		AL 3						
Oil/Grease/Organics	see chapter 7.10							

*) Must be evaluated plant-specifically, see Chapter 8

N: Normal Level

AL 1 (2, 3): Action Level

⁽¹⁾ with copper alloys in the system the pH value shall be maintained in the range 8.7 to 9.2⁽²⁾ with softened make-up water (pH > 7) the pH value of boiler water according to Table 11 - Table 13 should be considered

Table 11: Boiler water for drum boilers with saturated steam design.

BOILER WATER							
Boiler Type	Drum, saturated steam design						
Feed Water	conductivity > 30 $\mu\text{S/cm}$ (high-salinity content)						
Boiler Water Treatment			Alkaline				
Steam Pressure (MPa)			< 2		2 to 4		> 4
pH		N	*)		*)		*)
		AL 1	10.5	12.0	10.5	11.8	10.3 11.5
		AL 2	10.0	12.2	10.0	12	10.0 11.8
		AL 3					
Conductivity	$\mu\text{S/cm}$	N	*)				
		AL 1	pressure dependent according to Figure 24				
		AL 2	1.2 x AL 1				
		AL 3	1.5 x AL 1				
Alkalinity (A_p)	mmol/kg	N	*)		*)		*)
		AL 1	1	15	1	10	0.5 5
		AL 2	–	–	–	–	–
		AL 3	–	–	–	–	–
Silica (SiO_2)	mg/kg	N	*)				
		AL 1	pressure and alkalinity dependent according to Figure 25				
		AL 2	1.25 x AL 1				
		AL 3	–				
Phosphate (PO_4) ¹⁾	mg/kg	N	*)		*)		*)
		AL 1	10	20	8	15	8 15
		AL 2		30		25	
		AL 3					
Organics	see chapter 7.10						
Sodium in saturated steam ²⁾	$\mu\text{g/kg}$	N	*)		*)		*)
		AL 1		5		5	5
		AL 2		10		10	10
		AL 3					

*) Must be evaluated plant-specifically, see Chapter 8

N: Normal Level

AL 1 (2, 3): Action Level

¹⁾ if used²⁾ To protect the superheater the content of sodium in saturated steam should be determined by the commissioning and afterwards periodically. (Determination of the carry-over of boiler water depending on the load).

Table 12: Boiler water for drum boilers with superheated steam design.

BOILER WATER							
Boiler Type	Drum, superheated steam design						
Feed Water	conductivity > 30 µS/cm (high-salinity content)						
Boiler Water Treatment			Alkaline				
Steam Pressure (MPa)			< 2		2 to 4		> 4
pH		N	*)		*)		*)
		AL 1	10.5	11.8	10.5	11.7	10.3 11.3
		AL 2	10.0	12.0	10.0	11.8	9.5 11.5
		AL 3					
Conductivity	µS/cm	N	*)				
		AL 1	pressure dependent according to Figure 24				
		AL 2	1.2 x AL 1				
		AL 3	1.5 x AL 1				
Alkalinity (A _p)	mmol/kg	N	*)		*)		*)
		AL 1	1	8	1	5	0.5 2.5
		AL 2	—	—	—	—	—
		AL 3	—	—	—	—	—
Silica (SiO ₂)	mg/kg	N	*)				
		AL 1	pressure and alkalinity dependent according to Figure 25				
		AL 2	1.25 x AL 1				
		AL 3	—				
Phosphate (PO ₄) ⁽¹⁾	mg/kg	N	*)		*)		*)
		AL 1	10	20	8	15	8 12
		AL 2		30		25	
		AL 3					
Organics	see chapter 7.10						
Sodium in saturated steam ²⁾	µg/kg	N	*)		*)		*)
		AL 1		5		5	5
		AL 2		10		10	10
		AL 3					

*) Must be evaluated plant-specifically, see Chapter 8

N: Normal Level

AL 1 (2, 3): Action Level

⁽¹⁾ if used²⁾ To protect the superheater the content of sodium in saturated steam should be determined by the commissioning and afterwards periodically. (Determination of the carry-over of boiler water depending on the load).

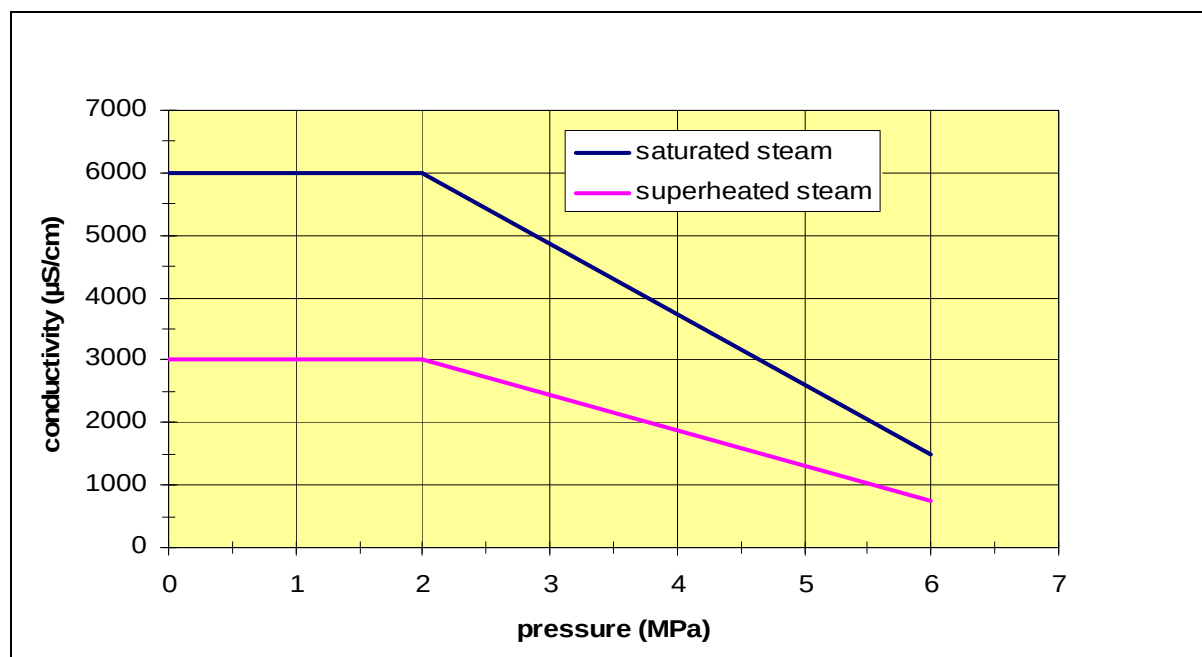


Figure 24: Drum boiler water (feed water with high-salinity), conductivity versus pressure.

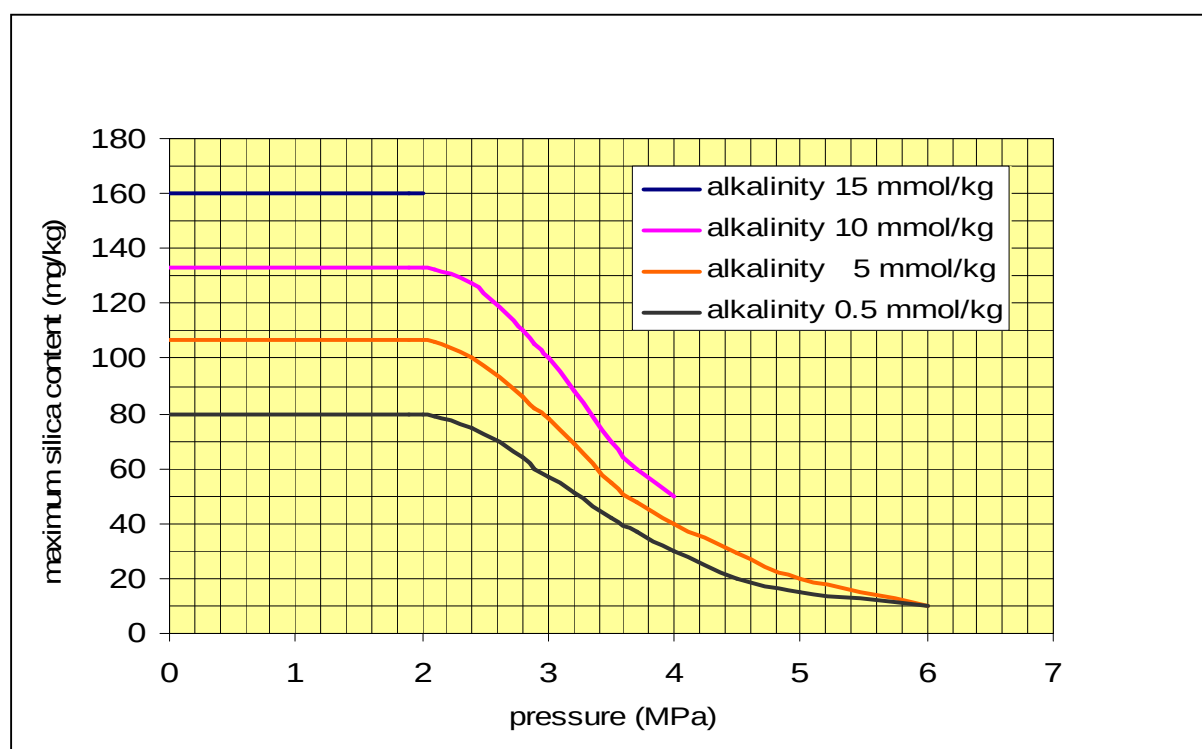


Figure 25: Drum boiler water (feed water non-demineralised), silica content versus pressure to achieve less than 0.020 mg/kg or 0.005 mg/kg respectively in the steam.

Table 13: Boiler water for drum boilers.

BOILER WATER			
Boiler Type	Drum, superheated steam design		
Feed Water	conductivity $\leq 30 \mu\text{S/cm}$ (low-salinity content)		
Boiler Water Treatment		Alkaline	
Steam Pressure (MPa)		≤ 6	
pH		N	^{*)}
		AL 1	10.0 11.0
		AL 2	9.5 11.5
		AL 3	
Conductivity	$\mu\text{S/cm}$	N	^{*)}
		AL 1	pressure dependent according to Figure 26
		AL 2	$1.2 \times \text{AL 1}$
		AL 3	$1.5 \times \text{AL 1}$
Alkalinity (A_p)	mmol/kg	N	^{*)}
		AL 1	0.1 1.0
		AL 2	– –
		AL 3	– –
Silica (SiO_2)	mg/kg	N	$< \text{AL 1}$
		AL 1	pressure and alkalinity dependent according to Figure 25
		AL 2	$1.25 \times \text{AL 1}$
		AL 3	–
Phosphate (PO_4) ⁽¹⁾	mg/kg	N	^{*)}
		AL 1	5 10
		AL 2	– 20
		AL 3	
Organics	see chapter 7.10		
Sodium in saturated steam ²⁾	$\mu\text{g/kg}$	N	^{*)}
		AL 1	– 5
		AL 2	– 10
		AL 3	

^{*)} Must be evaluated plant-specifically, see Chapter 8

N: Normal Level

AL 1 (2, 3): Action Level

⁽¹⁾ if used

²⁾ To protect the superheater the content of sodium in saturated steam should be determined by the commissioning and afterwards periodically. (Determination of the carry-over of boiler water depending on the load).

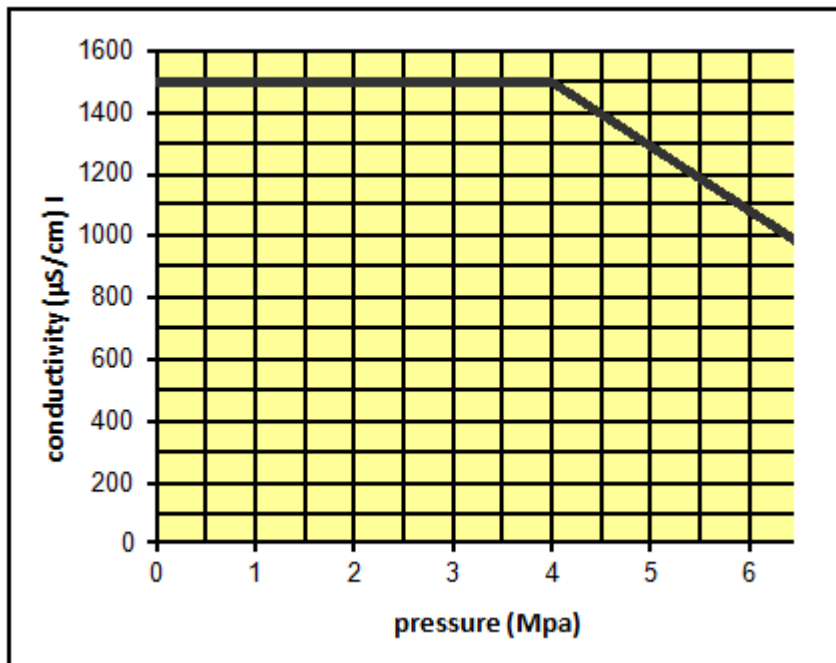


Figure 26: Drum boiler water (feed water with low-salinity), conductivity versus pressure.

7 Explanation of chemical specifications

The quality of water and steam is determined by chemical parameters.

7.1 pH value, alkalinity

The buffer system of the water sample is determined by the pH value and alkalinity.

7.1.1 pH value

The unit-less pH value is a very important unit of measurement for the acidic ($\text{pH} < 7$), neutral ($\text{pH} = 7$) or alkaline ($\text{pH} > 7$) reaction of liquids, particularly water samples of water-steam-circuits. Because of the definition of the pH-value (negative decadal logarithm of the concentration of hydrogen ions) any step of a pH-unit is an actual change of the acidic or alkaline concentration for a factor of ten!

For exact results the pH value must be measured electrochemically using pH-meter and electrodes, indicators give rough information only. The pH value changes significantly with the temperature and must be either noted together with the measuring temperature or measured at a reference temperature of 25°C (thermostated) see Figure 27. At low conductivity (specific conductivity $< 10 \mu\text{S/cm}$) is a reliable measurement of pH is only possible with difficulty and great care. A neutral salt may be added to the sample prior to measurement, or the measurement may be substituted by measurement of conductivity and calculation of pH. This is, however, only possible with known alkalising agents.

The pH value of feed water, boiler water, and condensate must be controlled to avoid attack on certain alloys or the dissolution of the iron protective layer. Further reference to the implications of pH is given in Chapter 4.3.3.

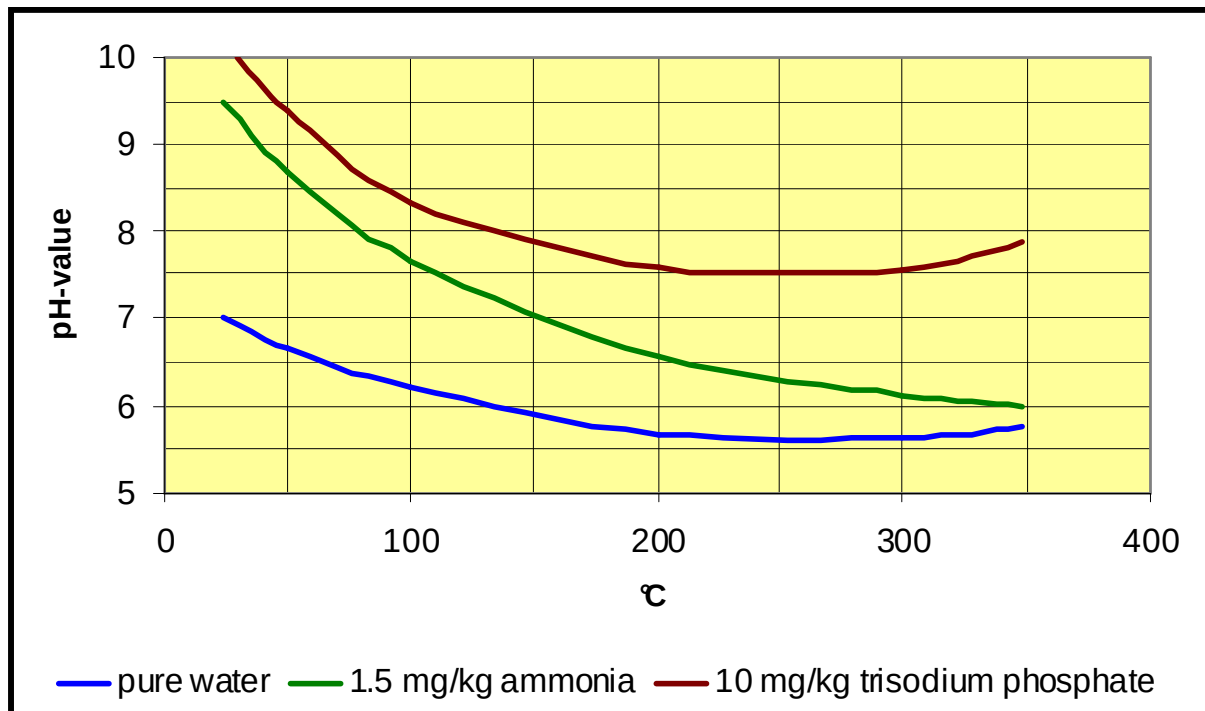


Figure 27: pH value at actual temperature of 1.5 mg/kg ammonia and 10 mg/kg trisodium phosphate in comparison with pure water.

7.1.2 Alkalinity

Alkalinity is the quantitative capacity of a water sample to neutralise strong acid and is divided into

- total alkalinity (titration to pH 4.3 by a standardised acid) and
- caustic alkalinity (titration to pH 8.2 by a standardised acid).

The total alkalinity corresponds to the equivalent concentration of hydrogen carbonate, carbonate, and hydroxide ions in water. Other buffering substances present as e. g. ammonia and phosphate are also included in the measurement.

The caustic alkalinity corresponds to the equivalent of hydroxide and carbonate concentration.

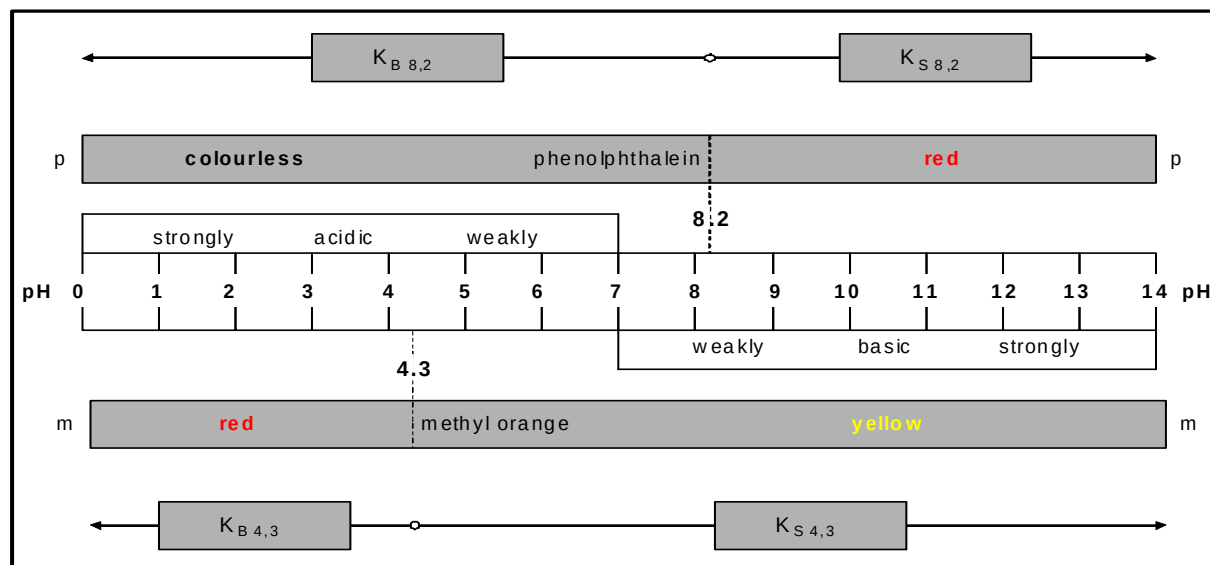


Figure 28: Interrelation between pH value and acid- (KS) respectively base-capacity (KB).

7.2 Conductivity

The **electrical conductivity** is a measure for the sum of all dissociated substances (salts, acids, bases and some organic substances) in liquids and is the actual substitute for the value of total dissolved solids/matter (TDS), particularly for TDS < 1 mg/l.

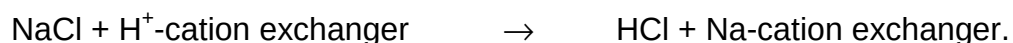
The unit for conductivity is Siemens (S) per metre (m) corresponding to $1/(\text{Ohm} \cdot \text{m})$ and is for the water-steam circuit traditionally expressed in $\mu\text{S}/\text{cm}$ ($10^{-4} \text{ S}/\text{m}$).

The conductivity changes strongly by the temperature and must be either noted together with the measuring temperature or measured at the reference temperature of 25°C (thermostated). In practise the conductivity is often corrected to the reference temperature by calculation. The temperature correction factor is not constant and depends on the type of electrical conductive matter and the absolute value of the conductivity, particularly < 0.2 $\mu\text{S}/\text{cm}$ (6).

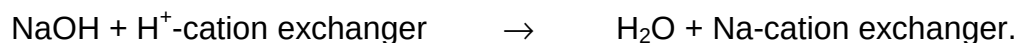
The conductivity of the purest water at 25°C is approximately 0.055 $\mu\text{S}/\text{cm}$.

Conductivity is the direct measured specific conductivity of any liquid.

Acid conductivity is the conductivity measured downstream of a strong acidic cation exchanger (sampling filter) which results in the elimination of any cation (like ammonia, sodium, potassium) and the emission of H^+ -cations. In that case, salts change to its free acids e. g.



Bases, however, like ammonium or sodium hydroxide reacts to water e. g.



Acids, also carbonic acid, are passing the cation exchanger without any effect.

This is an advantage for the indication of traces of salts (e. g. of condenser leaks) in water samples alkalisied with ammonia, because acids have a significant (3 to 4 times) higher specific conductivity than its neutral salts. On the other hand it prevents the indication of leaks of e. g. caustic soda in water samples.

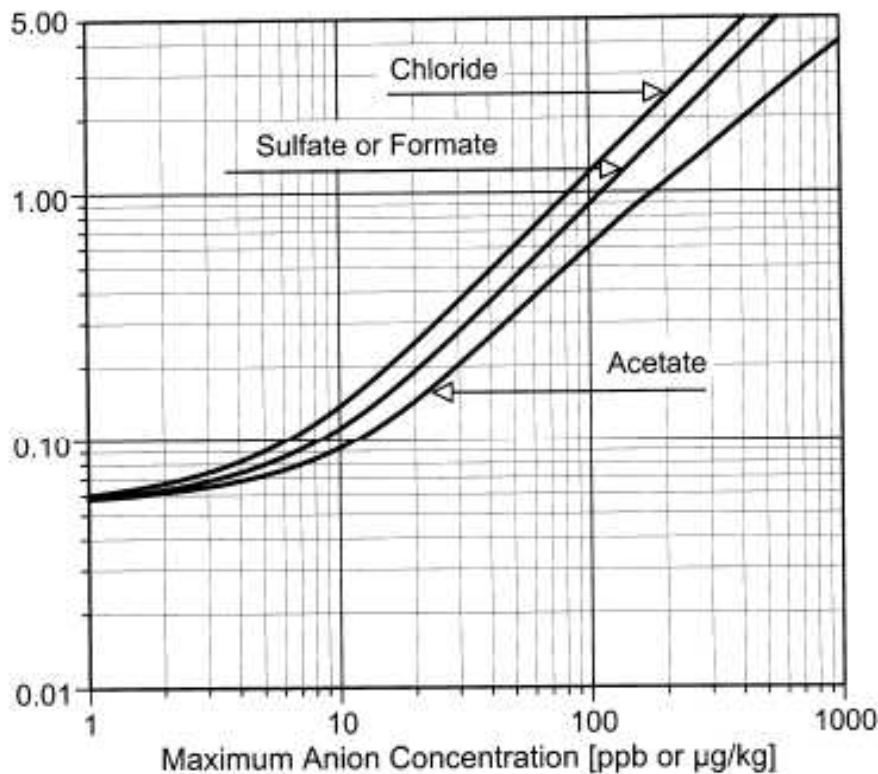


Figure 29: Acid conductivity in relation to different anions /15/.

Degassed conductivity is the conductivity measured after the sample has passed through a cation exchanger (acid conductivity) and a device (normally boiling) that strips the dissolved gases (in particular carbon dioxide) from the sample. Degassed conductivity may be interpreted as the acid conductivity without the conductivity contribution from carbon dioxide. In this sense the degassed conductivity measurement is sufficiently accurate, even though other compounds in the sample may also be volatile under the acidic conditions and possibly partly escape from the sample.

7.3 Oxygen

The concentration of dissolved oxygen in the water-steam circuit is of importance because it, on one hand, supports the formation of the protective layer in pure water and, on the other hand, may promote corrosion in water with even low concentrations of salts.

The assessments of oxygen concentration have to be made together with pH and acid conductivity. High purity of the water allows increased concentrations of oxygen and decreased pH, resulting in better protection of steel /16/.

The improvement of the protection is caused by an oxidation of the surface of the magnetite protective layer to hematite. Hematite has lower solubility and much finer crystalline structure and seals the porous magnetite structure /17/.

Different methods are applicable for the measurement of oxygen; these are described in VGB-S-006-T-00;2012-00.EN (4).

7.4 Hardness

Hardness is a measure for the sum of all alkaline-earth elements, like calcium and magnesium (rarely also barium and strontium) compounds in water samples. Hardness in the water-steam cycle leads to deposition on heated surfaces (hardness scale) and may in consequence lead to uneconomic operation, material over-heating, and to severe corrosion attacks underneath the scale.

The most useful method for determination of hardness is titration with EDTA. The SI-unit for hardness is mmol/l. 1 mmol/l corresponds to 100 mg/l CaCO_3 .

7.5 Phosphate

Phosphate in form of alkali phosphates – mostly tri-sodium phosphate – is used both as alkalisation agent and as scale inhibitor to prevent hardness scale.

The determination of the phosphate concentration is usually by means of spectrophotometer (9).

In contrast to sodium hydroxide (NaOH) phosphate contributes to acid conductivity and thus excludes the use of this parameter as a measure of boiler water purity.

7.6 Silica

Silica concentrations in the feed water of once-through boilers and the boiler water of drum-type boilers must not exceed the values in Table 2 to Table 13 because of the requirement concerning steam purity for turbine operation. The solubility of silica in steam increases with pressure.

Even when the specified values are complied with, silica deposits in the high pressure section of the turbine cannot be excluded under the most unfavourable conditions, especially in the presence of substances such as aluminium, which enhances the solubility of silica.

If there are differences between the silica concentration in the feed water and in the steam or if the silica concentration in the boiler water is higher than the product of concentration coefficient and silica concentration of the feed water, then the raw

water probably contains colloidal silica, which has not been retained in the make-up water treatment plant and has hydrolysed to form soluble silica in the boiler.

Applicable analytical methods for silica are described in the VGB handbook “Chemistry in power plants – Analytical methods” (9).

7.7 Iron and copper

Iron and copper may appear in the water-steam circuit in dissolved (mostly copper) or suspended as fine particles (mostly iron). Because of this the total iron or copper concentration must be determined analytically. The VGB-Standard on sampling VGB-S-006-T-00;2012-00.EN (4) is referred to in order to get representative samples from a 2-phase flow of particles in a fluid. Analytical methods for total as well as dissolved and suspended fractions are found in the VGB handbook “Chemistry in power plants – Analytical methods” (9). Because of the difficulties related to sampling and analysis both parameters are mostly suited for trend analysis of diagnostic parameters.

Iron and copper concentrations in feed water and steam are an indicator of the efficiency of conditioning. They supply information on the metal dissolution processes in the system and the metal take-up by the water as well as possible deposits in the boiler and turbine. Changes in iron and copper concentrations due to load fluctuations cannot be influenced by chemical measures.

The VGB guideline M412 (5) and Chapter 5.1.2 describe methods for removal of iron and copper corrosion products from the water-steam circuit.

7.8 Sodium

Sodium is used to condition the boiler water of drum-type boilers in the form of sodium hydroxide and tri-sodium phosphate, but it also occurs as a contaminant in the water/steam cycle through slippage from ion exchangers or heat exchanger leakage. Ingress of sodium to the steam may lead to deposits and caustic induced stress corrosion cracking in superheaters and turbine systems. Because of this the measurement of sodium in the steam is important (see Chapter 4.4.1.4).

The on-line measurement of the sodium level is usually performed with an ion-sensitive electrode, see VGB-S-006-T-00;2012-00.EN (4) and the VGB Handbook B 401 “Chemie im Kraftwerk” – “Analysenverfahren” (9).

7.9 Carbon dioxide

Carbon dioxide is a common contaminant in the steam water cycle that leads to an increase of acid conductivity.

Depending on the quantity of air entering the steam water cycle, as well as on cycle capabilities for degassing (condenser, deaerator) and demineralisation (condensate polishers), some residues will remain circulating through the systems.

Another source is thermal decomposition of organic matter (also organic conditioning agents) that has entered (been dosed to) the cycle. If an increase in acid conductivity can be attributed to carbon dioxide, relaxed action levels and schedules on acid conductivity can be defined, see Figure 30. In each case operation outside the specifications of this VGB-Standard should be assessed carefully according to operator and turbine supplier's experience as well as configuration and design of the components.

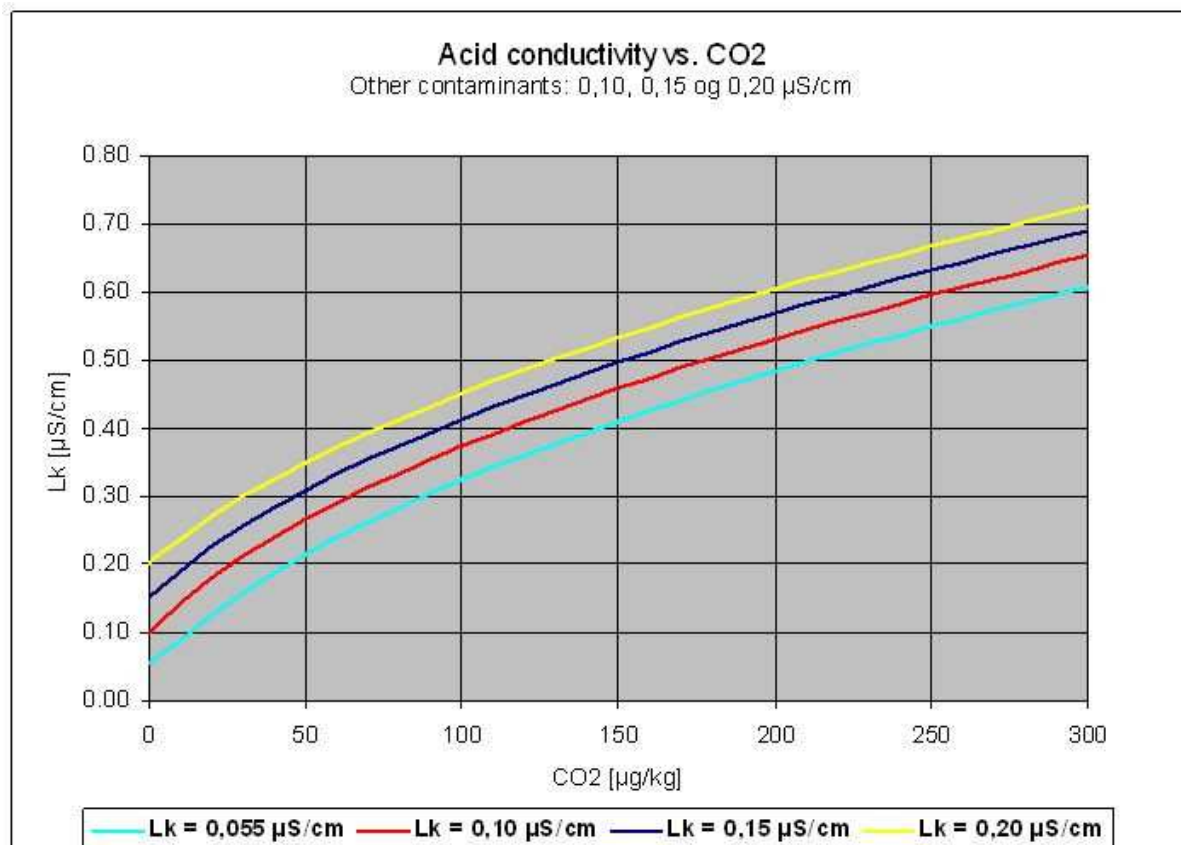


Figure 30: Influence of carbon dioxide (CO₂) and other contaminants on acid conductivity (Lk).

During outages the water/steam system may be contaminated with carbon dioxide because the vacuum is broken. An increased acid conductivity is acceptable during start up, if it is caused by carbon dioxide. This is foreseen in the specific action levels used during start up, see Chapter 6.

The determination of carbon dioxide is feasible using a degassed acid conductivity measurement, see Chapter 7.2.

7.10 Organic substances

Organic substances, which are carried with the feed water into the steam generator, can, after being concentrated in the boiler water of drum-type boilers, increase its foaming tendency, cause carry-over of boiler water droplets and thus indirectly affect the steam quality. Decomposition products of organic substances formed under

boiler conditions can directly affect the pH of boiler water and, if volatile, the steam quality (6).

Organic substances in the water are best detected by determining the dissolved organic carbon (DOC) content, see the VGB handbook "Chemistry in power plants – Analytical methods" (9) and VGB-S-006-T-00;2012-00.EN (4).

To evaluate the possible effects and means for removal of organics, the knowledge of the type of organics is very important /19/. It is recommended to strive for less than 0.1 mg/l. Even this value may be too high in special cases, depending on the nature of the organic matter and the make-up water demand. High make-up rates require a minimization of the DOC content, see VGB-M 407 (3).

Where organic substances can enter the steam water cycle from other sources, e. g. return of non-purified condensate in industrial power plants, continuous monitoring of the DOC content in the condensate or feed water is recommended (see VGB-M 412 (5)).

When operating with demineralised feed water, the ingress of organic contaminants usually can be detected due to a decrease in the pH of the steam compared to the feed water or an increase in the acid conductivity between feed water and steam as a result of the decomposition of organic substances. This may also be indicated by corresponding measurements of degassed conductivity.

Chapter 5.3.1.7 is referred with respect to the problems related to organic conditioning agents.

8 Analytical control of operation

An analytical control of the operation is absolutely necessary in order to identify deviations from normal operation soon.

8.1 Sampling of water and steam

It cannot be emphasised enough that:

"Poor sampling gives poor results"

Too often "chemists" carry out extremely sensitive and complex analyses, which undoubtedly are accurate, but if the sample does not truly represent the process stream (the bulk material) the results are meaningless and often misleading.

A number of factors must be taken into account in design and maintenance of a suitable sampling system for water/steam cycles, e. g.

- Proper materials of sample lines, valves, and coolers.
- Secure handling of the system
- Suitable length of and flow in sampling lines
- Considering isokinetic sampling whenever demanded (2-phase flow conditions)

- Proper Maintenance

Further recommendations and considerations of sampling systems are found in VGB-S-006-T-00;2012-00.EN (4).

8.2 Sampling points and parameters

The key sample points and key parameters are given in the tables of Chapter 6 for the different boiler types and chemistries, and the parameters are described more closely in Chapter 7. However, further sampling points and measurements are recommended in order to be able to track the chemistry of the water-steam cycle closely.

Table 14 shows the recommended sample point for the different types of power plants in accordance with VGB-S-006-T-00;2012-00.EN (4). Table 15 and Table 16 show recommendations for sampling points and parameters for boilers operated with demineralised and non-demineralised feed water, respectively. Here, recommended and optional monitors are distinguished, and the routine analyses (also performed during operation in the N-range) and the extended analyses performed for diagnostic purposes are surveyed.

These examples may be used as a starting point when assessing the chemical surveillance of a specific plant. Not all plants may have the sampling points indicated, e. g. district heating condensate or polished condensate for drum boilers.

Table 14: Recommended sampling points according to VGB-S-006-T-00;2012-00.EN (4) for different power plant types.

Position	Sampling point	Unit with once-through boiler	3-stage HRSG, HP once-through type	3-stage HRSG, all drum type	Unit with drum boiler, demineralised water	Unit with drum boiler, non-demineralised water
S-1.0	Make-up water	x	x	x	x	
S-1.1	Treated make-up water					x
S-2.0	Main condensate (downstream CPP)	x	x	x	x	
S-2.1	Raw condensate (upstream CPP)	x	x		x	
S-2.2	Condensate from LP-preheaters	x			x	
S-2.3	Main condensate upstream feed water tank	x			x	
S-2.4	Raw process return condensate	x	x	x	x	x
S-2.5	Rinsed process return condensate	x	x	x	x	x
S-2.6	District heater condensate	x	x	x	x	x
S-2.7	Reserve condensate tank	x	x	x	x	x
S-3.0	(HP) Feed water upstream ECO	x	x	x	x	
S-3.1	Feed water downstream de-aeration (side stream)			x		
S-3.2	IP feed water downstream feed water pumps		x	x		
S-3.3	HP feed water downstream feed water pumps		x	x		
S-3.4	Condensate from HP-preheaters	x			x	
S-3.5	Feed water downstream feed water tank					x
S-4.0	(HP) Boiler water			x	x	x
S-4.1	LP boiler water		x	x		
S-4.2	IP boiler water		x	x		
S-4.3	Boiler water downstream of flask	x	x			

Table continues on next page

Table 14: (continued) Recommended sampling points according to VGB-S-006-T-00;2012-00.EN (4) for different power plant types.

Position	Sampling point	Unit with once-through boiler	3-stage HRSG, HP once-through type	3-stage HRSG, all drum type	Unit with drum boiler, demineralised water	Unit with drum boiler, non-demineralised water
S-5.0	(HP) Live steam	x	x	x	x	x
S-5.1	LP saturated steam		x	x		
S-5.2	LP live steam		x	x		
S-5.3	IP saturated steam		x	x		
S-5.4	IP live steam		x	x		
S-5.5	Reheated steam	x	x	x	x	
S-5.6	(HP) saturated steam			x	x	x

Table 15: Recommended requirements for water steam cycle supervision for boilers with demineralised feed water.

Position	Sampling point	On-line monitors							Laboratory analyses					
		pH ⁽¹⁾	Specific conductivity ⁽²⁾	Acidic conductivity	Degassed conductivity ⁽³⁾	Oxygen	Silica ⁽⁵⁾	Sodium ⁽⁵⁾	Iron	Silica	Sodium	Copper ⁽⁶⁾	Phosphate	Organics, trace anions & cations
S-1.0	Make-up water		MR		CA		MR		EA	RA				CA
S-2.0	Main condensate (downstream CPP)		MR	MO	CA	CA		MR	EA	EA	EA	RA		CA
S-2.1	Raw condensate (upstream CPP)		MO	MR				MO	RA	EA	EA	RA		
S-2.2	Condensate from LP-preheaters			CA				CA	EA					
S-2.6	District heater condensate			MR				MR ⁽⁷⁾	EA	EA	EA			
S-3.0	(HP) Feed water upstream ECO	MR, ALS	MR ⁽⁸⁾ , ALS	MR, ALS	CA	MR, ALS		MO, ALS	RA, ALS	RA, ALS	RA/EA, ALS	RA, ALS		CA
S-3.x	Feed water other sampling points			CA					EA					
S-3.4	Condensate from HP-preheaters			MO					EA					
S-3.5	Feed water downstream of feed water tank		MO	MO		CA			EA					
S-4.0	(HP) Boiler water	MR ⁽⁴⁾ , ALS	MR, ALS	MR, ALS				CA	EA	RA, ALS		CA	RA, ALS	EA
S-4.3	Boilerwater downstream of flask			MR					EA		CA			CA
S-4.x	IP/LP boiler water	MO ⁽⁴⁾	MR	MR				CA	EA	RA		CA	RA, ALS	EA
Table continues on next page														

Table15: (continued) Recommended requirements for water steam cycle supervision for boilers with demineralised feed water.

Position	Sampling point	On-line monitors							Laboratory analyses					
		pH ⁽¹⁾	Specific conductivity ⁽²⁾	Acidic conductivity	Degassed conductivity ⁽³⁾	Oxygen	Silica ⁽⁵⁾	Sodium ⁽⁵⁾	Iron	Silica	Sodium	Copper ⁽⁶⁾	Phosphate	Organics, trace anions & cations
S-5.0	(HP) Live steam			MR, ALS	MO, ALS		MO, ALS	MR, ALS	RA, ALS	RA, ALS	RA/E A, ALS	RA, ALS		CA
S-5.x	LP/IP saturated steam with AVT			CA				CA	EA					CA
S-5.x	LP/IP saturated steam with caustic/phosphate			MO ⁽⁹⁾				MR, ALS	EA		RA/E A ALS			CA
S-5.x	LP/IP live steam			MR				CA	EA	RA	EA	CA		CA
S-5.5	Reheated steam			MR				CA	EA	RA	EA	CA		CA

Explanation (Table 15)

The colour marks a key parameter	MR: On-line monitor recommended MO: On-line monitor optional ALS: Action levels specified in chapter 6	The colour marks a parameter in routine analysis	RA: Routine analysis program EA: Extended analysis program CA: Campaign analysis program
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(1) Instead of measuring pH, it may be calculated from the difference between direct and acid conductivity

(2) Specific conductivity may be used to control ammonia dosing and pH, thus a key parameter in this mode of operation

(3) Degassed conductivity is optional depending on plant and mode of operation. When present, this parameter is a key parameter in superheated steam for turbine operation

(4) pH calculation according (1) does not work if phosphate is added into the boiler water

(5) common analyzer for either sodium or silica operating in multiplex mode is possible

(6) only relevant with copper alloy in the condensate / feed water system

(7) Sodium monitoring is recommended when the district heating system is operated with demineralised water conditioned with sodium hydroxide

(8) Specific conductivity may be used to control dosing of ammonia sodium hydroxide /phosphate and thus to control pH, i. e. it is a key parameter in this mode of operation, only for drum boiler

(9) Only relevant when phosphate is dosed to the boiler water

Table16: Recommended requirements for water steam cycle supervision for drum boilers with non-demineralised feed water.

Position	Sampling point	On-line monitors					Laboratory analyses							
		pH	Specific conductivity	Oxygen	Silica	Sodium	Total hardness	Alkalinity	Iron	Silica	Copper ⁽¹⁾	Phosphate ⁽²⁾	Oil, grease & organics	Additional Analyses depending on steam use
S-1.1	Treated make up water		MR				RA	RA		RA				RA/EA
S-2.0	Main condensate		CA	CA					RA		RA		RA/EA	
S-2.4	Raw return process condensate			CA					EA		EA		RA/EA	RA/EA
S-2.5	Rinsed return process condensate		MO			CA	RA	RA	EA		EA		RA/EA	RA/EA
S-3.0	Feed water	MO ALS	CA	MR, ALS	CA		RA, ALS		RA, ALS	RA	RA, ALS		RA/EA	
S-4.0	Boiler water	MR, ALS	MR, ALS					RA, ALS		RA, ALS		RA, ALS		
S-5.0	Live steam		MR			MO, ALS								RA/EA
S-5.6	Saturated steam		MR			MO, ALS								RA/EA

Explanation (Table 16)

		The colour marks a key parameter	MR: On-line monitor recommended MO: On-line monitor optional ALS: Action levels specified in chapter 6	The colour marks a parameter in routine analysis	RA: Routine analysis program EA: Extended analysis program CA: Campaign analysis program
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(1) Only relevant with copper alloy in the condensate/feed water system

(2) Only relevant when phosphate is dosed to the boiler water

In the tables, the terms “routine analysis” and “extended analysis” describe the minimal set of laboratory analyses necessary to check the state of the water/steam circuit and the broader set used to get more detailed insight into the conditions, e. g. to locate the cause of a chemical excursion. The idea is to minimize the effort and resources spent on laboratory analyses under steady and stable conditions and to maximize the effort when excursions and/or non-usual operating conditions occur. On the other hand, it is necessary to build up reference data for the operation under normal conditions, thus the extended program should run occasionally, even when no excursion has occurred. Figure 31 illustrates this balance in a flow diagram. Laboratory analysis may either be triggered as a scheduled task (routine analyses and extended analyses when no excursion has occurred for a longer period) or by excursions of the chemical parameters, either discovered by a monitor or in a routine analysis.

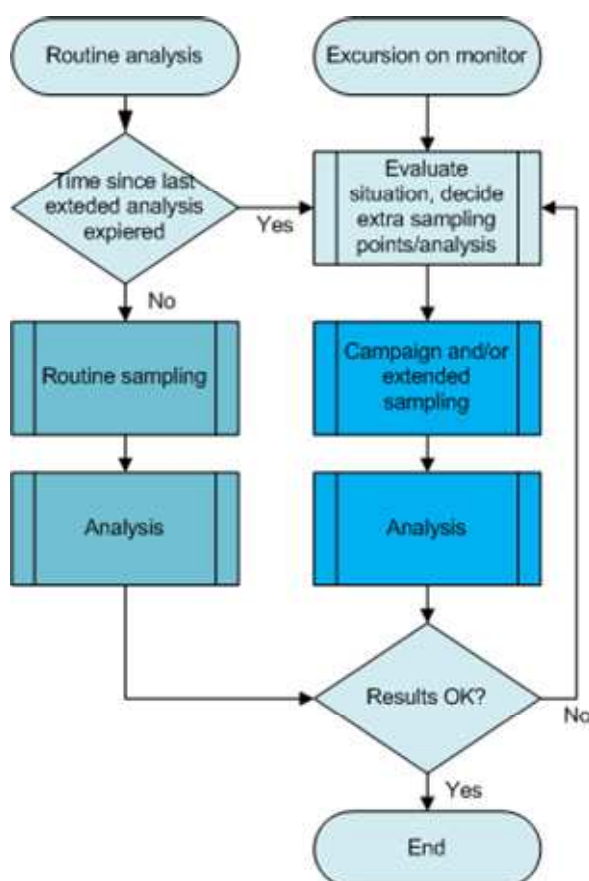


Figure 31: Flow diagram for laboratory analyses.

As a starting point for plants in steady operation, the frequency of the routine analysis could be weekly and the scheduled frequency of the extended analysis monthly. For new plants and subsequent to a significant change in operation mode for older plants it is recommended to run the extended program weekly for at least half a year.

The timing of the follow-up measurements when an excursion has occurred depends on which action level has been crossed as shown in Table 17.

Table 17: Schedule for follow-up measurements on excursions.

Triggers for action	Action level crossing	Action
Key parameters, iron, silica, or sodium	N	Plan extended analysis within 48 hrs
	AL 1	Target sampling plan according to disturbance, take action within 24 hrs
	AL 2	Target sampling plan according to disturbance, take immediate action

8.3 Quality control of measurements

The purpose of the laboratory analyses is to document the parameters not measured on-line; together with the on-line measurements they gradually build up a set of reference data describing the state of chemistry under normal operating conditions. Furthermore, the laboratory analyses serve as control of on-line monitors for e. g. silica and sodium.

The analysis methods used must be **fit for purpose** according to the tables in Chapter 6 and beside that verified and well proven. This means that the complete measuring chain from sampling to the final results has to be reviewed carefully. Since the levels measured are often very low, special care has to be taken to avoid contamination from the surroundings, sample containers and chemicals, including the demineralised water of the laboratory. Sufficient quality control to ensure reliable results should be carried out along with the analyses of the samples, and the uncertainty of the methods including the sampling step should be assessed in order to evaluate the results properly.

For detailed analytical methods refer to literature for instance to the VGB Handbook B 401 "Chemie im Kraftwerk" – "Analyseverfahren" (9). Quality control of the on-line monitors may be arranged according to VGB-S-006-T-00;2012-00.EN (4).

8.4 Specification of the optimal operation – definition of the N-range

As mentioned in chapter 6 (Table 2 to Table 13) the values for optimal operation, the N-range, should be set for each plant specifically. New and tight water/steam cycles well equipped with means to control the purity (high level instrumentation, condensate polishers, diversion of preheater condensates etc.) usually will operate well below AL1, whereas older units or units with simpler equipment may operate closer to AL1. Thus, the N-range – and thereby the optimal operation achievable – should be evaluated for each plant specifically.

The main ideas behind the N-range are that this set of limits defines the optimal operation for the given water-steam circuit, and that comparing the daily measurements with the N-range limits is an efficient means to keep the plant in optimal operation. When something in the process unexpectedly is altered, the use of the N-range limits will give an early warning. This is because the shift in process

values is typically discovered long before the action limit AL1 is crossed and the chemical excursion becomes serious.

As an example, Figure 32 shows the content of iron in feed water over a period of time. After the first 40 analyses, an erosion corrosion process¹ on the steam side of a heat exchanger slowly starts and gradually accelerates. Due to the increased iron content of the heat exchanger condensate, the level of iron in the feed water gradually increases and eventually leads to a severe contamination of the feed water as stipulated in the figure. However, in the initial phase the shift in iron level is not easily discernible due to random variation of the measured values. Even in the first undisturbed period, the random variation leads to a few high values above the AL1 and even above the AL2 limits, but the general level is well below AL1 (10 µg/kg) and the N-limit is estimated to 6 µg/kg. In the following period the increased level most likely will be noticed after 70 analyses, because the N-limit is repeatedly crossed. If only the AL1 limit is used, the disturbance would most likely be noticed after 85-90 analyses when this threshold has been crossed several times. With the typical analysis frequency this difference in recognition of the problem corresponds to several weeks in real time, and by use of the N-range limits proper actions would have been taken in due time, such that prolonged operation above AL1 would have been avoided.

The assessment of the N-range limits and the following comparison of current chemistry data with these will naturally focus the attention of shift and laboratory personnel on keeping the water/steam circuit operating optimally. In the long run focus on the optimal operation compared to operation according to AL1 levels will make a considerable difference with respect to lifetime of the components of the water steam circuit.

¹ This could for instance be a consequence of a reduction of the ammonia content of the feed water to extend the operational cycle of an ion exchange based condensate polishing plant.

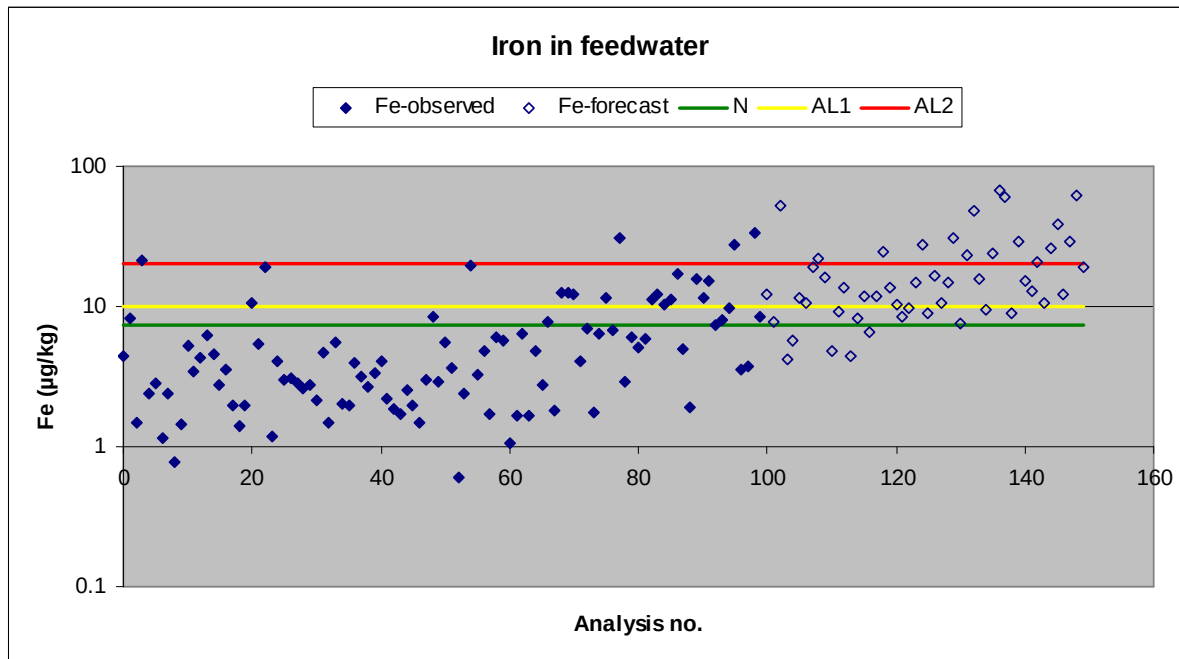


Figure 32: Iron content of feed water as analysed in a series of measurements covering a long period of time.

The procedure for setting the action level N limits should be characterized by these properties:

- It must be relatively simple and straightforward so that it may be repeated at regular intervals as a means to evaluate the long term water-steam chemistry.
- The limits should trigger extended analysis in 10 % of all routine analyses to secure the accumulation of reference data of the specific unit. From a statistical point of view, the limit must then be set such that 90 % of all results fall below the limit during a period of normal operation.

The basis of the evaluation is a data set corresponding to the extended analysis program mentioned in chapter 8.2 with at least 20 data sets covering a period of operation without major disturbances of the water/steam chemistry (for example weekly analyses over half a year). From these data the N-range limits may be evaluated by the statistical procedure described in the following example and further outlined in Appendix 1.

The data set under evaluation is initially sorted in increasing order, and a rank assigned to each result. The rank is simply the number of the result in the sorted order. Next the Percentile is calculated as:

$$\text{Percentile} = \frac{\text{Rank} \cdot 100\%}{N}$$

where N is the total number of results in the data set

Plotting the percentile versus the concentration (value of the result) gives the cumulative distribution curve of the data set. To obtain a curve for data of the water-steam circuit (pH is the only exception) that is easy to read, it is appropriate to use a logarithmic scale on the x-axis. The relevant percentiles of the data set, for example the 90 % percentile, may then be read directly from the cumulative curve (or from the table behind in a spreadsheet). This is illustrated for the first 40 results of the example above in Figure 33 and explains how the cited value for the N-limit has been found.

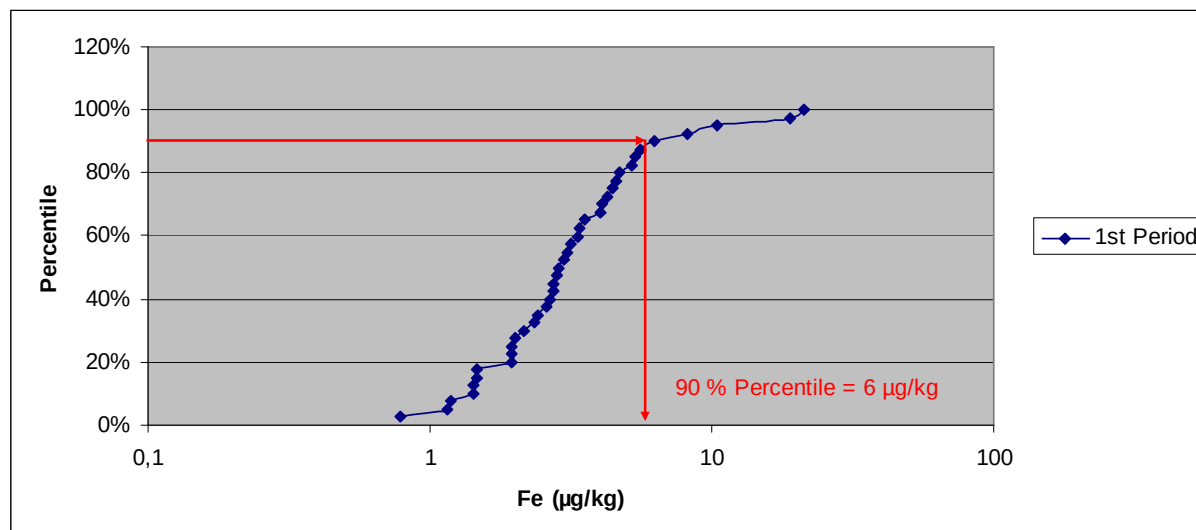


Figure 33: Distribution of iron measurements in Period 1 that covers the first 40 results of the previous figure.

In more general terms the x % percentile of a data set is the value that x % of all results is less than, i. e.

10 % percentile	10 % of all results fall below this value
20 % percentile	20 % of all results fall below this value
80 % percentile	80 % of all results fall below this value
90 % percentile	90 % of all results fall below this value

The percentiles may be calculated directly from a data set by most spreadsheet and statistical software packages commonly used. Thus, it is not even necessary to do the data processing described in relation to Figure 32, but it is advisable to do so for the key parameters to check that the cumulative distribution appears smooth and is of sigmoidal shape as in the example. N-limits are then chosen as round figures close to the 90 % percentiles (80 % percentile < N-limit ≤ 90 % percentile) for upward limited parameters. Correspondingly, for downward limited parameters, the N-limits are chosen close to the 10 % percentile (10 % percentile ≤ N-limit < 20 % percentile). For bidirectional limited parameters both sets of percentiles are used.

Looking at the distribution curves to compare different data sets (same sampling point and parameter over two periods, or same parameter in two different sampling points) is a means to detect subtle changes that are not easily seen otherwise. As an

example consider distribution curves of the two periods covering the first 40 (period 1) and the next 40 (period 2) results displayed in Figure 32. Not knowing the subsequent development, it would be difficult to tell from the trend curve whether there is a real difference in level between the two periods. Figure 34 displays the distribution curves for the two periods as well as the 90 % percentiles. From this presentation of the data it is evident that there has been a change in iron level between the two periods.

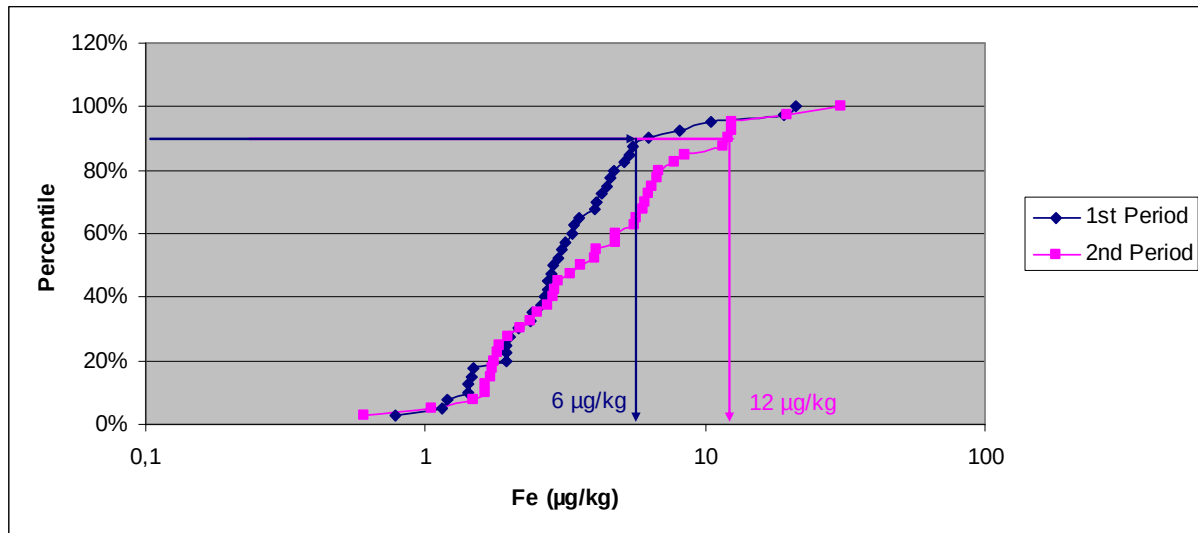


Figure 34: Cumulative distributions of two periods of the example data. The 90 % percentiles of the two periods are either 6 or 12 µg/kg.

Calculating the percentiles listed above together with the minimum and maximum values for a series of sampling points gives an overview of the complete water-steam circuit for the period examined. These values may conveniently be calculated and displayed in a standard spreadsheet or statistical software program as summary of the many results obtained over a period of operation. Figure 35 shows a real-life example for iron in the water-steam circuit covering a full year of operation with weekly analyses. In this so-called “Box-and-Whiskers” diagram the boxes show the typical ranges of the results, here the 80 % between the 10 % and 90 % percentile, and the lines show the minimum 10 % and maximum 10 %, respectively.

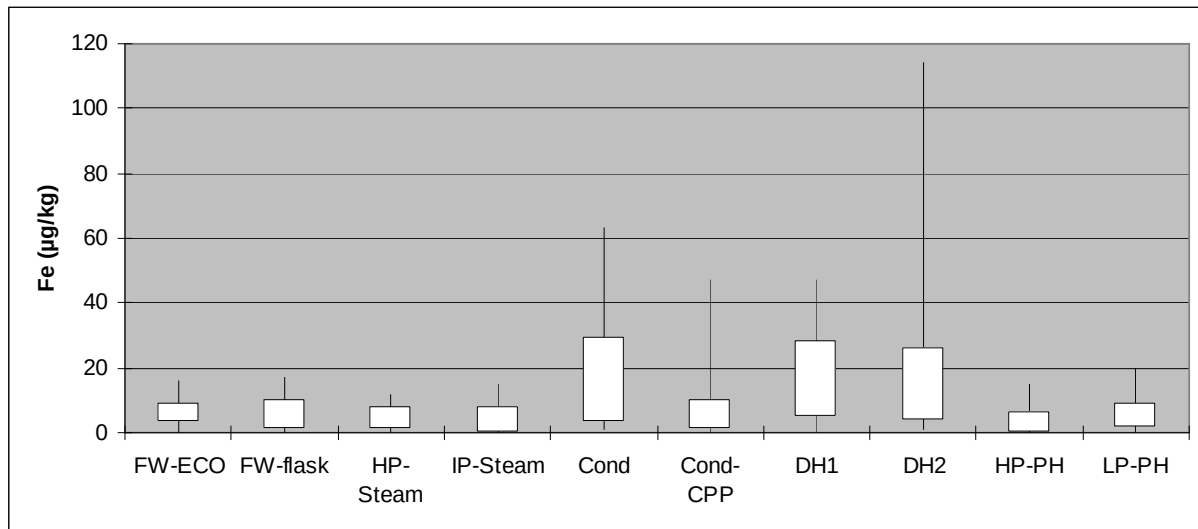


Figure 35: Overview of levels of iron in the water-/steam cycle of a once-through unit run on OT. The relative high level in the main condensate is removed by the condensate polishing plant ("Cond-CPP" is the label for polished condensate). This makes the condensate train downstream of the CPP, the major sources of iron in the feed water. The boxes mark the 10 % and 90 % percentiles, and the whiskers mark minimum and maximum values.

8.5 Monitoring and reporting

Parameters change on power plants and interrelate with each other, often in predictable ways but occasionally with unexpected side effects. It is strongly recommended that an interactive data base is operated with a facility to plot a minimum of any four parameters simultaneously over any time period to enable lateral thinking of chemical and temporal effects. This is often the case for plant based systems, through DCS technology, but it is strongly recommended that the same functionality and sophistication is applied to laboratory based measurements.

The integration of the action levels with the DCS technology and further reporting systems of the plant has to be considered. One way of doing this is outlined in table 8.8; however, the specific implementation is plant specific depending on the technology available and the organisation of the chemistry related tasks.

Table 18: Example of integration of action levels with DCS and reporting systems.

System	Action levels	Remark
DCS	AL1, AL2, AL3	Action levels implemented as alarms. Only those levels that demand action as soon as possible by the shift personnel are implemented.
Plant historian (Database with historic plant values and reporting facilities)	N, AL1, AL2, AL3	Automatic generation of reports covering the last 1 to 2 days of operation. Summary of the data from the on-line monitors is reported and compared to the action limits, e. g.: – 10 %, 20 %, 50 %, 80 %, and 90 % percentiles – Box- and whiskers diagrams – Trend curves for key parameters These reports are assessed by trained shift or laboratory personnel on a daily basis
Laboratory database (Historic laboratory measurements and simultaneous readings from on-line monitors)	N, AL1, AL2, AL3	(Automatic) generation of reports covering the last 1 to 2 months of operation. Data are summarized and compared to the action levels. These reports are assessed and commented by personnel with a thorough understanding of water/steam chemistry.

9 Annex

9.1 Internal cleaning and preservation

The internal cleaning and the preservation during standstills have a major impact on a failure-free operation.

9.1.1 Internal cleaning

The topic of internal cleaning plays an important role in reaching the aim of this VGB-Standard, enabling boiler operation that is as trouble-free as possible as well as good steam quality for the operation of turbines. If the water-steam system isn't cleaned properly and professionally problems for the operation of the plant will recur leading to poor availability and possible damage to the system.

In the power plant industry there are numerous company-specific or proprietary guidelines and specifications for internal cleaning and steam blowing. Independent guidance can be found in VGB guideline, VGB-R 513 "Internal Cleaning of Water-Tube Steam Generating Plants and Associated Pipe-work" (1) which is generally agreed upon by the power plant industry. This VGB-Standard is intended to give recommendations for:

- Flushing,
- alkaline boil-out,
- preoperational acid cleaning of new plants,
- chemical cleaning of plants under operation,
- steam blowing of water-tube generating plants and associated pipe-work upstream to the turbine, where required.

When selecting the type and performance of the cleaning procedures, agreement shall be reached between the (steam boiler/pipe-work/turbine) manufacturers and the plant user and be stipulated in writing. This agreement should be reached as early as possible in the design stage.

9.1.2 Preservation

Preservation means any method to avoid corrosion on the waterside of boilers, parts of it or auxiliary components made of low-alloyed steel during shut down and stand-by. It also includes storage and transportation, erection and commissioning of plant. This can be realized by excluding either oxygen or water respectively.

A sufficient present protective layer of iron oxides on the waterside of boilers (in operation for at least 1 month before shut down) can protect low-alloyed steel in presence of humidity or moisture and air for restricted time only. If non-demineralised

BFW/BW is used the time without preservation is restricted to 1 week, in case of the use of demineralised BFW/BW the shut down time without preservation should not exceed 2 weeks. Exceeding times require preservation methods by either

- wet preservation (in absence of air) e. g. by replacing of air by nitrogen or completely 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.

Details may be obtained from special papers (for example VGB-R 116 H “Preservation of Power Plant Systems” (8)).

High-alloyed or stainless steel may require particular preservation methods to avoid chloride induced pitting or SCC in special cases during transport, storage and stand by.

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

9.2 Operation above Action level 3

If the chemistry in an operating unit comes out of control and a key parameter exceeds the Action level 3, continued operation will result in damage. An assessment (based on exponential increase in life time consumption with action level) of a continued operation of a unit with once-through boiler is shown in Figure 36. It illustrates the lifetime consumption for every hour operation with acid conductivity of feed water in between 1 and 500 $\mu\text{S}/\text{cm}$. Operation time to expect collapse is also indicated. This is an example only and uncertainty of the evaluation is quite large. However, it illustrates the order of magnitude of damage.

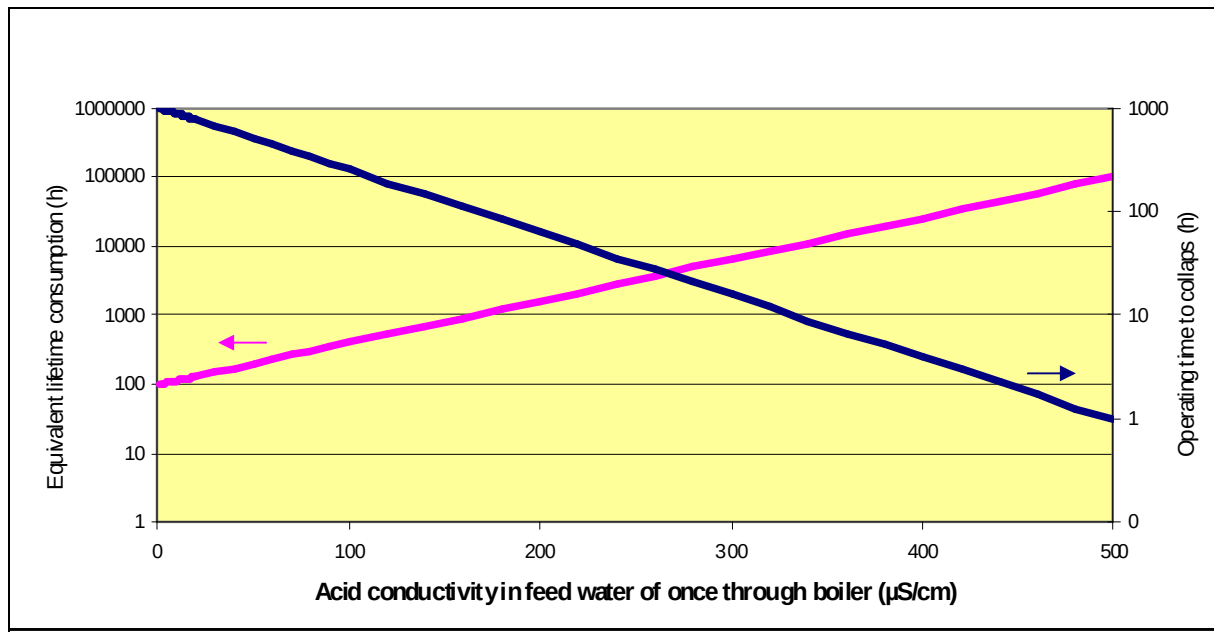


Figure 36: Example of lifetime consumption at operation above Action level 3 limit.

9.3 Warning examples

What may happen when the surveillance is not sufficient ...

On-site inspection and Samples of deposits
 $\Rightarrow \text{pH} = 11!$

Lab. investigation:
 Blade from row 12 broke due to metal fatigue caused by caustic induced stress corrosion cracking.

The images show: 1) On-site inspection of a turbine component with labels #22, #23, and pH=11. 2) A close-up of a broken turbine blade. 3) A micrograph of a metal surface showing fatigue cracks, with a 20 μm scale bar.

Figure 37: Example – on-site inspection.

Stress corrosion cracking induced by carry-over of boiler water to the steam at start-up leads to the damage. The carry-over could not be detected because of lacking surveillance (missing Na-monitor) of the IP-stage of the HRSG.

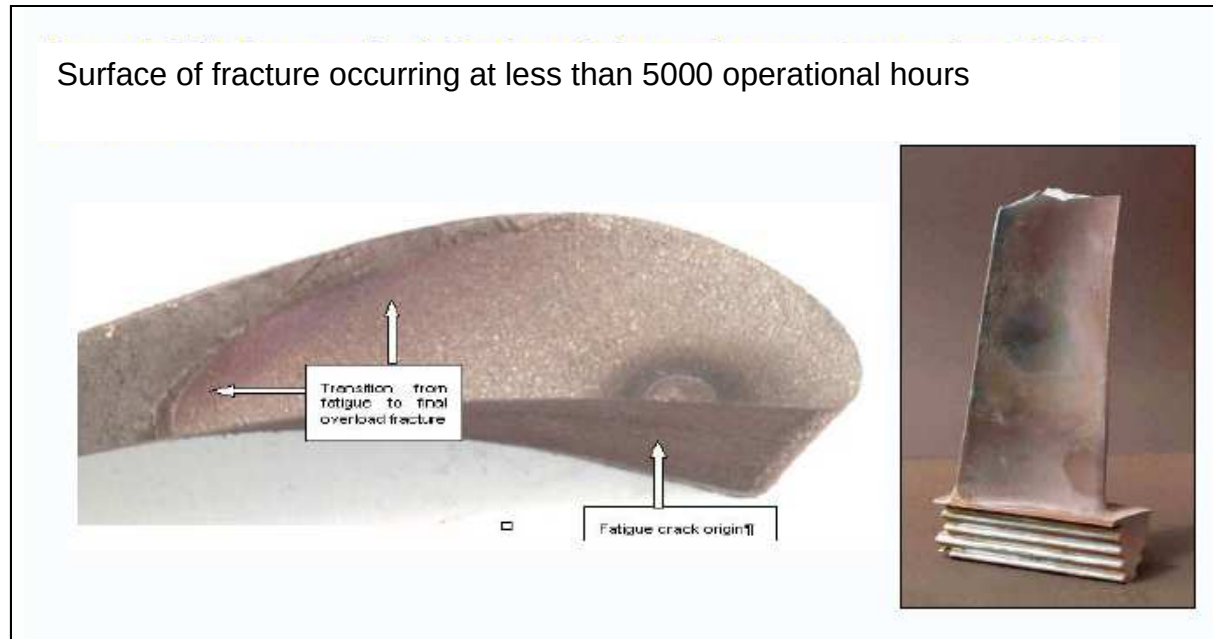


Figure 38: Example – fractured surface along blade L-1.

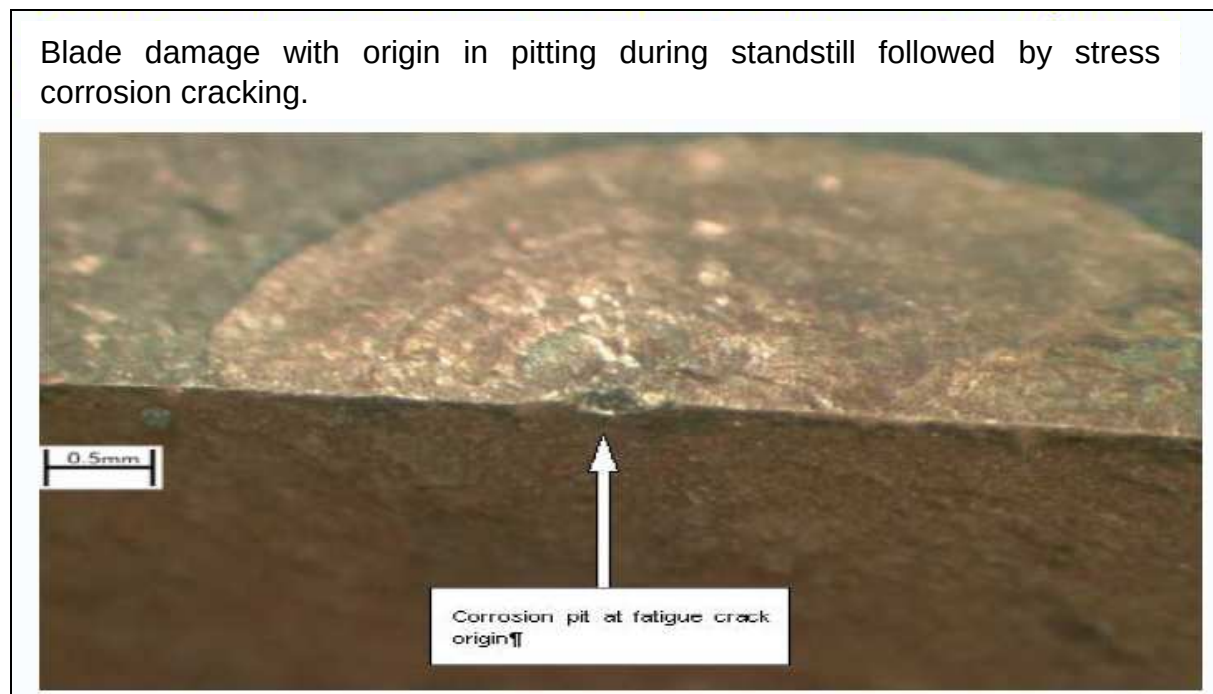


Figure 39: Example – blade damage.

Extended operation of the water-steam cycle with increased conductivity led to salt deposits on the turbine blades. Due to insufficient conservation during standstill,

pitting corrosion took place and gave rise to concentration of salts in the pit (crevice concentration) and finally to a metal fatigue fracture of the blade.



Figure 40: Example – fatigue break.



Figure 41: Example – notch effect.

This incident illustrates the consequences of insufficient surveillance of steam quality in combination with documented longer periods of operation above AL3 and repeated periods of standstill without conservation. This led to pitting corrosion as starting point of cracks and finally to tear off of the blade.



Figure 42: Example – shrinkage of material thickness.

The boiler tube fails as a consequence of the concentration of solid alkalisising agent due to local evaporation. This led to caustic corrosion that reduced the thickness of the material and finally perforated the tube.

9.4 Statistical procedures

In this appendix the statistical procedures and models behind the procedure to estimate the N-range limits (see Chapter 8.4) is described in depth. The purpose is to give a better understanding and a few handy tools for further data processing to those interested. A basic understanding of statistics is assumed.

As mentioned in Chapter 8 the statistically based N-limits serve more purposes:

- To function as warning limits to detect at an early stage changes in the processes of the water-steam circuit. In this respect the N- and AL1-limits function exactly as the alarm and control limits known from the X-charts of laboratory quality control.
- To ensure that even with the reduced analysis program run routinely more complete reference data describing the operation under satisfactory conditions are gathered and maintained.

Because random fluctuation overlay all results obtained both by on-line measurements and by laboratory analyses, it may not be evident when a change in a chemical parameter is caused by a change in the process. However, this is determined by means of the follow-up analyses on crossing the N-limits (or even AL-limits): Getting more results above the warning limits in a short period of time is highly unlikely, if the first one is a result of random variation. Thus, such a pattern most likely indicates a physical cause for the change in level. If the follow-up analysis does not reveal anything unusual, the first result may be seen as just a random incident. In this case, the follow-up analysis is not in vain, because it serves to build up the reference data of the plant in satisfactory operation.

Unlike the quality data of laboratory analyses (X-charts) the results for the chemical parameters of the water-steam circuit do not follow the normal distribution. The approach used here does not assume any specific distribution behind the data, just that they are drawn from a distribution that may be considered stable over time when the plant is operating within its typical conditions. However, experience shows that a logarithmic normal distribution may in many cases model the data rather well.

9.4.1 Determining the N-limit

The procedure is described in Chapter 8.4 but is summarized here:

	<u>Verbal description</u>	<u>Mathematical description</u>
1	Sort the data set in increasing order and assign a rank to each result. The rank is number of the result in the sorted order.	Sorting makes the N results appear in the order: $x_1, x_2, \dots, x_{i+1}, \dots, x_N$ where $x_i \leq x_{i+1}$ The rank is equal to the index i
2	Calculate the Percentile (in %) as the rank divided	For each result, x_i , the Percentile, P_i , is given by:

	<u>Verbal description</u>	<u>Mathematical description</u>
	by the total number of results	$P_i = \frac{100\% \cdot i}{N}, i = 1 \dots N$
3	Plot the Percentile (Y-axis) versus the result (X-axes). Use a logarithmic x-axis for results, except for pH. See Figure 33 for an example of the cumulative distribution plot.	Plot the data set (x_i, P_i) , $i = 1 \dots N$
4	Choose the N-value as a round figure near the 90 % percentile (upward limited parameter) or 10 % percentile (downward limited parameter). For bidirectional limited parameters use both.	Upward limited parameter: $80 \% < N\text{-limit} \leq 90 \%$ Downward limited parameter: $10 \% \leq N\text{-limit} < 20 \%$

For the example used in Chapter 8.4 the following table summarizes the outcome of the procedure.

The original data set has been sorted in increasing order, and the rank assigned according to the new order. The percentile has been calculated in column D, and the 90 % percentile may be read directly from the table.

Table 19: Example of integration of action levels with DCS and reporting systems.

	A	B	C	D
1	Period 1			
2	No. Of Meas.		40	
3	Meas. No.	Result	Rank	Percentile
4	9	0,8	1	2,5%
5	7	1,1	2	5,0%
6	24	1,2	3	7,5%
7	19	1,4	4	10,0%
8	10	1,4	5	12,5%
9	33	1,5	6	15,0%
10	3	1,5	7	17,5%
11	18	1,9	8	20,0%
12	36	1,9	9	22,5%
13	20	2,0	10	25,0%
14	35	2,0	11	27,5%
15	31	2,2	12	30,0%
16	8	2,4	13	32,5%
17	5	2,4	14	35,0%
18	29	2,6	15	37,5%
19	39	2,7	16	40,0%
20	16	2,7	17	42,5%
21	30	2,8	18	45,0%
22	28	2,8	19	47,5%
23	6	2,9	20	50,0%
24	26	3,0	21	52,5%
25	27	3,1	22	55,0%
26	38	3,2	23	57,5%
27	40	3,3	24	60,0%
28	12	3,4	25	62,5%
29	17	3,6	26	65,0%
30	37	4,0	27	67,5%
31	25	4,1	28	70,0%
32	13	4,3	29	72,5%
33	1	4,5	30	75,0%
34	15	4,6	31	77,5%
35	32	4,7	32	80,0%
36	11	5,2	33	82,5%
37	22	5,3	34	85,0%
38	34	5,5	35	87,5%
39	14	6,3	36	90,0%
40	2	8,1	37	92,5%
41	21	10,5	38	95,0%
42	23	19,0	39	97,5%
43	4	21,2	40	100,0%

9.4.2 The “Box-and-Whiskers” plot

This plot is a convenient way to summarize the ranges of results for a given parameter and period across a water-steam circuit. It may be helpful to elucidate the main sources in a mass balance. Figure 35 in Chapter 8.4 gives a realistic example of the plot, and the data set and calculated values are shown in Figure 43.

	FW-ECO	FW-flask	HP-Steam	IP-Steam	Cond	Cond-CPP	DH1	DH2	HP-PH	LP-PH
	Fe	Fe	Fe	Fe	Fe	Fe	Fe	Fe	Fe	Fe
Prøvetid	Res	Res	Res	Res	Res	Res	Res	Res	Res	Res
07-01-08 00:00	7	8	3	2	4	1	7	5	3	3
18-01-08 00:00	4	4	5	5	14	8	30	9	4	4
31-01-08 00:00	3	3	2	8	8	6	6	6	3	3
08-02-08 00:00	13	6	5	3	6	5	28	25	3	9
03-03-08 09:00	16	7	7	4	9	4	47	45	4	8
26-03-08 08:00	9	3	5	15	5	9	14	12	3	4
04-04-08 08:00	4	5	4	6	63	47	15	22	5	5
11-04-08 08:00	9	6	9	8	8	10	17	16	8	9
16-04-08 09:00	6	7	6	9	32	13	19	21	4	
06-05-08 09:00	4	3	7	5	11	7	8	7	3	3
15-05-08 09:00	3	4	5	5	10	5	5	4	3	4
15-05-08 09:00	3	4	5	5	10	5	5	4	3	4
23-05-08 09:00	4	11	4	4	8	11	5	8	4	3
11-06-08 08:30	0	2	2	0	1	1	0	1	3	0
17-08-08 08:30	6	5	6	2	35	3	25	114	15	9
13-08-08 00:00	8	4	1	0	3	2	7	7	0	3
13-08-08 00:00	8	4	1	0	3	2	7	7	0	3
22-08-08 08:00	5	17	0	1	6	2	9	7	0	20
03-09-08 09:00	6	5	4	6	10	1	11	9	3	1
12-09-08 08:00	6	1	2	2	7	4	9	2	4	3
12-09-08 08:00	6	1	2	2	7	4	9	2	4	3
19-09-08 08:00	8	10	10	8	6	3	8	24	5	4
10-10-08 08:30	1	0	12	0	27	2	19	22	12	5
23-10-08 08:00	4	1	2	0	2	0	3	6	1	1
05-11-08 08:00	12	8	2	2	12	0	19	24	0	5
13-11-08 08:00	9	7	2	2	17	7	11	17	4	2
27-11-08 09:00	7	0	0	0	18	2	33	38,3	1	3
15-12-08 09:15	4	2	5	3	6	2	3	7	4	2
05-01-09 08:30	5	12	8	2	29	7	19	18	6	9
15-01-09 08:15	7	8	3	2	4	1	7	5	3	3
Minimum	0	0	0	0	1	0	0	1	0	0
Percentile										
10%	3	1	1	0	3	1	4,8	3,8	0	1,8
20%	4	2	2	0,8	4,8	1,8	5,8	5	2,6	3
80%	8,2	8	6,2	6	17,2	7,2	19	22,4	4,2	6,2
90%	9,3	10,1	8,1	8	29,3	10,1	28,2	26,33	6,2	9
Maximum	16	17	12	15	63	47	47	114	15	20

Figure 43: Example of iron measurement for a once-through unit run on OT. The statistics displayed in the “Box-and-Whiskers” diagram are calculated below the data table.

9.4.3 Modelling of observed data

Experience shows that the results from the water-steam circuit may often be modelled rather well by the logarithmic normal distribution. This is convenient because the distribution may then be described by only two parameters, $\bar{x}_{\log}$ (mean value of log-transformed results) and $s_{\log}$ (standard deviation of log-transformed results). All relevant percentiles may then be calculated directly by functional

relationships based on these two parameters. The parameters of the model are estimated and used in following way:

<u>Verbal description</u>	<u>Mathematical description</u>
1 Calculate mean and standard deviation of the natural logarithm ($\ln(x)$) of the results Substitute results with value 0 (zero) with the detection limit of the analysis method, since $\ln(0)$ is not defined.	Calculate for $i = 1 \dots N$ and $x_i > 0$: $\bar{x}_{\log} = \frac{\sum_i \ln(x_i)}{N}$ $s_{\log} = \sqrt{\frac{\sum_i (\ln(x_i) - \bar{x}_{\log})^2}{N - 1}}$
2 Calculate the value corresponding to a given percentile by means of the inverse log-normal distribution function. This function is available in spreadsheets and statistical software programs in common use.	The value, x, corresponding to a given percentile, p, is calculated as: $x = N_{\log}^{-1}(p, \bar{x}_{\log}, s_{\log})$
3 Calculate and plot the smooth curve of the estimated distribution together with the observed distribution curve.	For $i = 1 \dots N$ calculate the values z_i: $z_i = N_{\log}^{-1}(P_i, \bar{x}_{\log}, s_{\log})$ where P_i is the percentile corresponding to each observed result, x_i (see 9.1 above) Plot the two data sets together: (x_i, P_i), $i = 1 \dots N$, - observed distribution (z_i, P_i), $i = 1 \dots N$, - model distribution
Explanation of the functions: The frequency function of the log-normal distribution is: The cumulative distribution (the probability to get an outcome $< x$) is then The inverse log-normal distribution function returns the x-value corresponding to a given probability (percentile):	$F_{\log}(x, \mu, \sigma) = \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{(\ln(x) - \mu)^2}{2\sigma^2}\right)$ $N_{\log}(x, \mu, \sigma) = \int_{-\infty}^x F_{\log}(t, \mu, \sigma) dt$ $N_{\log}^{-1}(p, \mu, \sigma)$ is the value of x for which $p = N_{\log}(x, \mu, \sigma) = \int_{-\infty}^x F_{\log}(t, \mu, \sigma) dt$

As an example of this data processing Figure 44 shows the distribution curves for iron in feed water ahead of ECO (the first data set of Figure 43).

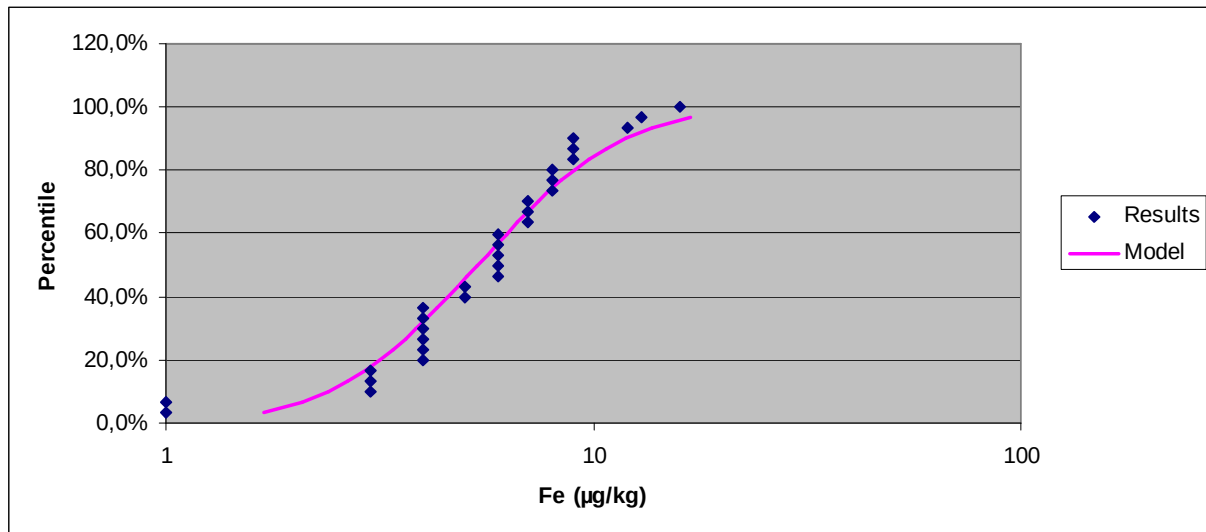


Figure 44: Observed and model cumulative distribution of iron in feed water (FW-ECO) from the example data above

9.4.4 Test of two estimated distributions

When comparing two sets of data from the water-steam circuit, for instance the same combination of sampling point and parameter over two periods of time or the same parameter and period in two different sampling points, it is often helpful to do a statistical test to support the conclusion. The test is based on log-normal distribution models for the two data sets (see 9.3 above) and answers the questions:

- Is it likely that the two data sets have the same standard deviation?
- Is it likely that the two data sets have the same mean value?

The test goes like this:

Verbal description

- 1 Determine the parameters describing the two data sets according to section 9.3.

- 2 Test if the two standard deviations may be assumed to be equal by means of an F-test.

If so, calculate a pooled value for the common standard deviation.

Mathematical description

Data set 1 is characterised by: $\bar{x}_1$ and s_1 . There are n_1 results in this set and thus n_1-1 degrees of freedom (f_1) of the standard deviation.

Data set 2 is characterised by: $\bar{x}_2$ and s_2 . There are n_2 results in this set and thus n_2-1 degrees of freedom (f_2) of the standard deviation.

Determine the F-test variable:

Verbal description

The F-distribution function is available in most spreadsheet or statistical software programs in common use.

Mathematical description

$$F_{test} = \frac{s_1^2}{s_2^2} \quad \text{if } s_1 \geq s_2$$

$$F_{test} = \frac{s_2^2}{s_1^2} \quad \text{if } s_1 < s_2$$

The test hypothesis is:

H_0 : s_1 is equal to s_2

Accept the hypothesis (assume equal standard deviations) if

$$F_{test} \leq F_{1-0.95}(f_d, f_n)$$

Reject the hypothesis if

$$F_{test} > F_{1-0.95}(f_d, f_n)$$

$F_{1-0.95}(f_d, f_n)$ is the value of the F-distribution (one-sided test) at 95 % confidence with f_d and f_n degrees of freedom of the standard deviation in denominator and numerator, respectively, of the test variable.

If equal standard deviations may be assumed, calculate the pooled standard deviation by:

$$s_{pool} = \sqrt{\frac{f_1 \cdot s_1^2 + f_2 \cdot s_2^2}{f_1 + f_2}}$$

Where f_1 and f_2 is the degrees of freedom for s_1 and s_2 , respectively.

- 3 Test if the two mean values may be assumed to be equal by means of a t-test.

If not so, a difference in level between the two data sets has been proved statistically.

The Student-t-distribution function is available in most spreadsheet or statistical software programs in common use.

If the standard deviations are equal, calculate the t-test variable by:

$$t_{test} = \frac{|\bar{x}_1 - \bar{x}_2|}{s_{pool} \cdot \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}}$$

If not, then use instead:

$$t_{test} = \frac{|\bar{x}_1 - \bar{x}_2|}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}}$$

Verbal descriptionMathematical description

The test hypothesis is:

$$H_0: \bar{x}_1 \text{ is equal to } \bar{x}_2$$

Accept the hypothesis (assume equal mean values) if:

$$t_{test} \leq t_{1-0.95}(f_1 + f_2)$$

Reject the hypothesis (i. e. prove a difference) if

$$t_{test} > t_{1-0.95}(f_1 + f_2)$$

$t_{1-0.95}(f_1 + f_2)$ is the Student-t distribution with 95 % confidence and f_1+f_2 degrees of freedom.

For example, consider a power plant running AVT for which an N-limit of 0.15 µS/cm for acid conductivity of the feed water upstream the ECO has been established. During a following period of operation there is a tendency to slightly higher values, and the N-limit is crossed occasionally, but not consequently. Is there a shift in level of the acid conductivity?

The data available for the two periods are:

Table 20: data for two periods.

Parameter	Reference period – data behind the N-limit of 0.15 µS/cm	Test period – data from routine and follow-up analyses
Number of results	43	10
Minimum	0.08	0.09
10 % percentile	0.10	0.10
90 % percentile	0.15	0.19
Maximum	0.18	0.21
Mean of log-transformed values	-2.21	-1.88
Standard deviation of log-transformed values	0.18	0.32

The test variable for equal standard deviations is:

$$F_{test} = \frac{0.32^2}{0.18^2} = 3.16$$

The table value of the F-distribution with 9 and 42 degrees of freedom is:

$$F_{1-0.95}(9,42) = 2.112$$

Since the test variable is greater than the table value, the conclusion is that the two standard deviations are not equal, i. e. a difference in range of the two periods has been proved.

Next, the test variable for equal mean values is:

$$t_{test} = \frac{|-2.21 + 1.88|}{\sqrt{\frac{0.18^2}{42} + \frac{0.32^2}{9}}} = 2.99$$

The table value of the Students-t distribution with 51 (42+9) degrees of freedom is:

$$t_{1-0.95}(51) = 2.008$$

Since the test variable is greater than the table value, a difference in mean values has been proved, i. e. a shift of the acid conductivity has been demonstrated from a statistical point of view.

10 Bibliography

10.1 VGB-Standards and guidelines in force

- (1) VGB-R 513 – Innere Reinigung von Wasser-Dampferzeugeranlagen und Rohrleitungen
VGB-R 513e – Internal Cleaning of Water-Tube Steam Generating Plants and Associated Pipework
- (2) VGB-R 131 – Abnahmemessungen und Betriebsüberwachung an luftgekühlten Kondensatoren unter Vakuum
VGB-R 131e – Acceptance Test Measurements and Operation Monitoring of Air-Cooled Condensers under Vacuum
- (3) VGB-M 407 – Konzeption, Spezifizierung und Leistungsnachweis von Anlagen zur Wasserentsalzung
- (4) VGB-S-006-T-00;2012-00.EN – Sampling and Surveillance for Water-Steam Cycles
- (5) VGB-M 412 L – Aufgaben und Methoden der Kondensatreinigung
- (6) VGB-M 418e – Organic Matter and Dissolved Carbon Dioxide in the Steam Water Circuit of Power Plants
- (7) VGB-M 413 – Schäden durch Fremdstoffeinbrüche in den Wasser-Dampfkreislauf und ihre Vermeidung
VGB-M413e – Damage from Ingress of Impurities into Water-Steam Circuits and its Avoidance
- (8) VGB-R 116 – Konservierung von Kraftwerksanlagen
VGB-R 116e – Preservation of Power Plant Systems
- (9) VGB-B 401 – VGB-Handbuch „Chemie im Kraftwerk“ – „Analysenverfahren“
- (10) VGB-M 404 – Wasserentsalzung mit Membranverfahren
- (11) VGB-M 405 – Wasserentsalzung mit Ionenaustauschern
- (12) VGB-R 450 L – VGB-Richtlinie für Kesselspeisewasser, Kesselwasser und Dampf von Dampferzeugern über 68 bar zulässigem Betriebsüberdruck, Ausgabe 1988
- (13) VGB-R 130 – Abnahmemessung und Betriebsüberwachung an wassergekühlten Oberflächenkondensatoren
VGB-R130e – Acceptance Test Measurements and Operational Monitoring of Water-Cooled Surface Condensers

10.2 Standards in force

- [1] EN 12952-12: Water-tube boilers and auxiliary installations – Part 12: Requirements for boiler feedwater and boiler water quality
- [2] EN ISO 8044: Corrosion of metals and alloys – Basic terms and definitions (ISO 8044:1999)
- [3] DIN 4304: Dampfturbinen – Begriffe, Einteilung
- [4] EN ISO 9963-1: Water quality – Determination of alkalinity – Part 1: Determination of total and composite alkalinity (ISO 9963-1:1994)
- [5] DIN EN 12953: Großwasserraumkessel
EN 12953: Shell boilers

10.3 Literature

The following references offer further information on the problems described on various places in the text or a more general account of the topics. The literature cited describes case studies and viewpoints of the authors and is thus not to be considered as binding statements of this standard. In general the literature contains further references for an in-depth study of a certain problem. To distinguish this kind of background information from the standards in force, is the literature cited in slashes (/x/).

- /1/ REACH Verordnung: EG 1907/2006, Anhang XV dossiers: PROPOSAL FOR IDENTIFICATION OF A SUBSTANCE AS A CATEGORY 1A OR 1B CMR, PBT, vPvB OR A SUBSTANCE OF AN EQUIVALENT LEVEL OF CONCERN
- /2/ Videm, K.: Corrosion of Steel in High-Temperature Water – The Influence of Oxygen in the Water and of Preformed Oxide Coatings in: Papers of the Seventh Scandinavian Corrosion Congress (7th NKM), Royal Norwegian Council for Scientific and Industrial Research – SINTEF, May 1975, Trondheim, 444 - 456
- /3/ Roberge, P.R.: Corrosion Engineering, McGraw-Hill, New York, 2008
- /4/ R.K. Freier, Wässrige Lösungen, Bd. 2
- /5/ Flow-accelerated Corrosion (FAC) in Fossil and Combined Cycle/HRSG Plants, International Conference, June 29, 2010 - July 01, 2010 in Washington DC, USA
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