



The International Association for the Properties of Water and Steam

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Technical Guidance Document: Chemistry Management in Generator Water Cooling during Operation and Shutdown

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Summary

This Technical Guidance Document applies to all generators with water-cooled windings. From the operating side, adherence to a suitable water chemistry regimen as well as proper layup practices help to avoid or mitigate flow restrictions. Other influencing factors are design and materials. It is emphasized that this is an IAPWS Technical Guidance Document and that, depending on local requirements, the normal or target values will need to be customized for each case, depending on the actual conditions of operation and maintenance.

This Technical Guidance Document contains 40 pages, including this cover page.

Further information about this Technical Guidance Document and other documents issued by IAPWS can be obtained from the Executive Secretary of IAPWS (Dr. R.B. Dooley, bdooley@iapws.org) or from <http://www.iapws.org>.

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1 Nomenclature and Definitions

Term	Alternative or Acronym	Definition
Alkaline Treatment		Using water to which an alkalizing substance (e.g., NaOH) has been added, typically with pH 8.5 to 9
Clogging		In this document, restrictions of flow in filters and strainers due to deposits
Conductivity	Specific Conductivity Direct Conductivity	Electrical conductivity of the water sample as measured directly without any treatment [1]
Corrosion		An irreversible interfacial reaction of a material with its environment which results in consumption of the material or in dissolution into the material of a component of the environment [2].
Electrochemical Potential	ECP	The electric potential of an electrode of selected material (here it is Cu) compared to a reference electrode in a selected medium (here it is the generator cooling water)
Generator Cooling Water System	GCWS	Closed cooling water system that removes the heat produced from the generator. It comprises the cooling of the stator as well as the rotor, if applicable.
High-oxygen treatment		Using water where the dissolved oxygen level is kept high, usually near saturation

Term	Alternative or Acronym	Definition
Hollow conductor	Hollow strand	Strands with small channels for the cooling water, inserted into the stator bars
Low-oxygen treatment		Using water where dissolved oxygen is kept low, typically <10 µg/kg
Neutral Treatment		Using high purity water with no additives; pH is limited by limiting conductivity, typically to < 0.2 µS/cm
OEM		Original Equipment Manufacturer
Oxidation		In this document, the transformation of a metal on its surface into its oxide(s)
Plugging		In this document, restrictions of flow in cooling channels due to deposits
Roebel transposition		Bends of the sub-conductors within a stator bar in order to minimize eddy currents, named after Mr. Roebel
Stator bar		Element of the winding of the stationary part of the generator (stator), bearing high voltage and high currents. The stator bar is composed of an array of solid sub-conductors and hollow conductors
Stator winding		Winding of conductors in the stator where the electric current is generated. In large generators the winding is an array of electrically connected stator bars.
Water chamber	(Clip)	Hollow body at the end of a stator bar to connect the array of hollow conductors with the water supply hoses. If it serves at the same time as an electric connection, it is frequently called a “clip”.

2 Introduction: Purpose of Document and How to Use it

This document is applicable for all generators where the winding is cooled with water.

The purpose of this document is to provide guidance on the choice and optimization of a water treatment regimen to assist operators of generating plants in minimizing equipment damage and in maximizing plant reliability.

The guidance document can form the basis of, but should not restrict, other derivative guidelines around the world.

IAPWS has issued a series of Technical Guidance Documents (TGDs) for chemistry control of conventional fossil and combined cycle plants [3]. The purpose of this document is to provide further guidance on the choice and optimization of a water treatment regimen for generator water cooling to assist operators of generating plants in minimizing equipment damage and in maximizing plant reliability. To avoid the major types of damage in generator water cooling, equal emphasis must be given to the operating as well as to shutdown environments, and these are discussed within this document. The guidance can be used directly by chemists and plant operators, and to develop international, national, company, and manufacturer's guidelines.

The primary objectives of this document are to: a) highlight the chemistry-related problems that can exist in generator windings, b) indicate how these problems occur and can be avoided, c) provide a set of water chemistry requirements that will provide optimum protection for the generator, and d) provide sufficient discussion that the reader can harmonize water chemistry and actual plant configurations.

It is emphasized that this is an IAPWS Technical Guidance Document representing the cumulative experience of IAPWS Power Cycle Chemistry (PCC) Working Group members. For its use, a general principle has to be followed:

The success of any water chemistry guidance ultimately depends on the operating experience and the lack of any serious failures, damage, and deposits. Thus, the guidance must be linked closely with comprehensive monitoring of related generator performance data and with inspection results during shutdown periods.

Experience has indicated that the Normal/Target values in Section 5.1 will provide good reliability and availability if they are customized for each plant to account for actual conditions of operation, the equipment installed, the materials, and the chemical treatments used. Customization will follow the roadmap approach in Section 6, which includes refinement of OEM specifications, or development of specifications from scratch if OEM specifications are not available.

It is further emphasized that these guidance values should not be considered as manufacturer's guarantees. Each manufacturer should provide a set of target values representing the plant as designed, and these may be slightly different from the operating guidance provided in this document.

Throughout this document, conductivity limits are provided in units of $\mu\text{S}/\text{cm}$. It is recognized that conductivity units of mS/m are preferred in the SI system; this document uses $\mu\text{S}/\text{cm}$ to be consistent with the most common industrial practice worldwide. All conductivities and pHs in this document refer to water samples cooled at $25\text{ }^\circ\text{C}$.

3 Background

All considerations in this document are based upon the operating conditions in a generator cooling water system: use of demineralized water, temperature between $10\text{ }^\circ\text{C}$ and $75\text{ }^\circ\text{C}$, pressure below 10 bar.

3.1 Overview of generator water cooling and the related chemistry

The history of generator water cooling is summarized in reference [4]. In the early days of direct water cooling from 1960 to 1965, little consideration was given to the chemistry of the generator cooling water. Conductivity of the water has to be restricted in order to limit phase-to-ground currents. In order to prevent magnetic particles from entering the generator winding, the cooling water system must be free of unalloyed steel, which greatly simplifies the requirements on water quality. However, it was evident that the cooling water systems had to be operated with demineralized water, which also eliminates concerns regarding corrosion of the structural materials [5, 6].

In consequence, generator windings are directly cooled with a dedicated closed-loop cooling water system, the Generator Cooling Water System (GCWS).

Cooling of the winding is achieved by inserting strands with small cooling channels between the solid copper strands used for conducting electricity, commonly termed as hollow conductors. Traditionally, they are made of copper, but stainless steel is also used.

So far about 2000 directly water-cooled generator stators have been produced worldwide, not including the former USSR and China where reliable data are only partially available. Of these 2000 generators, about 80 also have water cooling of the rotor. Some of these generators have reached more than 250 000 successful operating hours [4].

3.1.1 Generators with copper hollow conductors

In the absence of oxygen, copper is stable and does not corrode in pure water [7]. With oxygen, copper oxides are formed that slowly dissolve in the water. In order to remove the dissolved copper as well as other impurities, purification in a side-stream mixed bed is foreseen. To limit the copper oxidation, two distinctly different approaches were chosen by the original equipment manufacturers (OEMs):

- Low-oxygen chemistry: keeps the oxidation of copper as low as possible
- High-oxygen chemistry: formation of an oxide layer that slows down further oxidation

Low-oxygen chemistry was chosen by Siemens, Brown Boveri, and later Westinghouse, and their technology followers (licensees, etc.); high-oxygen chemistry was chosen by General Electric and followers. British companies (AEI, GEC, and Parsons) opted for a hybrid approach, by having the system closed to air, but with a deadend head tank open to the atmosphere. Such systems are in fact of the low-oxygen type, but with frequent incursions of air-saturated water.

An alternative strategy to counteract the occurrence of plugging was found in the 1970s by alkalization of the cooling water [8, 9], which was first implemented in 1979 [10, 11]. Since then, more than 260 of the 2000 generators above have used this technology.

Looking back on more than 50 years of experience in the industry, these methods of water treatment have been rewarded by the absence of significant loss of wall thickness, pitting corrosion, and stress-corrosion cracking, as long as the water was not acidic. Only a few chemistry-related problem areas have emerged with copper hollow conductors [4, 12]:

- Flow restrictions and plugging of hollow conductors in the stator
- Crevice corrosion in the brazing between hollow conductor and water chamber (“clip-to-strand leak”)
- Plugging of strainers at the generator inlet
- Deposits on insulating hoses

While generic clip-to-strand leaks are essentially specific to a certain OEM series of generators, it is not an issue of water chemistry, but its solution is in the use of a more stable braze. Strainer plugging is also specific to one OEM.

The buildup of deposits on the insulating hoses of AC applications like stator bars is slow and usually solved by the longterm replacement of the hoses. In the case of very low oxygen levels, such deposits are more frequent with water-cooled DC applications in field windings (generator rotors) and rectifiers.

The main chemistry-related issue is therefore plugging of stator copper hollow conductors by copper oxides. It is estimated that about 10 % to 20 % of the 2000 water-cooled generators worldwide (not including the former USSR and China) suffer from flow restrictions within the first 25 years of operation.

3.1.2 Generators with stainless steel hollow conductors

Since the introduction of stainless steel hollow conductors in 1972, no problems related to corrosion and deposits have emerged with plant operation [13, 14]. They also do not

require special layup during shutdown except that the water in the system should have a low conductivity before draining [13]; see also Section 5.1.3.

3.2 Flow restrictions with copper hollow conductors

3.2.1 Mechanism for flow restrictions

In water, copper together with oxygen reacts to form Cu^+ and Cu^{2+} hydroxides and oxides. The resulting layers are very thin (on the order of $1\ \mu\text{m}$) and will not cause any flow restrictions. However, if the oxides are released to the water and re-deposit locally at preferential sites, the hollow conductor cross section will be impaired and in extreme cases will even plug fully.

The mechanism of growth of flow restrictions can be separated into four steps [15]:

- (1) Oxidation of copper surfaces
- (2) Release of copper oxides
- (3) Migration of released copper oxides
- (4) Re-deposition of migrating copper oxides

Only the combination of these four steps leads to flow restrictions. Water chemistry is one of the parameters of influence, but it should be recognized that other parameters such as design and operating conditions can have an important impact. Not all plugging problems can be blamed on bad chemistry; good chemistry may not provide a cure for everything.

While the mechanisms of steps (1) and (2) are quite well understood and step (3) is rather self-evident, little research is available on step (4), the question of why the copper oxides deposit and at which locations.

(1) Oxidation of the copper

With low-oxygen chemistry, all oxygen entering the system is fully consumed by the copper surfaces to form cuprous and cupric oxide. Otherwise, any incoming oxygen would accumulate in the system and the oxygen concentration in the water would increase towards saturation, which does not happen in low-oxygen systems. This full consumption of oxygen is therefore completely independent of any low-oxygen water chemistry scheme (e.g., alkaline treatment).

With high-oxygen chemistry, a copper oxide layer forms and hinders further access of oxygen to the copper, thus slowing down the oxidation rate. This oxide layer is steadily dissolved in the water. The thickness of the oxide layer is then determined by the balance between the oxidation rate and the dissolution rate.

It should be recognized that both types of chemistry employ no reducing agents, and therefore even low-oxygen chemistry provides an oxidizing water treatment [16]. Therefore, the reaction products with these two chemistries will be similar [15].

In low-oxygen systems and in neutral-pH systems, cuprous oxide (Cu_2O) will be predominant, while in high-oxygen and in alkaline systems the oxide will be mainly cupric oxide (CuO); usually a mixture is found. Variations in the oxygen level or the pH will act to alter this mixture. Phase changes, especially with accompanying changes in density of the oxide layer, will modify the compactness of the oxide layer and may loosen or even detach parts of it.

The morphology of the oxides is also influenced by the system water chemistry. Dense polyhedral oxides are typical for high-oxygen or alkaline water chemistry, and for low-oxygen or neutral water chemistry flower-shaped needles predominate, but usually there is a mixture of the two.

(2) Release of the oxidized copper

The copper is released from the copper surfaces either as particles (e.g., oxides, hydroxides) or dissolved as ions (Cu^+ and Cu^{2+}).

Particle release is usually related to spalling of deposits, for example by phase changes (from Cu^+ to Cu^{2+}) during transient operation like inadequate layout, by changes in the electrochemical potential (ECP) [17], or by mechanical stresses caused by high water velocity or turbulence. Dissolution of copper oxides (see below) may also release particles that were bonded by the oxide.

In water and in the presence of oxygen, copper dissolves into the boundary layer by the formation of Cu^+ and Cu^{2+} ions. Depending on solubility limits, some of the copper ions are transformed into precipitated copper oxides and copper hydroxides. The dissolution progresses until the solubility limit is reached. Then a covering layer of precipitated copper oxide/hydroxide is formed. The release rate of copper will then depend on how much dissolved Cu^+ or Cu^{2+} is removed from the boundary layer and replenished by the oxidation (step (1)).

The release rate can then be described by mass transfer kinetics:

$$dm/dt = k(C_B - C_W) \quad \text{Equation (1)}$$

where

dm/dt	mass transferred per unit of time (release rate)
k	mass transfer coefficient
C_B	copper concentration in the oxide/water boundary layer
C_W	copper concentration in the bulk liquid

The mass transfer coefficient k is determined by the mechanical transport with the flowing water and by diffusion. It includes the effect of various parameters, such as the water velocity and turbulence, flow geometry, surface finish, and temperature.

C_W is mainly determined by the effect of the mixed bed, step (3).

Of these parameters, only C_B is influenced by the water chemistry. The copper concentration in the oxide/water boundary layer will be at or near saturation, which corresponds to the solubility limit of copper ions and depends on chemical conditions, for instance pH, and thermodynamic parameters [18].

It is observed that, while the solubility of copper oxides increases only moderately with temperature, the release rate shows a stronger increase [8]. The difference is evidently caused by the mass transfer coefficient, which increases with temperature.

It is useful to remember that other parameters besides water chemistry, like flow velocity and temperature, also influence the release rate. Such parameters are usually related to design.

Figure 1 shows that at low oxygen concentrations, the release rate rises steadily with oxygen concentration. Here the release rate depends directly on the oxidation rate. At high oxygen concentration, the release rate decreases and achieves a relatively low value due to the slowing of the reaction by the cupric oxide layer that has grown in the high-oxygen system. It is important to remember that the release rate with high-oxygen chemistry is nevertheless larger than with low-oxygen chemistry. The release rate with both chemistries decreases by more than a factor of 10 when the pH is raised to 8.0 or 8.5 [8, 11].

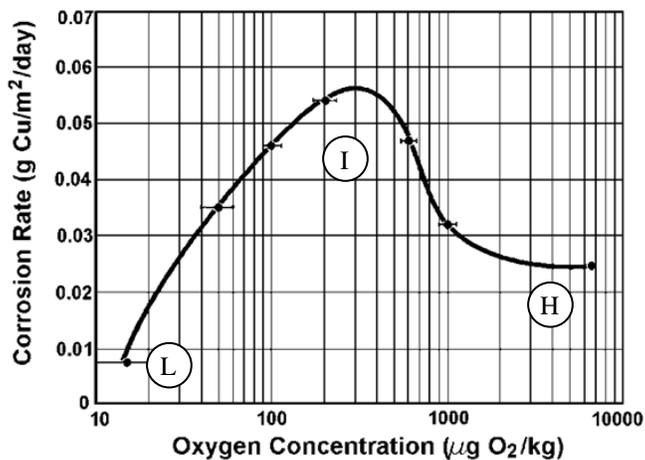


Figure 1. Copper release rate as a function of oxygen concentration [8]. L and H indicate the regions for low- and high-oxygen chemistry, respectively, and I the intermediate region.

(3) *Migration of the released copper*

Once the copper is released into the water, it is circulated in the system until it is removed somewhere. This is done either by the mixed bed, by the filter, or by deposition which is predominantly inside the copper hollow conductors of the stator bars.

The copper concentration in the system is determined by the equilibrium between the release rate and the removal rate.

Consequently, a higher mixed-bed flow rate and an efficient full-flow filter with fine mesh cartridges (Section 4.3.2) are effective for lowering the copper concentration in the cooling water and leaving less copper for deposition and plugging in the winding.

(4) *Re-deposition of the migrating copper*

Investigations on oxide deposits show that re-deposition preferentially takes place at the hollow conductor inlets as well as the outlets, and also at places of flow disturbance inside the hollow conductors, that is, at places of elevated turbulence. These deposits are mainly locally grown crystals from Cu^+ and Cu^{2+} to Cu_2O and CuO , often with suspended oxide particles embedded. Sedimentation of particles is usually a secondary effect at flow restrictions that have been built up by crystal growth.

There is little published research on the mechanism of re-deposition. Basically, the same effect as in step (2) (copper release) takes place. However, with re-deposition, the mass transfer goes in the opposite direction ($C_W > C_B$), Equation (1).

In order to obtain crystallization, the concentration in the water must be above the solubility limit, $C_B > \text{saturation}$. Because the crystallization process takes copper ions away from the boundary layer, C_B will decrease. In order for the crystallization process to continue, C_B will therefore need to be replenished from C_W . Here the same mass transfer parameters as for Equation (1) are applicable, which could explain why the crystallization preferentially takes place at elevated water turbulence.

This indicates that stator bar design may influence the tendency for the precipitation of copper oxides.

3.2.2 Mitigation of flow restrictions

The influencing parameters in steps (1) to (4) offer solutions for avoiding or mitigating excessive deposits in the hollow conductors. The application of a suitable water chemistry regimen is one of them. It should, however, be kept in mind that this is not the complete picture as some root causes are related to the design of the stator bars and the cooling water system, e.g., flow geometry and velocity, mixed-bed flow rate, etc. [15]. Many problems originating in design cannot be remedied by plant operation efforts.

Good water chemistry during all operating conditions (Section 4) is essential to avoid excessive oxide deposits. This comprises normal operation as well as the conditions when the generator is shut down.

Water Chemistry during Normal Operation

Today there are five different water chemistries applied, each following its own strategy (Table 1). It should be mentioned that all these water treatment regimens have their success, but none is without failures.

Table 1. Strategies for normal-operation water chemistry to prevent plugging of copper hollow conductors.

Type of Water Treatment	Keep Oxidation Low	Keep Release Rate Low	Direct Transport into Ion Exchanger	Keep Re-deposition Low
Low-oxygen / neutral	x			
Low-oxygen / alkaline	x	x		
High-oxygen / neutral		x	x	
High-oxygen / alkaline		x		
Cationic Purification ^a			x	x

x objective for the respective water treatment

^a treatment for temporary use only

The target for low-oxygen treatment is to operate within region L of Figure 1, with an oxygen level of <10 µg/kg. This can be obtained by having the system sealed against air, for example by eliminating any ingress of air and applying a hydrogen or nitrogen gas blanket at a pressure slightly above atmospheric.

The target of high-oxygen treatment is to operate within region H of Figure 1, with an oxygen level near saturation with air (4–5 mg/kg at 60 °C). This can be obtained by leaving the system open to air and a continuous feed of air.

The intermediate region I in Figure 1 is usually avoided, because there is a transition between Cu₂O and CuO that may destabilize the oxide layer [17].

The most common causes for elevated oxygen levels in low-oxygen systems are ingress of air by leaky flanges, valves, or pump sliding seals, use of significant quantities of aerated makeup water, opening parts of the system for maintenance, or inadequate layup. It must also be recognized that air may even be drawn into an over-pressured system by a water-jet effect. Gas-to-water leakage within the stator can also lead to detrimental oxygen ingress with the impurity of hydrogen. In generators that are operating in air (e.g., hydroelectric generators), ingress via the insulating hoses is also a source of oxygen.

Common causes for insufficient aeration in high-oxygen systems are hydrogen leaks into the water that replace the air blanket of the water tank. In addition, oxygen is consumed slowly by the copper surfaces in the system. Regular or continuous feed of oil-free air is required to maintain high oxygen levels. In order to avoid acidic pH, the air should be filtered for carbon dioxide.

Alkaline pH is achieved by a controlled addition of NaOH to the cooling water [9]. The target value is a pH of 8.5–9.0 [12].

The "cationic purification" method defies the strategies of all the other types of water treatment. The system is kept fully aerated without carbon dioxide removal, which will result in a slightly acidic pH, ~ 6.0–6.5, due to the formation of carbonic acid from the

carbon dioxide present in air. Électricité de France (EdF) implemented this successfully as a temporary treatment on some generators in their nuclear fleet [19]. It should be noted that this treatment requires profound knowledge of copper solubility and deposition criteria, as well as expert supervision. If applied excessively or if poorly controlled, there is the risk of material damage, especially to the copper and to the brazing connections of the hollow conductors with the water chambers. This method is not recommended for permanent application and therefore is not included in this document.

Consideration has also been given to the use of reducing agents or inhibitors for low-oxygen cooling water. Potential problems are the incompatibility of the agent with the low conductivity limits required for generator operation, and the need for its replenishment when consumed or removed by the system's mixed bed. Moreover, unexpected side effects may occur. Some inhibitors have caused a compacting of oxide deposits, thus rendering them more difficult to remove. Consequently, there is good reason to recommend maintaining the simple chemistry of the copper/water system.

Some generators have oxygen scavengers combined with the side-stream mixed bed. Techniques are either the use of ion-exchange resin loaded with a reducing agent (sulfite, ascorbic acid, hydrazine), or the use of palladium-catalyzed resin to recombine oxygen with the dissolved hydrogen gas [10, 20, 21]. These side-stream devices have the disadvantage of having a slow “clean-up” time constant [22], and oxygen may be more rapidly consumed by the winding than by the scavenger. In generators with slow oxygen consumption (for example with alkaline treatment) or large side-stream water flows, this technique may nonetheless be beneficial. However, it requires extra supervision and maintenance, and unwanted side-effects such as degradation of the mixed-bed resin and possible migration of the palladium into the system need to be considered [21].

Layup during Shutdown

Corrosion-resistant materials such as copper and stainless steel in the generator cooling water system (GCWS) together with the high purity water do not necessitate special corrosion protection measures for layup. However, many water-cooled generators worldwide have experienced plugging of copper hollow strands or clogging of strainers caused by increased oxide release and migration at the lower pH due to ingress of CO₂ from air, frequently closely coinciding with outages. Often the consequences of inadequate layup may be cumulative and only realized several years later.

The best method of layup during shutdown is to keep water chemistry under the same conditions as during normal operation. This is, however, usually not feasible during outages. In such cases, the hollow conductors should be completely drained and subsequently dried. Under dry conditions, the oxide layers are stable.

This applies independently of the type of water chemistry regimen and especially concerns low-oxygen systems as well as high-oxygen systems.

3.2.3 Removal of flow restrictions

If the winding shows indications of flow restrictions, it is suggested to take swift corrective action [23]. Parameters for monitoring flow restrictions are provided in Section 4.4. Mechanical and/or chemical cleaning is effective in removing flow restrictions [24]. Removing flow restrictions at an early stage reduces the risk of severe plugging of conductors that may be very difficult to remove later.

However, cleaning does not eliminate the root cause. Control of operating conditions and water chemistry, and possibly also the design parameters/features, should be critically reviewed in an effort to reduce or eliminate further flow restrictions and plugging in the future.

4 Requirements for Generator Water Chemistry

4.1 Water chemistry parameters

Table 2. IAPWS key parameters for routine chemical monitoring of the cooling water system. (pH is not included because in high purity water it would involve instrumentation that is not compatible with the requirements in the cooling water system, see 4.1.2)

Parameter	Continuous	Periodic
Conductivity	x	
Oxygen ^a	x	
Copper		x
Sodium ^b		x

^a Oxygen monitoring is not required, but still suggested, in high-oxygen systems in which air is continuously injected into the system.

^b Only with alkaline treatment using NaOH

Table 2 lists the IAPWS suggested chemical monitoring parameters and their frequency [12, 25]. Periodic means once a week, or more often when instabilities in the values are observed.

The Electrochemical Potential (ECP) is an additional monitoring parameter which gives useful information. As it is not yet commonly used, it is not included in Table 2.

Other chemistry parameters may also be routinely monitored, but their value would need to be scrutinized regarding their usefulness. Too many data points may lead to a situation with more questions than answers.

It should be considered that any removal of water from the system has to be compensated by addition of makeup water which may destabilize generator water chemistry (Section 4.3.3). Therefore, withdrawal of water for sampling should be minimized (e.g., < 2 liters per week) or where possible employing a sampling loop with water return (Section 8.1.2).

Except for conductivity (Section 4.1.1) and the associated monitoring, the other requirements of this section on water chemistry parameters are not needed with stainless steel hollow conductors.

4.1.1 Conductivity

Conductivity is a key parameter of the generator water specifications and has to be measured and recorded continuously. Conductivity data are usually referred to a temperature of 25 °C. The requirements for sampling are listed in Section 8.1.1.

All original equipment manufacturers (OEM) have two conductivity limits for the water in the main stream of the system:

- Normal conductivity limit. A low conductivity value is prescribed in all designs for normal operation, because there is no reason for a clean, closed cooling system to have elevated conductivity. Depending on OEM, values between 0.3 and 2 $\mu\text{S}/\text{cm}$ are common. Systems operating with alkaline water treatment will have a higher normal conductivity limit, because the alkalizing agent NaOH will provide background conductivity.

In order to limit excursions in pH (see below), conductivity should be kept $<0.15 \mu\text{S}/\text{cm}$ with neutral and $<2 \mu\text{S}/\text{cm}$ with alkaline water treatment.

For formulating water specifications, some tolerance to the above-mentioned values is practical (Section 5.1).

- Maximum conductivity limit. The main purpose of this limit is to avoid the risk of boiling in the insulating water hoses due to heating from currents induced in the conductive water by the high voltages present. The heating also depends on the size of the hoses and the water flow, so no conductivity limit can be universally stated. Therefore, the limit should follow the specification of the OEM.

Depending on OEM and design, values between 6 and 20 $\mu\text{S}/\text{cm}$ are common. A maximum level of 10 $\mu\text{S}/\text{cm}$ is widely employed. These values are usually quite over-conservative, but there is no sound reason why conductivity in a high purity cooling water system should become so high under normal conditions.

Systems operating with alkaline water treatment will have the same maximum conductivity limit, because the limit is set for overheating protection.

In many designs, there is also a conductivity measurement at the mixed-bed outlet, which is used for monitoring its performance. However, since the mixed bed saturates normally from the copper that it absorbs with time, it does not give a distinct conductivity indication.

4.1.2 pH

Direct pH measurement in high purity water is a delicate, error-prone procedure. Special instruments would be required with low conductivity such as in generator cooling water.

The electrode membranes of commercial pH instruments would either let sample backflow into the electrolyte, or pass electrolyte into the stator water, depending on pressure conditions. For on-line measurements, the sample would have to be discarded after passing through the instrument, which would require unacceptable quantities of makeup water.

The efforts of employing a suitable instrument are however not necessary, as pH can be indirectly controlled by measurement of conductivity, Figure 2 and [22, 26]. Thus, with a conductivity of $0.15 \mu\text{S}/\text{cm}$, pH will automatically be between $6.5 < \text{pH} < 7.8$ (if the only contributors are caustic and carbonic acid), which is considerably better than the precision of a pH meter.

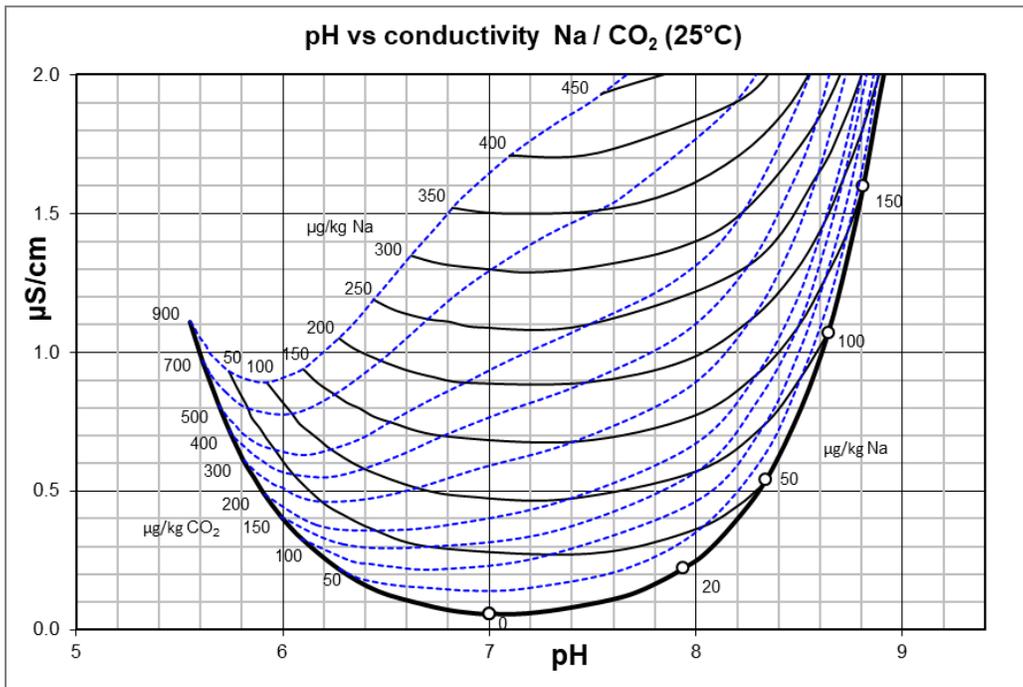


Figure 2. Conductivity and pH of mixtures of NaOH with CO_2 solutions in high purity water, at 25°C . Pure CO_2 is represented by the left-side border curve, pure NaOH by the right one. Values in between are for mixtures.

A conductivity limit of $0.5 \mu\text{S}/\text{cm}$ would permit pH to be $5.9 < \text{pH} < 8.3$. At pH 5.9 the release rate of copper would, however, be excessively high; it is therefore suggested to take action to keep conductivity at $0.15 \mu\text{S}/\text{cm}$ or below unless it can be assured that the resulting pH is not acidic. In this case, spot on-line measurements with a suitable laboratory instrument can be useful (Section 8.4).

With alkaline treatment, conductivity can also be used as a substitute for pH measurement. In this case, the information has to be supplemented by regular analysis of the alkalizing agent (Na^+). Here the conductivity is compared to the theoretical conductivity of NaOH. Smaller conductivity indicates the presence of an anion, thus lower pH [22].

It is better to have no pH meter than one that gives unreliable data. Conductivity is a good substitute parameter.

4.1.3 Oxygen

Oxygen is also an important control parameter for the chosen water chemistry regimen (low-oxygen or high-oxygen).

The target for oxygen is to keep the oxygen concentration outside the intermediate region of Figure 1, because there is a transition in preference between Cu_2O and CuO that may destabilize the oxide layer [17].

The target for low-oxygen treatment is to operate within region L of Figure 1, with an oxygen level $<10 \mu\text{g}/\text{kg}$. Such a low level is chosen because any oxygen entering the system will result in an unwanted buildup of Cu_2O which has a low solubility and stays on site.

The target of high-oxygen treatment is to operate within region H of Figure 1, with an oxygen level near saturation with air (4–5 mg/kg at 60 °C). Here, the buildup of oxides is controlled by the solubility of CuO and the removal by the mixed bed (Section 4.3.2).

For formulating water specifications, some tolerance to the above-mentioned values is practical (Section 5.1).

A selection of suitable instruments is available. They are installed into a dedicated closed sampling loop with sample return to the system.

With high-oxygen water chemistry, oxygen measurements are unquestionably of direct use for verifying that the oxygen level is kept sufficiently high.

It should also be considered that an oxygen level below saturation indicates a lower partial air pressure than the total pressure. The gap may be due to hydrogen, which can create a potentially explosive gas mixture in the stator water tank.

With low-oxygen systems, the information may however be inconclusive. Ingress of oxygen into a low-oxygen system will cause a rise of oxygen concentration, which is counteracted by removal of oxygen through consumption on the copper surfaces. Consider the following two cases:

- The copper may have a surface that consumes oxygen only slowly (tight oxide layer). Then any small quantity of oxygen entering the system will contribute to a visibly increased oxygen level, even though the situation may not be detrimental.
- The copper may be very reactive, consuming oxygen rapidly (thin, porous, or no oxide layer). In such a case, oxygen ingress will not generate an increased oxygen level, even though it may produce enough oxides, oxide migration, and localized copper oxide deposits to cause plugging.

Oxygen concentration should therefore always be evaluated in correlation with the speed of oxygen consumption within the system. High oxygen values may not necessarily be bad if at the same time the consumption rate is low. On the other hand, low oxygen values combined with a rapid consumption rate may be detrimental in the long term.

The oxygen consumption rate can be measured when, for example, air-saturated water is brought into the system (e.g., addition of makeup water) [22].

4.1.4 Copper

Copper concentration is a useful indicator of copper corrosion and release in the generator.

Here again, the copper concentration is governed on the one hand by the release of copper, and on the other hand counteracted by removal in the filters and ion exchangers, as well as by deposition in the winding. As a result, values of copper concentrations are not conclusive of the actual copper release.

Copper concentration has proven to be a useful relative indicator when compared within a user group of similar generators. Typical values for total copper with neutral water chemistry are ca. 5 µg/kg in low-oxygen systems, and 5-15 µg/kg in high-oxygen systems. With alkaline water treatment, copper concentrations are considerably lower.

The copper concentration can be measured with grab samples. Sampling is delicate, however; instructions are given in Section 8.1.3. Grab samples give only a spot-check, which is generally sufficient for regular routine monitoring.

Alternatively, the copper concentration can be determined using an integrated sample (Section 8.2) [27].

The copper release of the system is best measured by taking a representative resin sample from the mixed bed at the same occasion each year. For this, a commercial sludge sampler or a similar improvised tool is helpful. The amount of copper in the resin bed has to be determined. It should be presented as grams copper per square meter of system "hot" copper surface (generator winding) per year. A comparative empirical value may indicate if oxide deposits are less likely to become a problem. It is therefore suggested to perform such an analysis on a regular basis and to observe the trend.

In addition, the quantity of oxides removed in the filter should also be measured or at least estimated (including any material settled on the vessel bottom).

The result of such measurements on the mixed-bed resin and the filter will give the release rate as grams ionic copper and grams particulate copper per square meter of system "hot" copper surface per year. It would be useful if the OEM, or a user group, keeps a comparative database for the specific type of generator. One OEM has found that with their generators on low-oxygen chemistry, a release rate above 5 mg/m²/d correlates with a risk of hollow conductor plugging.

4.1.5 Electrochemical Potential (ECP)

Phenomena such as corrosion and deposition are affected by the ECP. The ECP is a complex parameter; it is a mixed potential obtained by a corroding metal and the balanced redox reactions that are influenced by oxidizing and reducing agents in the water, pH, temperature, impurities, etc. The ECP is therefore a summary parameter that describes the electrochemical reactivity better than any single parameter, including oxygen-concentration.

The ECP probe consists of a copper electrode, a reference electrode, and a temperature sensor, and is installed into a dedicated closed sampling loop with sample return to the system.

Laboratory investigations by EPRI have indicated a correlation between copper release, oxide deposition, and ECP [17]. Suitable ECP sensors have been developed, and their use in generators with high-oxygen as well as with low-oxygen chemistry has been demonstrated [28, 29].

It must be considered that both high-oxygen and low-oxygen chemistry represent, as mentioned in Section 3.2.1, oxidizing water treatment, and therefore the differences in ECP may not be large. However, the ECP is more sensitive to variations of the pH [15].

Tentative ECP specification values have been developed [28]. They relate to the stability of Cu_2O oxide film for low-oxygen systems and the stability of CuO oxide film for high-oxygen systems [17]. Future application will lead to a refinement of the technology.

Even though ECP monitoring is seen more as a scientific tool, it is nevertheless suggested to consider this technique for routine monitoring. With more widespread use, a broader database for the evaluation of these data will become available. Its cost is probably less than some other less useful analyzers sometimes used in generator cooling water systems.

4.1.6 Other

Iron is frequently measured in grab samples from the generator cooling water system. Given the uncertainties of sampling particulate species such as iron, the value of such data is questionable. Once it has been established that the system does not contain any carbon steel elements (which should be the case in the first place), iron analyses are no longer useful.

Generator cooling water systems usually carry a significant load of organic matter. Organic materials, like filter cartridges, ion-exchange resin, gaskets, etc. are usually found in such a system, with no purification device capable of removing them. Thus, with time, organics may accumulate in generator cooling water, often producing a foam that floats on the water of the compensation tank. However, no damages have been related to organics in this system. Nevertheless, their decomposition products have in some cases been found to lead to increased conductivity and also to solubilize copper which challenges the stability of the

oxide layers. It is very seldom that chemical analyses for organics are conducted for specific troubleshooting, e.g., in case of increased conductivity. Organics are certainly not a routinely measured parameter.

Sometimes substances that are uncommon in a generator are also analyzed. Unless they serve to solve a very specific problem, such analyses are of questionable value.

4.2 Layup

Appropriate layup is important with all types of water treatment regimens. It mitigates or even eliminates risks regarding corrosion of materials and detachment of oxide layers which in turn can cause hollow conductor plugging. Severe damage due to inappropriate layup has been experienced [15]. There are three options for layup, Table 3:

Table 3. Options for layup with copper hollow conductors.

Type of Layup	Leave System Running	Shut Pumps and Leave System Filled with Water	Drain and Dry
Short-term layup ^a	x	x	
Long-term layup			x

^a Short-term means 3 days or less. The 3-day limit is not rigid and may be extended by a few days or even decreased depending on qualified experience.

Leave the system running

If the generator is not the cause of the outage, the gas and the GCWS can remain under in-service conditions, even for long-term layup. In such a case, the generator water chemistry has to be kept within specifications for normal operation and monitored. This type of attention may not be guaranteed during long periods of plant shutdown, thus this option is not included as a standard option for long-term layup. However, this option is perfectly viable and may be preferable for plants that lack the resources or procedures to facilitate appropriate drying of the winding.

Generators with pre-identified stator bar end leaks or where leaks are suspected are a major concern when the gas pressure is lowered below the water pressure and the pumps are in operation, because external cooling water may then leak into the generator. For these generators, leaving the system running is only viable with a pressurized cover gas in place. Other generators may operate the GCWS at the owner's prerogative with the water pressure higher than the gas pressure. Note that during purging of the hydrogen, replacing it with CO₂ and finally with air, the pressure of the cover gas is seldom kept above the water pressure. Generally, this is acceptable because the water pressure is higher than the gas pressure only for a short time.

Shut off pumps and leave the system filled with water

This option presumes that the original generator water chemistry is maintained during the layup period. Although the 3-day limit is somewhat arbitrary, experience has shown that for most systems the water chemistry can be maintained for that length of time without circulation. Extending that time period will require monitoring the water chemistry to ensure that it is held within the OEM specifications.

For this option, it is necessary to ensure that the generator stays filled with water up to the top. This may be easier for systems with a positive pressure water head, that is, where the water level is at a higher elevation than the uppermost point of the stator. In systems with a negative pressure water head, when a water tank is situated lower than the stator, a sufficient gas overpressure can avoid vacuum in the stator and with this the risk of air in-leakage. Other measures are also possible, for example the use of isolation valves to the winding.

Drain and dry the winding

Copper surfaces, either bare or with oxide, do not change into a deteriorating condition when dry. Reactions, however, take place readily when they are wet, within a time frame of a few hours.

Simple draining of the stator will not make the winding dry. A good part of the stator bars will still be filled with water and the drained bars will be wet and filled with moist air.

This is especially a major concern for low-oxygen generators, where transformation of Cu_2O into CuO may cause oxide mobilization.

High-oxygen units are also affected, but with different mechanisms. Entrance of air into a partially drained stator winding will lower pH in the water film (by the CO_2 in the air). Stator bars left filled with water will transform to a low-oxygen environment, because the oxygen is consumed by the copper. Such chemistry changes will upset oxide morphology and stability. Another risk factor appears when the generator has had an out-of-specification operating history with periods of low oxygen; then the exposure to air may mobilize oxides rapidly at re-start and plug the stator.

In order to properly lay up a water system or to evacuate the system for the performance of a dielectric withstand test (Hipot Test), a method of removing all of the moisture from copper surfaces must be employed. The method consists of the following basic steps:

- Draining the water from the system
- Isolating the components with copper surfaces from the rest of the system
- Blowing down with a series of strong blasts with oil-free compressed air
- Pulling a vacuum on the system
- Monitoring dew point or insulation resistance

Vacuum drying alone, without previous blow-out of the water, will not be successful. Several hundred liters of water will still remain in the winding after draining, which is too large an amount to be removed via vacuum pump.

For low-oxygen units, the use of pure-grade nitrogen at an adequate overpressure is a useful addition to draining and drying, especially in specific cases when there are doubts about the quality of drying or when drying is not feasible. It is simple to add and easy to control, but it should not be used as a substitute for draining and drying.

4.3 Special features

4.3.1 Component design

The design of stator bars influences their performance with regard to hollow conductor plugging.

In Section 3.2.1, parameters that influence the susceptibility for plugging are identified:

- Elevated temperature: the copper release rate increases with temperature.
- Intrusion of untreated air: Carbon dioxide lowers the pH and increases copper release.
- Low purification flow of the mixed bed: a low flow leads to less removal of copper from the water.
- Hydrodynamics: areas of turbulence increase the susceptibility for plugging. This is widely observed at field inspections where deposits are predominantly at the inlet and outlet of the hollow conductors [11, 15]. Turbulences are caused by flow geometry (e.g., sharp edges at inlets and outlets), around deposits, with rough (or corroded) surfaces, and with excessive velocity of water flow.

The opening cross section of the hollow conductors plays a pivotal role for the susceptibility to plugging. Narrow openings or deformations at the Roebel transpositions are frequently associated with plugging.

It must be acknowledged that many design features are predetermined by prioritized requirements that cannot easily be changed. For example, the cross sections of hollow conductors cannot be greatly increased since they have to fit into the available space.

There is no specific “bad design”; performance of all designs is basically good, but most OEMs have nevertheless in some cases experienced plugging.

4.3.2 System design

For generator cooling, closed cooling water systems are used. Such a system comprises the following components in full flow, listed in flow direction: generator, recirculation pump, cooler, and filter. In addition, there is an expansion tank, either in the main stream before

the pump or in a side stream (usually a head tank on top of the generator), or even in a dead end. There is also a side-stream purification loop with a mixed-bed filter.

Makeup water which serves to compensate water losses is usually introduced either into the purification loop upstream of the mixed bed or into the expansion tank. Gases that may collect in the system are vented off via the expansion tank or by a dedicated gas detraining tank.

The design of the cooling water system influences the performance with regard to hollow conductor plugging.

Each water treatment method has some special requirements on system design. There are, however, some requirements that are applicable to all types of water treatments.

General requirements

- **Filters:** There should be full-flow filters, filtering the full recirculating water flow. It is useful to have them as 2×100 %, with one filter in standby, so that the filter can be changed without shutting down the cooling water system. Various types of filters are in use worldwide such as stainless steel mesh filters, sintered filters, wound fiber filters, and pleated filters. Sizes in use vary from 1 to 80 μm. There is no overriding evidence to suggest one type is better than another; all can do the job. Most common are wound polypropylene filters of 1–20 μm with the most typical being 5 μm.

In order to avoid uncontrolled ingress of organic substances, new filter elements should be thoroughly rinsed with demineralized water before they are put into use. This helps to avoid uncontrolled water chemistry and conductivity spikes when taking the filter into operation.

- **Handling of gas-to-water leakage:** Leaks may introduce CO₂ into the water if it is present as an impurity in the hydrogen, especially after filling the generator when there is still some CO₂ left over in the gas.
- **Mixed-bed resin:** resin fully in the H⁺/OH⁻ form is used, with some methods for alkaline treatment additionally using resin in the Na⁺/OH⁻ form. Gel-type resin gives the best performance, but macroporous resin is used by some utilities. It is advised to only use fresh factory-regenerated resin. Recycled and regenerated resin usually cannot attain the required quality standard for the generator cooling water system whose functionality is directly related to the plant's availability.
- **Makeup water:** its use should be minimized (Section 4.3.3).
- **Layup during shutdown:** proper layup (Section 4.2) must be feasible.

High-oxygen chemistry

- Materials compatibility: some materials are poorly compatible with oxygenated water. Attack has been experienced with certain brazing alloys [30] and certain sliding pump seals. For high-oxygen chemistry, a related assessment of all materials is recommended.
- Providing aeration to achieve a high oxygen level: injection and distribution of purified air (oil-free and CO₂ removed) into a full-stream water tank is required.
- Handling of air in-leakage: such in-leakage may, for example, develop at leaking flanges of sub-atmospheric piping. The associated CO₂ from the entrained air will lower pH and can destabilize the oxide layers.
- Handling of gas-to-water leakage: large hydrogen leaks may displace the air needed for high oxygen levels in the water. Also, explosive hydrogen / air mixtures may develop.
- Sizing of the mixed bed: copper release with high-oxygen treatment is higher than with low-oxygen treatment (Figure 1). Therefore, a large mixed-bed flow is required to keep the copper level in the water under control. Flow rates of 10–30 m³/h are typical. Also, the high release rate charges the mixed bed faster and therefore larger quantities of resin are required for a useful running time. Quantities of 250–1000 L are typical.

Low-oxygen chemistry

- Air-tightness of the system: very critical, and sometimes hard to achieve. Even with water overpressure, air may be pulled in by jet effects.
- Deaeration of the system: a gas blanket of hydrogen or nitrogen has to be applied in the expansion vessel (e.g., stator water tank or head tank).
- Handling of gas-to-water leakage: standard grades of hydrogen contain quantities of oxygen that, when leaking into the water, may increase the oxygen concentration and in consequence lead to plugging of the hollow conductors.
- Sizing of the mixed bed: water flows of 1–4 m³/h and resin volumes of 30–130 L are typical. Larger flows and volumes are possible.

Alkaline Treatment

Alkaline treatment is applied additively to high- or low-oxygen treatment.

- Materials compatibility: a check for compatibility of all materials is recommended. Laboratory investigations have shown that alkaline water reduces the stability of a certain braze [31].

- Alkalizer system: additional hardware is required and needs to be monitored and maintained. The alkalizer system needs to be safeguarded against overdosing, which could cause a generator trip. Alkalizer refill requires handling of chemicals.
- Monitoring: there are additional monitoring requirements, like periodic Na^+ analyses.
- Mixed bed: this will be exhausted with the NaOH which is used for alkalization. It is not recommended to run without or with only a very small ($< 500 \text{ L/h}$) mixed-bed flow. Operating with only a mixed bed fully in the Na^+/OH^- form is also not recommended [9]. The options are either a small H^+/OH^- mixed-bed flow (e.g., $1 \text{ m}^3/\text{h}$) together with a sufficiently sized resin volume, or the use of a dual bed, that is two mixed beds in parallel, one being in the Na^+/OH^- form, the other (with a smaller water flow) in the H^+/OH^- form [9, 32]. The dual bed, however, requires special expertise and supervision.

4.3.3 Withdrawal of water from the system

Withdrawal of water from the system leads to refilling with makeup water. Makeup water should have an adequate quality to fit the requirements for the water treatment regimen:

- High-oxygen chemistry: if makeup water is used in significant quantities, it should be air-saturated and free of CO_2 in order to avoid destabilization of the oxide layer.
- Low-oxygen chemistry: makeup water should be free of oxygen and of CO_2 .

If such is not available, the use of makeup water must be minimized and strictly controlled. This refers especially to regular withdrawals for water samples. Situations such as leaking valves, etc. should be dealt with as a priority to help minimize makeup water addition.

It is suggested to use an integrating water meter to control the usage of makeup water.

It should be mentioned that in most plants of the former USSR, the cooling water system had a continuous blowdown, with deaerated condensate as makeup, taken after the polishers to remove ammonia.

4.3.4 Filling and refilling of the system

Filling / refilling the water

The safest way to refill the generator cooling water system is to ensure that the water in the system is at the proper level of dissolved oxygen during and at the completion of filling.

With low-oxygen chemistry, the system should first be evacuated and then filled with nitrogen. The water, when added, will then not be in contact with air to pick up oxygen.

With high-oxygen chemistry, it should be ensured that the filling water does not become acidic by carbon dioxide when in contact with air. Some contact may be difficult to avoid; in such cases the water should be purified as soon as possible using the mixed bed.

Filling / refilling the hydrogen

For operation, the frame of most generators is filled with hydrogen. When the seal oil pumps are not operating, or during outages for safety reasons, the hydrogen is removed and replaced by air. In order to avoid an explosive mixture, the process has an intermediate step of filling the frame with carbon dioxide. When at this point a gas-to-water leak occurs, substantial amounts of carbon dioxide will enter the water, lowering the pH and dissolving part of the oxide layers. High copper levels in the water are an indication for this.

4.3.5 Commissioning

Attention must also be given to the conditions at the first installation of the generator. Adequate protection during transport is obvious. During commissioning, appropriate conditions for the windings have to be provided: operate with water at or near the requirements for normal operation and provide appropriate layup during idle periods.

It is strongly emphasized that water should attain the correct quality as quickly as possible during commissioning. Conditions out of specification should be minimized. It is important that the generator withstands commissioning without developing excessive or unfit oxide layers.

4.3.6 Cleaning of the cooling channels

It is suggested to remove flow restrictions at an early stage of detection, which reduces the risk of severe plugging of conductors that may be very difficult to remove later. (Section 3.2.3).

4.4 Physical parameters

Optimum water chemistry is a pre-emptive measure. If the generator nevertheless develops flow restrictions, corrective actions can still be taken; the sooner they are taken, the more successful they are in mitigating future issues. It is therefore important to continuously monitor the generator for flow restrictions [23]. Key physical parameters for monitoring are listed in Table 4. Trends in the measured data should be monitored for early detection of situations out of normal.

Table 4. Recommended parameters for routine monitoring for flow restrictions.

Parameter	Importance	Monitoring Frequency
Winding / bar temperatures	critical parameter	c
Winding water flow	critical parameter	c
Δp winding inlet to outlet	important indicative information	c
Δp over filter / strainer	important indicative information	d
Δp gas to water	important parameter	c
Gas-to-water leakage	important parameter	d
Consumption of makeup water	good indicative information	d

Δp = pressure difference
c = continuous; d = daily

Winding and bar temperatures, as well as the hydraulic parameters (winding flow and pressure drop) are direct indications for reduced cooling water flow. The other listed parameters give an early warning for risk factors regarding hollow conductor plugging. Information on the interpretation of the data is given in Section 8.5.

5 Tables of Chemistry Limits

5.1 Table of water chemistry limits

5.1.1 Copper hollow conductors with high-oxygen chemistry

Table 5. Generator cooling water specifications for high-oxygen chemistry.

Parameter	Unit	Normal / Target Values	Application Range
Conductivity @ 25 °C	$\mu\text{S}/\text{cm}$	≤ 0.2 ≤ 2	Neutral water treatment Alkaline water treatment ^a
Oxygen	$\mu\text{g}/\text{kg}$	≥ 2000 ^b	All

^a alkaline water treatment means a stable pH between 8.5–9.0

^b as close as possible to saturation with air

5.1.2 Copper hollow conductors with low-oxygen chemistry

Table 6. Generator cooling water specifications for low-oxygen chemistry.

Parameter	Unit	Normal / Target Values	Application Range
Conductivity @ 25 °C	$\mu\text{S}/\text{cm}$	≤ 0.2 ≤ 2	Neutral water treatment Alkaline water treatment ^a
Oxygen	$\mu\text{g}/\text{kg}$	≤ 20 ^b	All

^a alkaline water treatment means a stable pH between 8.5–9.0

^b as low as reasonably achievable

5.1.3 Stainless steel hollow conductors

Table 7. Generator cooling water specifications for stator windings with stainless steel hollow conductors.

Parameter	Unit	Normal / Target Values	During Shutdown
Conductivity @ 25 °C	μS/cm	< 0.3	< 0.3 ^a
Oxygen ^b	μg/kg	-	-
Copper	μg/kg	<10	-
Iron	μg/kg	< 10	-

^a if stator is left filled, or before draining

^b no requirements regarding oxygen

5.2 Limits for normal operation

The rationale for the normal values and targets is given in Section 4.1.1 (conductivity), Section 4.1.3 (oxygen) and in reference [13] (stainless steel hollow conductors).

Tables 5–7 give limit values for normal operation which includes some tolerance for practical use [12, 17b]. The goal, however, is to achieve better values.

- The goal is to keep conductivity <0.15 μS/cm.
- For low-oxygen treatment, the goal is to operate with a lower oxygen level of <10 μg/kg.
- For high-oxygen chemistry, the goal is to operate with an oxygen level close to equilibrium with air, which is usually > 4000 μg/kg.
- The specification for alkaline treatment is a pH of 8.5–9.0. The goal is to keep the pH stable within this range; a typical control parameter (Section 4.1.2) is to keep conductivity at 1.5±0.1 μS/cm.

The normal values in Table 5–7 represent the accumulated experience of the IAPWS Power Cycle Chemistry (PCC) Working Group. The limits in these tables after modification through use of Section 6 are considered as the normal operating values during stable operation. They represent the current state of knowledge and research worldwide to avoid the damage mechanisms delineated in Section 3. They are therefore consistent with long-term plant reliability.

However, it should be kept in mind that water chemistry is not the only factor for avoiding problems related to corrosion and deposits, as some root causes are related to the design of the stator bars and the cooling water system, such as flow geometry and velocity, mixed-bed flow rate, etc.

5.3 Development of Action Levels

If water quality is outside normal operation levels, then the reason for the degraded quality must be determined, and corrective action taken to restore operation within the normal limits as soon as is practicable.

It is strongly suggested that each plant operator, chemist, or owner develop a set of Action Levels that are supported by management and define when the operators must take action in response to values outside the limits.

The conductivity limit of 0.2 $\mu\text{S}/\text{cm}$ can be increased if it can be shown that the water is not acidic. With high-oxygen treatment, however, elevated conductivity is usually due to ingress of carbon dioxide which turns the water acidic. However, a limit above 0.5 $\mu\text{S}/\text{cm}$ should not be chosen, because it would indicate poor chemistry control in such a pure water system.

5.4 Development of shutdown limits

There is a limit on conductivity to prevent boiling in the insulating water hoses, which could lead to local loss of cooling and high-voltage electric discharge that could destroy parts of the generator. The limit value, which depends on generator and system design, has to follow the specification of the OEM (Section 4.1.1). A shutdown level of 10 $\mu\text{S}/\text{cm}$ is widely employed.

The required actions also have to follow the specifications of the OEM. In some designs, the generator is tripped automatically with no delay, in another with some delay. Other designs call for manual generator trip, within a limited time, and other designs link this shutdown requirement with the simultaneous loss of cooling water flow.

5.5 Operating outside the limits for normal operation

Operating the generator outside the range defined in Sections 5.1 and 5.2 increases the risk for damage by corrosion and by flow restriction, which can in the worst case destroy the generator. The actual risk can, however, be assessed by proactive monitoring.

5.5.1 Monitoring for corrosion

This can be done by visual or endoscopic inspections. It usually requires disassembly of parts of the components.

The most critical item is the oxide layer on the hollow conductors. An inspection of the conductor inlets and outlets in the water chambers will give an indication if corrosion deposits are present. If bare bright metal is visible, it can be expected that material loss is taking place. Its quantity and rate should be determined.

The brazings at the hollow conductor ends are also sometimes subject to corrosion [30]. However, this is usually hardly detectable by visual inspection; water leaks will be the final indication.

5.5.2 Monitoring for flow restrictions

This has been treated in Section 4.4.

5.6 Operating with inadequate layup

Operating the generator with inadequate layup (Section 4.2) will destabilize the oxide layers, which can subsequently flake off and cause flow restrictions. They can, in the worst cases, destroy the generator winding. Proactive monitoring for flow restrictions will indicate if such a situation is occurring. The drawback is that sensitive monitoring requires the generator to be in operation, so an adverse situation may be detected only at a late moment with little time to consider appropriate remedial action (e.g., reduce load or shut down generator).

6 Road Map for the Choice and Optimization of the Water Treatment Regimen

The water treatment regimen strongly interfaces with the provisions given by the system design. It is therefore useful to start the optimization of the water treatment regimen from the applicable OEM specification.

The road map is illustrated in Figure 3.

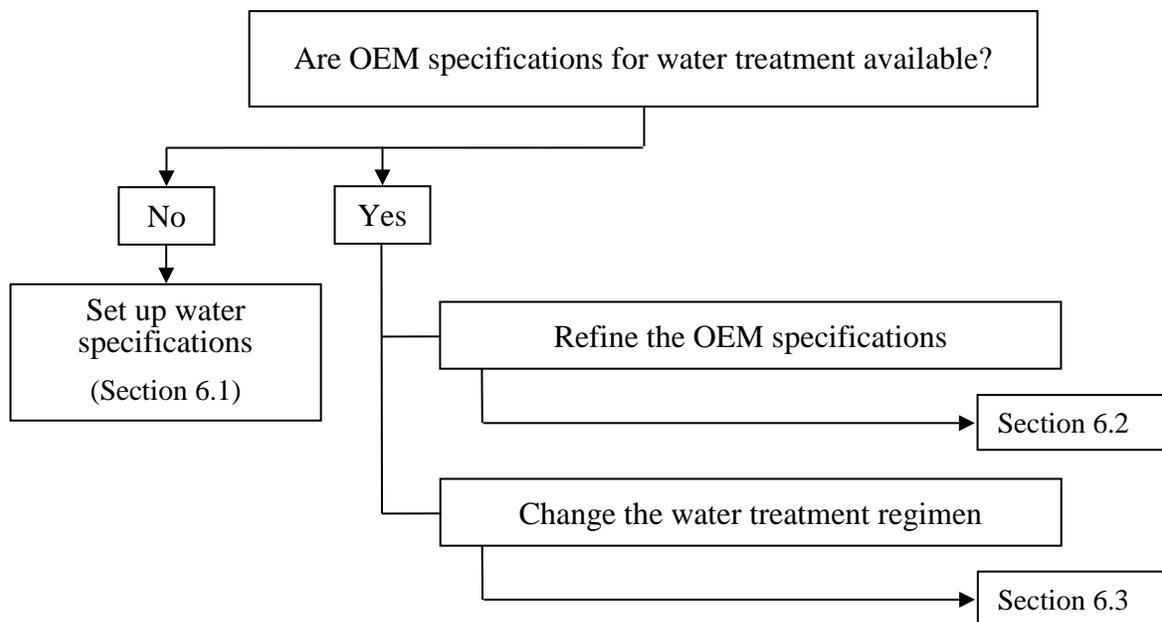


Figure 3. IAPWS Roadmap to develop plant-specific generator cooling water specifications.

6.1 Setting up water specifications

The first step will be the choice of the water treatment regimen:

1. Clarify what is possible: check which set of pre-conditions listed in Sections 4.3.1 and 4.3.2 are fulfilled. If required, the cooling water system has to be modified appropriately.
2. Select the regimen that best fits your organization and constraints (e.g., for supervision, maintenance, etc.). Remember that all these water treatment regimens have their success, but none is without failures.

The next step will be setting up the requirements for operation and monitoring and the water chemistry specifications using Sections 4 and 5.

6.2 Refining the OEM specification

Usually the OEM provides water specifications for the generator. It may however be desirable or even useful to adapt these specifications to specific plant conditions, and to include experience from other OEM and plant operators. The idea of this Section is to harmonize the OEM specification with this Technical Guidance Document (TGD).

Section 4 of the TGD lists the requirements and Section 5 the quantification for generator water chemistry, especially water chemistry parameters, methods for layup, and parameters for monitoring. They may be applied additively to the OEM specifications.

Although this TGD represents the state of the art, it may nevertheless be possible that it contradicts some parts of an OEM specification, especially on some special or unique features of a generator. In such cases, it is suggested to clarify the situation with the OEM. Legal aspects and warranties must also be considered.

6.3 Changing the water treatment regimen

Although not advised, it may be useful in specific cases to convert the water chemistry from one regimen to another.

Usually a cooling water system and its components are designed for a specific water treatment regimen. When changing the regimen, changes in the cooling water system may be required. Such a step should therefore be carefully planned, and considerations taken on design, materials, available hardware, and on the current condition of the hollow conductors [12, 33, 34].

The associated transition in oxide structure may render the oxide layers unstable. In order to achieve a defined oxide structure, a chemical cleaning should be considered at the beginning of the conversion.

6.3.1 Converting from neutral to alkaline treatment

Generally, it is possible to convert from neutral to alkaline treatment or vice versa without substantial modifications in the generator cooling water system.

In order to achieve a defined oxide structure, a chemical cleaning should be considered at the time of the regimen conversion.

Low-oxygen chemistry

Conversion can usually be done without further modification of the cooling water system. Depending on the method of alkalization, it may, however, be useful to reduce the mixed-bed flow or to apply a larger mixed bed in order to delay exhaustion of the mixed bed by the alkalizing agent (NaOH) [9].

High-oxygen chemistry

Ultimate care has to be taken that carbon dioxide (from air) is kept out of the system, as even traces will jeopardize the pH of alkalization [22], Figure 2. This is especially a concern for the air injected for maintaining high oxygen levels, the makeup water, and also possible air in-leakage.

High-oxygen systems usually have a large mixed-bed flow. In order to achieve a reasonable runtime of the mixed bed (it will exhaust with the injected NaOH), either the mixed-bed flow has to be reduced, or a dual-bed system has to be applied [9]. The latter, however, requires special expertise and supervision.

Some materials may degrade by the combined action of oxygen and alkaline pH. While this is a minor problem with expendables that can be replaced by other materials (e.g., pump seals), it may be a problem with parts of key components (e.g., brazings of the hollow conductors). A thorough review of materials and their stability is therefore advised. Generally, however, gentle alkalization ($\text{pH} < 9$) mitigates corrosion of the used materials.

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8 Appendix

8.1 Water sampling

The requirements for proper sampling for corrosion products in water are delineated in IAPWS Technical Guidance Document TGD 6-13 [27]. There are, however, different preconditions in generator cooling water systems, and procedures can be simplified.

8.1.1 Conductivity

Conductivity has to be measured continuously. The sensor should be immersed into the main stream pipe of the cooling water system after the coolers and before the generator. This ensures the lowest temperature and the absence of a gas/water mix that would compromise the measurement. Alternatively, the sensor can be placed in a designated sample loop. For reliability reasons this loop should be used exclusively for the sensor, not shared with other instruments or any sampling devices. Here it has to be assured that any delay is small, e.g., less than 30 seconds, and that the sample flow is never shut off (e.g., remove the handles from associated valves).

The conductivity of water is dependent on temperature. Conductivity data are usually referred to a temperature of 25 °C. Instruments with appropriate temperature compensation must be used. The nearer the sample temperature is to 25 °C, the smaller is the error from temperature compensation.

8.1.2 Sampling loops

A sampling loop with water return to the system permits continuous sample flow for instruments and integrated samples. It can also be used for grab samples without the necessity of long flushing.

The sample should be withdrawn from the cooling water system after the coolers and before the generator. This assures the lowest temperature and the absence of a gas/water mix that would compromise instrument function. The sample return should go to a suitable place downstream of the generator.

The withdrawal point should be at the main stream pipe of the cooling water system, and, if not available, at the vent of a component like the (operating) mechanical filter. In no case should a water drain connection (e.g., cooler drain) be used if analysis for suspended species has to be made.

The sampling line should be of stainless steel and with a diameter to support sufficient flow even when grab samples are taken. Provided that the withdrawal point is on the high pressure side (e.g., before the main flow control valve) and the return point at the low pressure side of the system, a tube with 9 mm (or 3/8") inner diameter will generally be sufficient.

The loop should be equipped with a flowmeter. The typical flow range is 2–5 L/min.

8.1.3 Grab samples

There is a problem with representative sampling for copper, especially when a significant fraction of particulate copper is present. It is good practice for such sampling to have a continuous sample flow [27]. This is, however, not possible in closed generator cooling systems.

Best would be to use a sampling loop as described above, with the grab sample taken directly from the loop (short T-connection for the sampling valve). If a sampling loop is not available, the sample should be taken locally (no long sample lines) at a suitable withdrawal point as specified for the sampling loop.

Sampling lines for grab samples should have small inner diameter (typically 6 mm or ¼”) to provide fast sample flow to avoid settling of particles. All related materials should be stainless steel.

Taking the sample:

- Open the valve fast and wide open, then immediately reduce to a small flow, on the order of 300–500 mL/min.
- Let the sample flow continuously until a minimum of at least a 10-fold volume of the sample tube, but no less 200 mL, has been flushed. Leave sample flow running constantly and discard the flushing water.
- Transfer the sample into an appropriate pre-cleaned container.

If the total quantity of copper has to be determined, the sample bottle may be pre-loaded with a small amount of concentrated nitric acid [27]. If suspended copper is also to be determined, no nitric acid should be employed. Experience has shown that copper concentrations in generator cooling water systems are such that adding nitric acid at sampling is not necessary.

8.2 Integrated sampling for copper

An integrating corrosion product sampler can be used to obtain time-integrated, representative samples of particulate and dissolved corrosion products, with the particles being collected on an acid-digestible filter of pore size 0.1 to 0.45 μm and the dissolved fraction on an ion-exchange (cation) membrane filter placed after the particle filter. The volume of filtered sample fluid is also recorded. The sampler is installed in a dedicated sampling loop. Details are given in the above-mentioned IAPWS Technical Guidance Document [27].

8.3 Copper analysis in grab samples

In order to avoid losses or contamination in the filtering process, the following procedures have proven to be useful:

- Use only samples that have not been acidified.
- Digest one part of the sample at ca. 95 °C with 1–3 mL concentrated nitric acid per 100 mL of sample. → Fraction “Cu total”.
- Run the other part of the sample over an acid-digestible filter of pore size 0.1 to 0.45 µm. Digest the filter at ca. 95 °C in 1–3 mL concentrated nitric acid per 100 mL of water. Run a blank with a new filter. → Fraction “Cu suspended”.
- Analyze these two fractions with a detection limit of 2 µg or preferably better. Using less sensitive methods may not give useful results.

The digestion temperature of ca. 95 °C is needed to dissolve Cu₂O. A lower temperature is possible for systems with exclusively CuO as the suspended species.

Typically, 50 mL of sample are sufficient for Fraction “Cu total”, and 200–1000 mL may be required for the Fraction “Cu suspended”, then to be dissolved in 50–100 mL acid.

The concentrations for “Cu total” and for “Cu suspended” are given directly by the analysis of the respective fraction. The concentration of “Cu dissolved” is calculated by the difference.

Direct measurement of “Cu dissolved” in the filtrate may introduce errors by losses or contamination and is therefore less reliable. Such analysis can, however, be used to check the consistency of the measurements.

8.4 pH analysis in grab samples

There are many ways to measure pH in high purity water. The following simple procedure has been proven to achieve adequate accuracy of generator cooling water monitoring.

Required for measurement:

- portable pH meter with associated single combination electrode (combines electrode and reference electrode into one body)
- plastic beaker 100 mL
- flexible plastic tube to fit sample connection, outlet end max. 3/8” outer diameter
- plastic bottle 100–150 mL for the storage of the electrode tip (e.g., wide-neck bottle with a hole in the cover to hold the electrode in a fixed position)

- 1 M KCl (76 g/L) or 1 M NaCl (59 g/L) solution in high purity water for electrode storage (“soak solution”). It is very important that the product is prepared with high purity chemicals that do not contain any traces of acid or alkali and yield a strictly neutral solution.
- buffer solutions at pH 4, 7, and 9 (or 10)
- plastic beakers to accommodate the buffer solutions and electrode during calibration

Preparations

- Calibrate with buffer solutions, using as the last buffer of this series one with the pH closest to the expected value for the sample.
- Soak the electrode for at least 30 minutes in the soak solution in order to wash out buffer residues, and to fill the liquid junction of the diaphragm with high conductivity neutral water.
- This preparation is valid for a period of up to 4 hours; between measurements, the electrode should be charged in the soak solution. Change the soak solution if it gets contaminated.

Measurement

- Place the sample tube outlet at the bottom of the beaker and let the sample flow slowly so there is no turbulence carrying water from the surface back into the beaker (to avoid pick-up of CO₂ from air).
- Insert the electrode into the lower part of the beaker.
- Let sample flow for 3–5 beaker volumes, then withdraw the sample tube slowly from the beaker, avoiding back-flow of water from the surface.
- Wait a few seconds until the reading has stabilized (10–30 seconds).
- Take and record the instrument reading.
- After the measurement, immediately return the electrode to the soak solution.

8.5 Relevance and interpretation of physical parameter data

Winding and stator bar temperatures

A rise in bar and winding temperatures (at reference load) indicates a deterioration of cooling, that is, a reduced cooling water flow through the stator bars. This is a strong indicator for hollow conductor plugging, but other causes should also be considered.

It is exclusively the temperature rise across the generator (outlet minus inlet temperature) which is significant for diagnosis. However, the temperature rise is also dependent on the generator load (MVA); it increases approximately with the square of the load. Therefore, for evaluation and monitoring trends, the temperature data should always be normalized to a reference load [23].

The global temperature rise over the generator gives only limited information. It is an indirect measure for the cooling water flow, which is better measured directly with a flowmeter.

Individual bar temperatures can be measured by temperature sensors either on the outlet water hoses of the bar, or in the stator slot between two bars. These temperatures give good information on the cooling of a stator bar in relation to the others. For this, it is necessary to group stator bars with regard to their designed hydraulic resistance, for example to separate bars that have other components like phase connectors in series. Bar temperatures within a group should be within a certain bandwidth, which depends on generator design. Typical bandwidth is on the order of ± 3 °C; bars warmer than 5 °C above the group average are definitely poorly cooled.

It is acknowledged that not all generators are equipped for individual bar temperature measurements. In those plants, it is recommended to measure annually the water flow through the individual bar by ultrasonic methods [23]. This of course requires opening the generator. An upgrade to temperature measurements is an alternative here.

Winding water flow and pressure drop

An increase in hydraulic resistance (winding water flow and pressure drop) of the winding is also an indicator for hollow conductor plugging.

The pressure drop increases with the square of the flow. Therefore, for evaluation and monitoring trends, all pressure-drop data should be normalized to a reference flow [23].

Long-term study of trends, especially comparing with the situation at commissioning of the new generator, identifies the presence of deposition in the hollow conductors. A 10 % increase in pressure drop must already be considered significant.

Pressure drop across filters and strainers

Frequent increase of pressure drop across the system filter and the strainer (if there is one) indicates increased corrosion product release and transport in the system, which is relevant to the risk of hollow conductor plugging (Section 3.2.1).

Therefore, the frequency of filter and strainer changes should be recorded and trends noted. If the frequency increases, stator bar temperatures and winding water flow/pressure drop should be given additional attention.

Gas-to-water conditions

In order to prevent water entering the generator frame in case of a leak in the generator cooling water supply, the gas pressure is always kept higher than the water pressure. Too high overpressure, however, increases the volume of possible gas-to-water leaks.

Gas-to-water leaks replace the oxygen in the stator water tank that is necessary for maintaining the required oxygen level in generators with high-oxygen chemistry. In generators with low-oxygen chemistry, the in-leaking gas may bring oxygen (as an impurity) into the system. A gas-to-water leak in a tight system can be as low as 20 liters/day, and most OEM indicate a range up to 500 liters/day as acceptable for long-term operation.

Usage of makeup water

Addition of makeup water can destabilize the system chemistry (Section 4.3.3). Recording the daily quantities of makeup water may point to unnecessary actions on the system that have increased makeup requirements. Under normal operation, the system should not need more than 1 m³ of makeup per year (there are generators that require only 20 L per year). It is recognized that such a limit is ambitious. It is feasible, however, especially if discipline is kept with water sampling (Section 8.1.3) and the system is inspected for water leakage in each shift. With high-oxygen chemistry, the restriction for usage of makeup water is more relaxed. During maintenance and outages, there may be a need for larger quantities of makeup; in those cases the situation is controlled and limited in time.