

GUIDE ON STATOR WATER CHEMISTRY MANAGEMENT

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1 INTRODUCTION

In early generator technology, the heat losses were removed by gas cooling, either with air or with hydrogen. Water cooling was introduced in 1956 by AEI (UK) with a view to accommodate larger generator power outputs.

For stator water cooling, the stator bars are equipped with hollow strands/conductors or with cooling tubes embedded between the individual solid copper strands/conductors. Traditionally these cooling tubes were commonly made of copper. Other materials, such as stainless steel can also be used. In some cases field windings are also water-cooled, but due to the larger-sized cooling ducts the problems associated with copper corrosion (i.e., Water Chemistry management) are of lesser importance.

There are cooling systems for the water and gas coolants consisting of heat exchangers, circulating pumps for water, fans for gas, filters, and any connecting features. Cooling water for stator cooling is purified by ion exchange, and its dissolved oxygen concentration is designed for either to very low levels (usually less than 20 ppb, but sometimes up to 50 ppb) or to high levels (greater than 2 ppm), depending on the manufacturer.

Table 1 summarizes the number of water cooled generators and their respective water chemistries. In Russia and China there is an additional comparable amount of water cooled generators; they are mostly based on low-oxygen water chemistry.

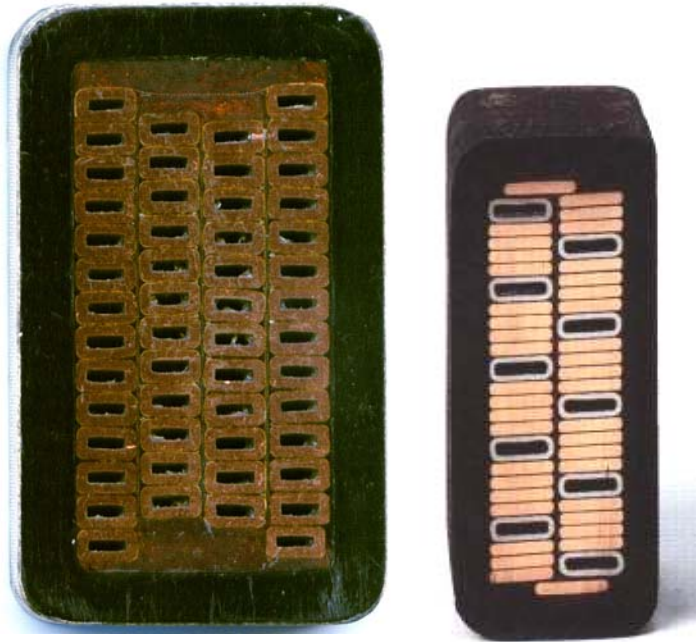


Figure 1 Water Cooled stator conductors

Part of the world	Stators	Rotors	Stator water chemistry		
			high oxygen	low oxygen	alkaline
World ex Russia & China	2000	80	1100	900	200

Table 1: Number of delivered water cooled generators and their water chemistries (status 2009)

Corrosion-related performance has generally been good, but nevertheless a few issues have emerged on an industry-wide scale [1].

- ❑ **Plugging of copper hollow conductors.** If the stator cooling water contains oxygen, the hollow conductors release dissolved copper and / or copper oxide particles that, when re-depositing preferentially, may cause flow restrictions in the strands and thus impair cooling. This is the key chemistry related problem in stator water cooling [2], and will be discussed in more depth in this guide document.
- ❑ **Clip-to-strand leak.** Copper hollow conductors are usually brazed into the coil end water box ("clip"). It is known and considered in design that the usual brazing materials will dissolve slowly. A certain type of braze however produces acid as well as a corrosion potential between braze and copper such that the copper is corroded at a considerably higher rate. The corrosion rate is influenced by stator water chemistry, but the comprehensive solution is to select a more suitable braze material. Although this problem is limited to specific materials, a substantial number of generators have been affected [3].

- ❑ **Conductivity of water.** The electric conductance of water causes the generation of heat across the stator bar insulating hoses. It is required to keep the water below boiling because a steam blanket may cause electric discharge that can destroy the connecting elements. This is especially critical under out-of-normal low flow conditions. The acceptable conductivity limit depends on design and operating conditions. Usual limit values for safe generator operation are 5..to.20 $\mu\text{S}/\text{cm}$ [1].
- ❑ **Deposits on insulating hoses.** These are no general concerns for AC applications, as on stator bars, but have been observed on water cooled DC applications like rotor bars or rectifiers in case of very low oxygen [1][4].

2 CORROSION AND PLUGGING OF COPPER HOLLOW CONDUCTORS IN WATER COOLED GENERATORS

Plugging of the stator hollow copper conductors has affected practically all designs and manufacturers and all water chemistry regimes. Consequences have ranged from a benign increase in stator pressure drop to the destruction of the coil because of partial meltdown of stator bars.

Depending on design and manufacture, the inside dimensions of stator coil hollow conductors are typically 3 to 10 mm wide, 1 to 3 mm high, 3500 to 12000 mm long, and they are packed into the stator bar with numerous bends (Roebel transpositions). These small cross sections and the bends make the hollow conductors susceptible to plugging by copper oxides that are generated in the cooling water system (Figure 2).



Figure 2: Hollow Conductors with Copper Oxide Plugging at the Water Inlet End [9].

Deposition of copper oxides is reported to be heaviest at the outlet end of the conductors, but deposits have also been experienced inside the hollow conductor at bends or at local deformations, and even at

the inlet end. Such plugging of hollow conductors has led to industry-wide equipment failures and production losses.

It should be noted that this is not strictly a corrosion failure; it is caused by the re-deposition of copper oxides that were formed by reaction of copper with oxygen. Actual material loss due to this oxidation is minimal, on the order of a few micrometers. Nevertheless, without this small amount of corrosion and release of the corrosion products into the cooling water, the subsequent re-deposition and ensuing plugging would be impossible.

2.1 Chemistry of copper

Although copper is fairly passive in air and completely in de-aerated pure water, it is rapidly oxidised in water under certain conditions of dissolved oxygen, pH and temperature. Two oxides of copper are known, namely copper (I) or cuprous oxide Cu_2O (red) and copper (II) or cupric oxide CuO (black). In generators, a mix of these oxides is always found, predominantly Cu_2O with low concentrations of dissolved oxygen, and predominantly CuO with higher levels of oxygen.

The following Pourbaix diagram (Figure 3) shows the different phases of copper and its oxides with respect to its metal potential and the pH of the aqueous medium.

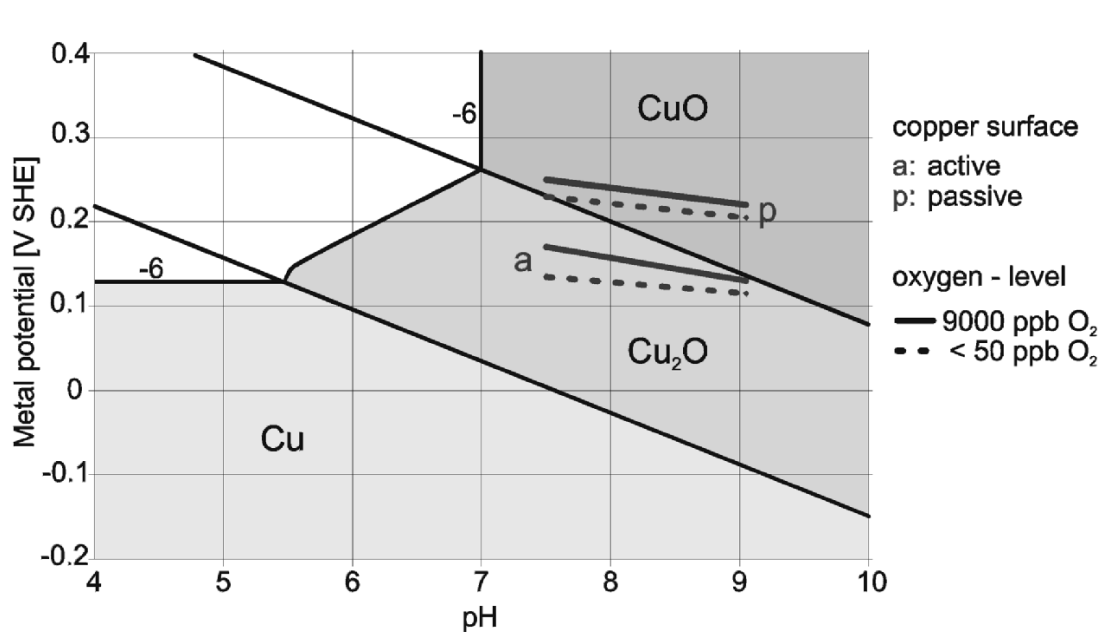


Figure 3: Pourbaix Diagram and Potential of Passivated (Black CuO Layer) and Active (Freshly Pickled) Copper Specimens [5].

The metal potential may be altered by the amount of dissolved oxygen present. Under conditions of low oxygen (<100 ppb) and neutral to alkaline pH, the formation of red Cu_2O is favoured. However, once air is introduced and dissolved oxygen increases, it rapidly changes to the black CuO or a mixture of oxides.

Either oxide forms a stable layer. However, altering either pH or dissolved oxygen or both may shift the equilibrium to a point where a mixture of oxides is found, resulting in instability. This causes the oxide to lose its adherence resulting in migration and deposition elsewhere in the water circuit.

Research results [6][7] indicate that under generator cooling water conditions the solubility of copper oxides is dependent on pH and also, to a lesser degree, on temperature. Figure 4 analyzes the conditions in pure water. Neutral pH is 6.64 at 50°C, and 6.13 at 100°C, but the dissolution of Cu_2O and CuO produces OH^- ions and the water will therefore be slightly alkaline. It is seen that the solubility of both CuO and Cu_2O at 100°C are higher than at 50°C, but the change is less pronounced for CuO .

This dependence of solubility on temperature is also seen at slightly acidic and at moderately alkaline pH values, such as encountered with neutral or alkaline generator water treatment. The trend can however be reversed and solubility at 100°C may be smaller than at 50°C in the following cases:

- at acidic pH, which is within the range of some stator water treatment regimes
- at elevated alkaline pH (for example with NaOH , $\text{pH}_{25^\circ\text{C}} > 10$), which is however not relevant for generator water chemistry

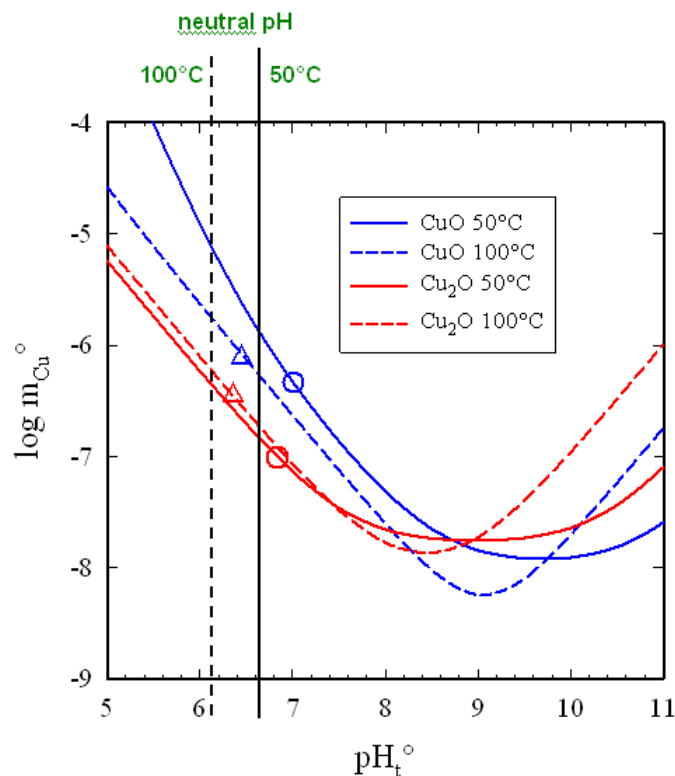


Figure 4: Solubility of Cu_2O and of CuO as a function of the pH at temperature. The vertical lines indicate the neutral pH at 50°C and 100°C, resp. The circular and triangular points indicate the solubility limits in pure water at 50 and 100°C, resp. Because the dissolution of Cu_2O and CuO produces OH^- ions, these points are at a slightly higher pH than neutral [7].

2.2 Mechanism of Plugging

Under the conditions typically found in pure water systems, copper does not react with water in the absence of oxygen [8]. In practice, however, oxygen is in many cases introduced into a generator cooling system, resulting in oxidation of copper hollow conductors. This may occur either inadvertently by in-leakage, or with the make-up water, or inherently, for example by in-diffusion through the insulation hoses in machines where the gas between rotor and stator is air, or intentionally, by leaving the system open to air.

As already mentioned before, the oxide layer formed in a generator system is very thin (a few micrometers) and does not, as such, cause any plugging. But once it becomes mobilized and re-deposits at selected critical spots, those locally accumulated oxides may become thick enough to cause flow restrictions or even full plugging of the hollow conductor. A model for the plugging mechanism of the hollow conductors [9] is shown schematically in Figure 5.

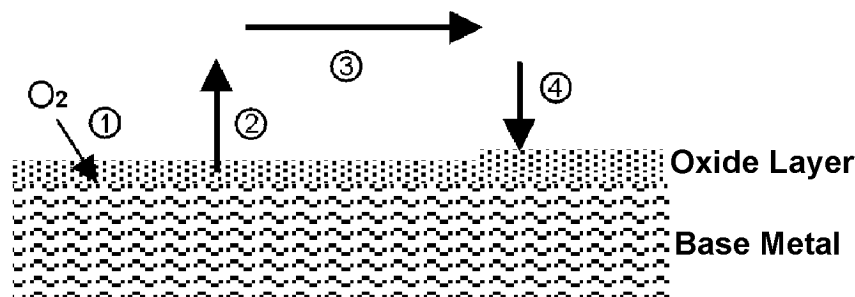


Figure 5: Schematics of the Mechanism for Hollow Conductor Plugging - (1) Oxidation of the Copper, (2) Release of the Oxidized Copper (Particle or Ion), (3) Transport of the Released Copper, (4) Re-deposition of the Migrating Copper [9].

(1) Oxidation

At low-oxygen conditions, all oxygen entering the system is fully consumed by the metallic copper surfaces; otherwise the oxygen content in the system water would increase towards saturation. At high oxygen conditions, dense oxide layers are formed that hinders further access of oxygen to the copper and thus lessens further oxidation.

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). Figure 3 illustrates that all points are close to the $\text{Cu}_2\text{O}/\text{CuO}$ boundary in the Pourbaix (potential-pH) diagram for the $\text{Cu}-\text{H}_2\text{O}$ system. The Pourbaix diagram is for equilibrium conditions, which are different from the dynamic conditions in a cooling system. Therefore, a changing and potentially unstable mixture of oxides may be present in a generator.

The morphology of the oxides is also influenced by the system water chemistry. Figure 6 gives an example of specimens in high-oxygen water (dense polyhedral layer), and in low-oxygen water (flower shaped needles piled one on another on the surface). Alkalisiation of the water also promotes polyhedral oxide structure. The dense polyhedral layer, which, due to its geometry, has a larger area of contact and may therefore, be expected that have better adhesion than the monoclinic form.

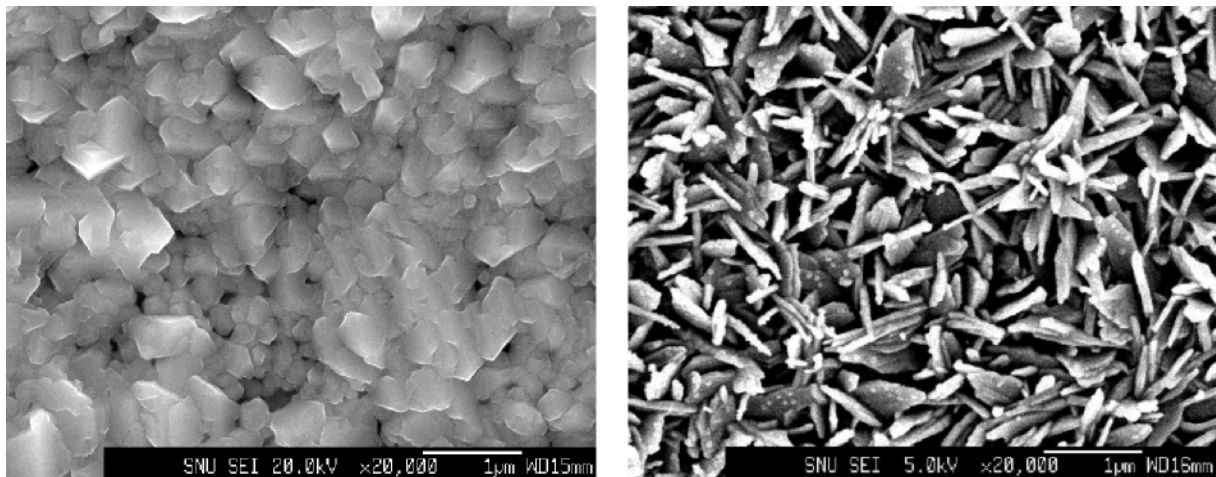


Figure 6: Copper Oxides: Dense Polyhedrons (Left) and Flower-Shaped Needles (Right) Formed in High- and Low-Oxygen Water, Respectively [3].

(2) Release

The first publication on flow restrictions in electric generators was presented in 1974 by the Allianz Center of Technology [10]. The authors investigated the release rates of copper in high purity water (Figure 7). They found that copper release is low at very low and also at high oxygen levels, but has a maximum in the 100 to 500 ppb range. Also, an increase in pH reduces copper release considerably; suggesting that alkalization of the stator water could be beneficial. In consequence, alkaline water treatment was closely investigated and then implemented in the late 1970's [4][11], Figure 8.

It should be noted that these data refer to the release rates and not to the total oxidation rate. The difference between those two rates is the quantity of copper corrosion products (oxides) that stays in place on the metal surface.

As is common with metals that form soluble oxide layers, the copper release rate increases with water velocity. This is due to a more rapid mass transfer from the oxide layer into the bulk liquid, resulting in an increased dissolution rate of the oxide layer.

The copper is released from surfaces as:

- dissolved copper ion (Cu^+ and Cu^{++})
- particle or as colloid (CuO , Cu_2O , and possibly also Cu)

The blue colour of spent ion exchange resin from generator cooling systems is evidence of the release of copper ions, whereas the clogging of strainers and fouling of mechanical filters is a result of particle release.

An investigation made through EPRI [12] showed that particle release plays an important role. The particle release seems to be connected to phase changes between Cu_2O and CuO , possibly by stresses from the change of structure. Such phase changes are initiated by variations of the electrochemical potential. They take place, for example, when the oxygen concentration is changed from its normal range (either less than 20 ppb or greater than 2 ppm) to intermediate concentrations (100 - 500 ppb).

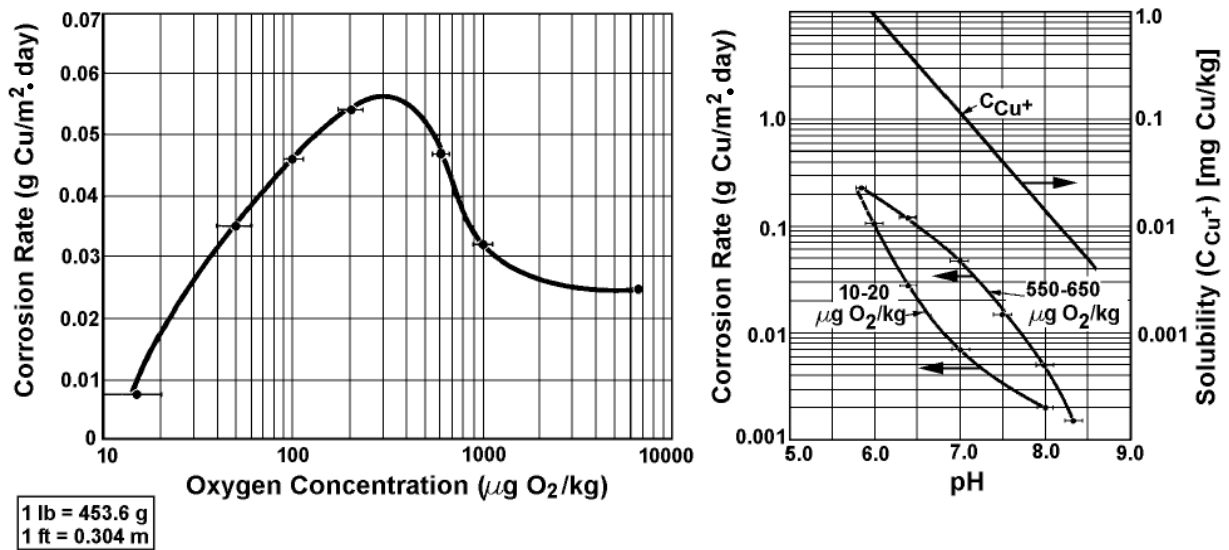


Figure 7: Copper Release Rates at Various Water Chemistry Conditions [10]

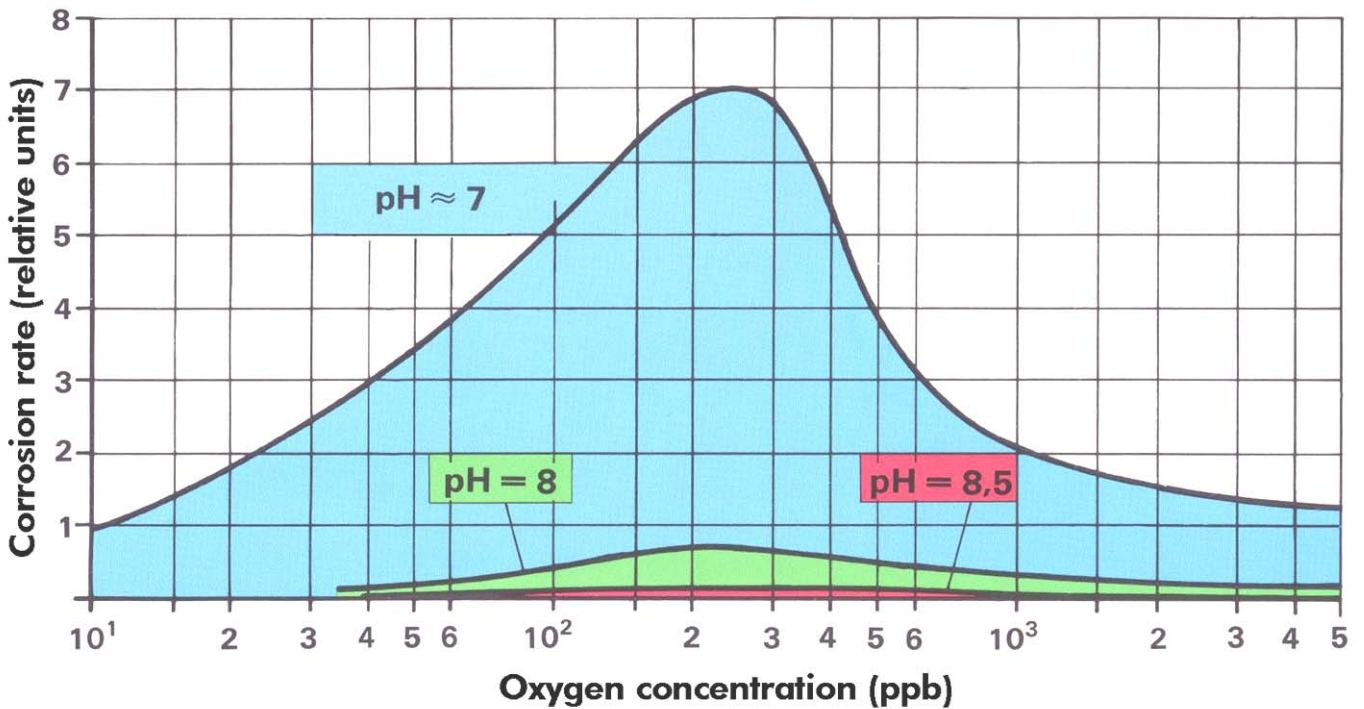


Figure 8: Copper Release Rate as a Function of Oxygen Concentration and pH [4]

(3) Transport

Once the copper and its corrosion products (CuO, Cu₂O) are released to the water, they migrate with the water flow until it is either removed by the ion-exchanger and the mechanical filters / strainers, or until it re-deposits in the system, usually at localized sites in the hollow conductors of the generator winding.

(4) Re-deposition

Re-deposition of copper and oxide particles may take place by gravitational, centrifugal, field stress or other mechanical forces. While some deposits are clearly a mechanical accumulation of oxide flakes, it does not explain the dense layers evidently grown slowly at exposed sites, like conductor inlets (Figure 2). Crystallographic growth onto the seeding oxide crystals at the copper surface provides a mechanism of re-deposition. Here the structure of the seeding crystals is of relevance for the future properties of the deposit layer.

Variations of solubility of copper ions throughout the system are also an important vehicle for driving copper transport and re-deposition. Copper will be released the most where copper solubility is highest, and be re-deposited where it is lowest. Hydrodynamic conditions influencing the mass transport from the liquid to the metal surface also play an important role. The deposit growth at conductors' inlet, as seen in Figure 2 may possibly be related to such hydrodynamic effects.

2.3 Water chemistry options

A good water chemistry regime is essential in eliminating the root cause of plugging. Today there are five different water chemistries being applied (Table 2).

Type of Water Treatment	Keeps Oxidation Low	Keeps Release Rate Low	Direct Transport into Ion-Exchanger	Keeps Re-deposition Low
Low-oxygen / neutral	x			
Low-oxygen / alkaline	x	x		
High-oxygen / neutral		x		
High-oxygen / alkaline		x		
Cationic purification			x	x

x - target parameter for the respective water treatment

Table 2: Strategies for Water Chemistry to Prevent Plugging of the Stator Hollow Conductors

Water chemistry specifications for low- and high-oxygen treatment have been specified in EPRI guidelines which represent industry consensus [13]:



Low-oxygen treatment

A low-oxygen system is defined as a system normally operating with 20 µg/l (ppb) of dissolved oxygen or less. Target is a stable oxygen level as low as possible, ideally zero. According to the EPRI guideline the generator should be scheduled for shutdown and correction if the oxygen level is > 50 ppb.

A low oxygen regime may be obtained with a well maintained system that has no leaks and hence no make-up. If periods between outages are limited the initial increase in oxygen level will have little effect on the winding condition.

Low-oxygen treatment can also be obtained by having the system sealed against air (for example, by a hydrogen or nitrogen gas blanket at a pressure slightly above atmospheric).

Problems arise when de-aeration is violated by air in-leakage. Common causes for air in-leakage in low-oxygen systems are leaky flanges, valves or pump sliding seals, use of significant quantities of aerated make-up water, opening parts of the system for maintenance, or inadequate lay-up. It must also be recognized that air may even be sucked into an high-pressure system by a water-jet effect.

High-oxygen treatment.

A high-oxygen system is defined as a system normally operating with 2 mg/l (ppm) of dissolved oxygen or more. Target is a stable oxygen level corresponding to saturation of water in the water tank with air. According to the EPRI guideline the generator should be scheduled for shutdown and correction if the oxygen level is <1 ppm.

High-oxygen treatment is obtained by leaving the system (for example the water tank) open to air.

Problems arise when aeration is insufficient. Common causes for insufficient aeration in high-oxygen systems are hydrogen leaks into the water that replace the air cap in the water storage tank. In addition, oxygen is consumed slowly by the copper surfaces in the system. Regular or continuous feed of air may be necessary to maintain high oxygen levels.

Alkaline treatment

Alkaline is normally understood to operate with a pH between 8.5 and 9.

Alkaline treatment is obtained by adding a small amount of dilute sodium hydroxide solution (NaOH) to the stator cooling water.

Problems may arise when the pH is not kept stable, for example either by irregular addition of NaOH, ingress of contamination, or by in-leakage of carbon dioxide from air.

Alkaline pH originated in low-oxygen water treatment regimes. Some high-oxygen systems have also been converted to alkaline with promising results.

Additional Techniques

The "cationic purification" method defies the strategies of all the other types of water treatment. The system is kept at a slightly acidic pH ~ 6.0 - 6.5 by means of carbon dioxide from air. Under these conditions, copper oxides are slowly dissolved and Cu-ions are removed in the ion exchanger. This is intended as a temporary treatment and not suitable for permanent operation.

Consideration has been given to the use of reduction 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 filter. Moreover, unexpected side effects may occur. Some may cause 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, without the use of such products.

Some generator cooling water systems have oxygen scavengers combined with the side-stream mixed bed filter. This is achieved either by using scavenger-loaded ion exchangers (sulphite, ascorbic acid, hydrazine), or by using a Pd-catalyzed resin to recombine oxygen with the dissolved hydrogen gas. Those side-stream devices have the disadvantage of having a slow "clean-up" time constant, and oxygen may be more rapidly consumed rather by the copper surfaces 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 interesting. However, it requires extra supervision and maintenance.

3 SOLUTIONS

3.1 Water treatment

Figure 9 shows the chemical parameters for the different water treatment regimes, in combination with the copper release rates. Table 3 summarizes the technologies presently used by the different manufacturers or operators. However, it should be mentioned that all these water treatment regimes have their success if operated properly, but none is without failures.

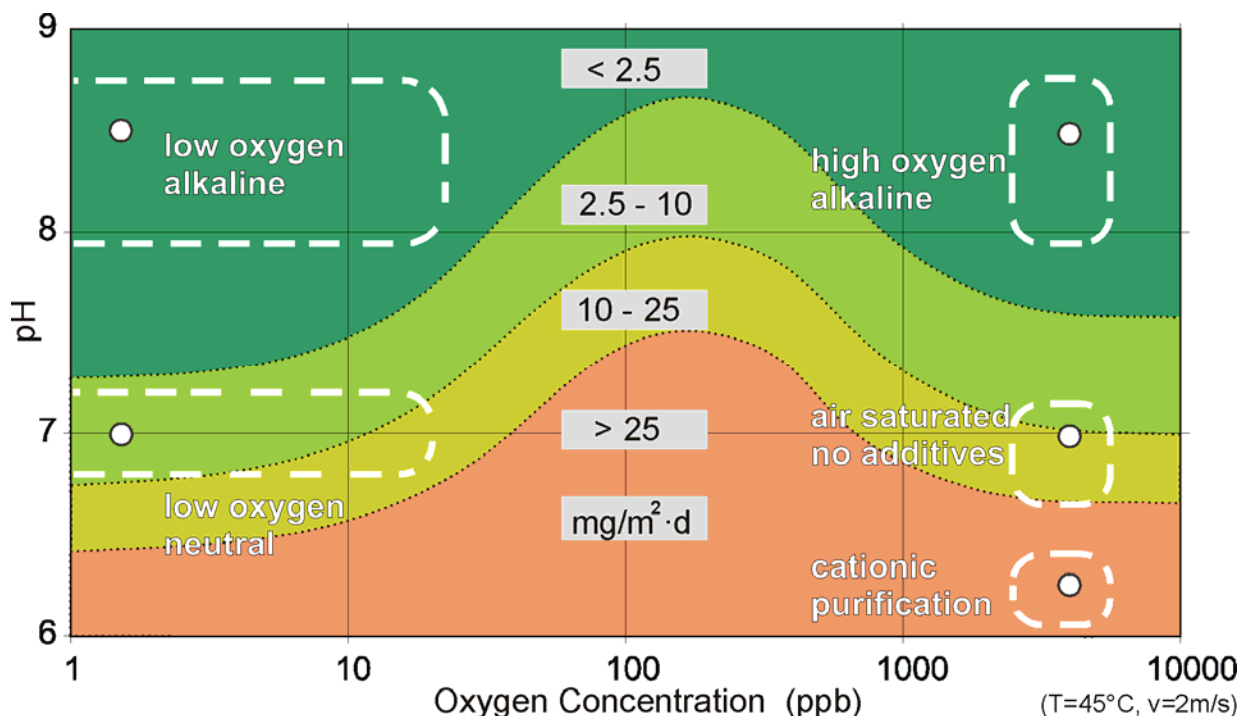


Figure 9: Summary of Copper Release as a Function of Oxygen Concentration and pH (Operating Areas of the Different Water Chemistry Regimes) [9].

Type of Water Treatment	Manufacturer / Operator
Low-oxygen / neutral	Alstom-GEC, Alstom-BBC, Westinghouse, Ontario Power (Canada), Siemens
Low-oxygen / alkaline	Siemens, Eskom (South Africa), Parsons
High-oxygen / neutral	General Electric, Alstom-Belfort, Ansaldo, Hitachi, Toshiba
High-oxygen / alkaline	Siemens, Eskom (South Africa)
Cationic purification	EdF (France)

Table 3: Water Treatment Technologies Applied by Different Manufacturers and Operators

Low oxygen / Neutral pH

This regime is usually preferred when the system can be excluded from contact with air. It is the simplest method of stator water treatment as it requires - besides an airtight system - only keeping water conductivity very low, which is easily achieved in a closed cooling loop by means of a side-stream mixed bed. Only very thin oxide layers are formed.

It must however be acknowledged that prevention of air ingress may be in some cases difficult. The most important measures for preventing oxygen from entering the system are:

- ❑ monitoring potential points for ingress of air (pumps, o-rings, seals, valves, flanges and joints etc; air may be sucked in by water jet even in components subjected to high pressure)
- ❑ de-aeration of makeup water to the cooling water circuit, if not available: strictly limiting the quantities of make-up water
- ❑ blanketing of cooling water storage and make-up tanks with hydrogen or nitrogen
- ❑ extended lay-up of the generator at shut down periods such that it does not get into contact with air (replace water by filling the stator winding with nitrogen, then vacuum dry the hollow conductors below the dew point at the coldest point)

It should be noted that contact with air is also accompanied by traces of carbon dioxide that will lower the pH of the water. Traces of carbon dioxide may also be present in the hydrogen that cools the stator core and field windings in turbo generators, and which may enter the water in case of leaks and by diffusion through the PTFE hoses.

Low oxygen / alkaline pH

This treatment has the basic features of a low oxygen operation. With alkaline treatment, the water is alkalinized by adding a small concentration of sodium hydroxide, in order to lower copper oxide solubility and thus the chance of migration of oxides. The quantity of oxides produced however is as with neutral treatment.

The same requirements as mentioned above for low oxygen/neutral pH treatment apply. In order to achieve a constant low solubility, it is very important to keep the pH value stable.

Alkalization can be achieved in two different ways:

- ❑ injection of a diluted NaOH solution via an injection pump, controlled by conductivity [4].
- ❑ constant leaching of NaOH from an ion exchanger

One method is the use of a dual bed demineralizer, consisting of a mixed bed filter followed in series by a weakly acidic cation exchanger, loaded with a measured quantity of NaOH. The cation exchanger provides constant high purity water, that leaches an equilibrium concentration of NaOH from the cation exchanger [4].

Another method is the use of a dual bed demineralizer, consisting of a mixed bed filter in parallel to a strongly acidic cation exchanger, loaded with NaOH. The Na concentration is controlled by suitable adjustment of the water flow through these two ion exchange beds [14].

Possible ingress of carbon dioxide traces are buffered by the alkalizer and therefore have smaller influence on pH than with neutral treatment.

High oxygen / neutral pH

This possibly can be regarded as the simplest form of stator water treatment, and is put into practice where oxygen cannot be excluded from the system. In this treatment regime, the objective is to form evenly distribution stable oxide layers (CuO).

There is always some dissolution of the oxide layer, but the dissolved copper is trapped by the ion exchanger. However, the risk of forming thick oxide layers cannot be excluded. In order to achieve a stable oxide layer, oxygen levels must be maintained high (e.g. forced air flow into the water tank) at all times. By introducing air, carbon dioxide is also added to the system. It is thus imperative to have a large mixed-bed flow (>10% of stator water flow).

With high-oxygen treatment, carbon dioxide is brought to negligible levels by the large mixed-bed water flow.

High oxygen / alkaline pH

This treatment has the basic features of high oxygen treatment. Here again, the water is alkalized in order to lower copper oxide solubility and thus limiting the chance of migration of oxides.

The same constraints and techniques as described above for alkaline treatment and high oxygen treatment apply.

Cationic purification

This is another variation of high oxygen treatment. The system is kept fully aerated which will result in a slightly acidic pH, ~ 6.0 - 6.5 due to the carbon dioxide from air. For a period of several months a single-bed cation exchanger replaces the mixed-bed ion-exchanger. Copper oxides will dissolve and the copper ions are removed in the cation exchanger and the generator is kept free of oxide deposits. After this "cleaning period", the mixed-bed filter is put back into normal function again. This operating cycle is repeated at regular intervals. It should be noted that this treatment requires profound knowledge of copper solubility and deposition criteria, as well as expert supervision.

3.2 Monitoring

Conductivity. With each of these water treatment regimes, continuous on-line conductivity monitoring assures that high purity water is used.

pH. Measuring pH in high purity water is difficult and may be unreliable. Conductivity is commonly used to indirectly monitor the pH: the known relationship between pH and conductivity for acid and caustic solutions automatically gives the extremes between which the pH must lie (Figure 10).

Oxygen monitoring helps to determine if the system operates within the correct operating range. A continuous on-line instrument is a good investment for detecting some types of adverse situations. However, if oxygen is consumed rapidly in the hollow stator coil strands (made of copper), the water may not show increased oxygen concentration despite a possible oxygen ingress.

Copper. Regular copper analysis in grab samples may give reference values for trending. More useful however is the measurement of the integrated copper release of the generator by analysis of the spent mixed-bed resin [1]. Comparison within a reference user group will indicate out-of-normal situations.

ECP (Electrochemical Potential). This is a novel technique with promising results [1]. ECP may indicate risk conditions for stator bar plugging [12]. By its nature, it also responds to conditions of system pH and oxygen concentration.

In addition, to these chemistry related parameters, the following plant parameters will give important information on the water flow conditions of the hollow conductors [15]:

- ❑ Stator water flow and stator winding pressure drop
- ❑ Stator water inlet and outlet temperature, together with stator water flow and generator load
- ❑ Individual bar temperatures (outlet water hoses), together with generator load
- ❑ Stator slot RTDs (to a lesser degree)
- ❑ Gas-to-water pressure
- ❑ Hydrogen leakage rate
- ❑ Make-up water consumption

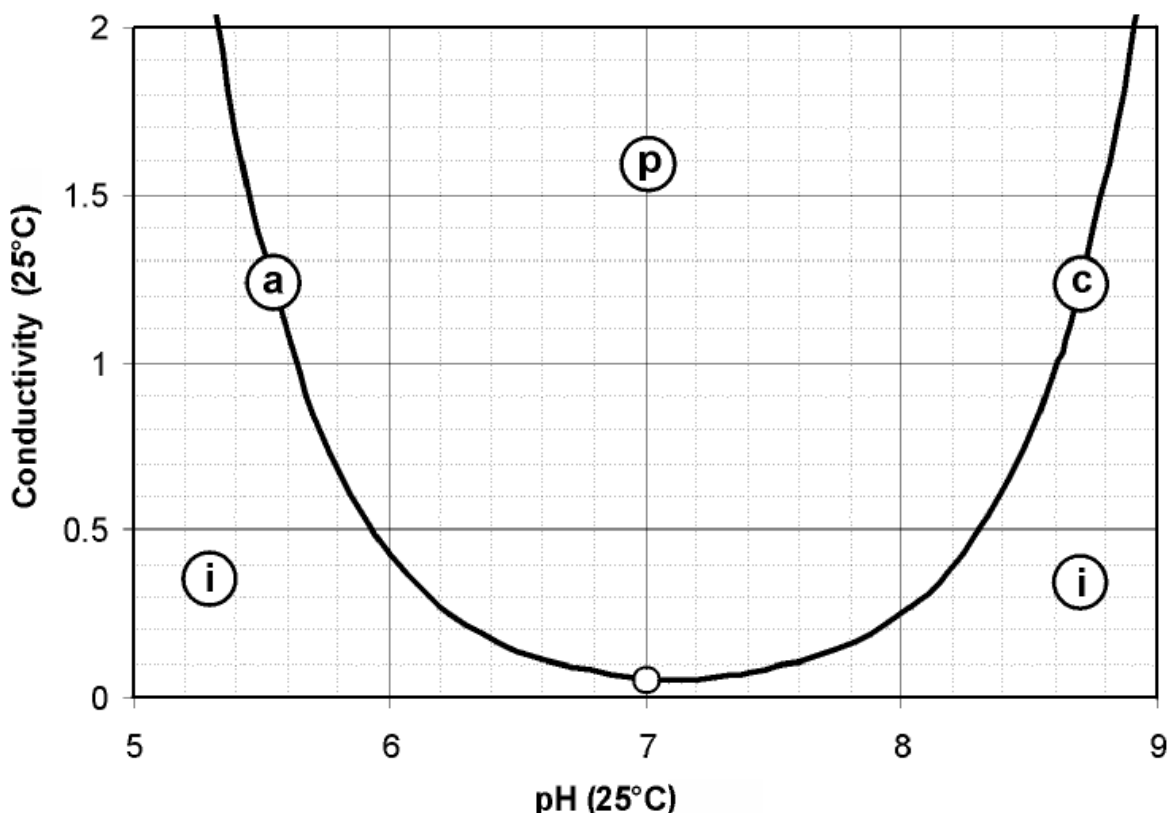


Figure 10: Conductivity ($\mu\text{S}/\text{cm}$) Versus pH: (a) Relation for Strong Acids, (c) Relations for Strong Caustic, (i) Impossible Region, (p) Region for All Possible Electrolytes

3.3 Maintenance

Besides electrical and mechanical maintenance, chemical maintenance is also required. This takes the form of:

- Replacement of ion exchange resin
- Cleaning / replacing of filters
- Maintenance and calibration of sensors
- Inspection of the stator coolant bars for corrosion products and - if required - followed by
- Mechanical and / or chemical cleaning

3.4 Cooling water system design and materials

It should be observed that each type of water chemistry is related to certain design features, and vice versa. Changing water chemistry therefore also means including a review of system design.

General system arrangement

All types of stator cooling water systems provide recirculation pumps, coolers, mechanical filters in the main stream, and ion-exchange filters in a side-stream.

A basic necessity is an expansion tank in order to accommodate the variations in water and system volume during the various changes in operation (e.g. temperature, water losses and refill etc). There are 3 different options for configuration:

- (1) Main stream stator water tank, usually placed close to the pumps suction side or at the top of the generator
- (2) Side-stream head tank, usually at the top of the generator housing
- (3) Dead-end head tank, usually placed at the circulation pump suction side at a level above the generator

High oxygen water chemistry requires option (1), with the tank vent open to air. Consistently high oxygen levels are achieved by continuously blowing air into the tank below water level.

Low oxygen water chemistries can use all three options. Options (1) and (2) require a gas blanket free of oxygen, usually hydrogen, but nitrogen is also used. The head tank in option (3) may be open to air if only small mass transfer between the system and the tank takes place. It may however also be useful to give this tank an oxygen free gas blanket.

Filters, strainers

Every stator cooling water system has a full-stream device to catch particles and debris. Most systems have a mechanical filter with elements with selectivity between 1 and 50 micrometer. There are also systems that use only a strainer between 50 and 200 micrometers that also perform as needed.

It cannot be said in a general manner that the finer the filter is, the better the performance of stator bars. That depends on the conditions in the stator water system. If the copper is in the dissolved form, then the function of the mechanical filter is reduced to being a simple barrier against debris. If there are, however, significant quantities of copper oxides migrating in the system, then fine filtration is required.

Generally, high oxygen units need filters with a finer selectivity, e.g. 1-20 micrometers, low oxygen systems may use a wider range.

When changing type or selectivity of filter elements, the implications for the overall hydraulic performance of the stator cooling water system have to be considered.

As new filter elements usually contain residues and impurities from fabrication, they have to be flushed thoroughly before putting them into service.

Ion exchangers

Usually fresh mixed bed resin, with strong acidic cation resin, and strong basic anion resin in 1:1 equivalent ratio is employed.

The side-stream water flow that has to be cleaned with the mixed bed is between 0.5 and 20% of the stator water flow, depending on system design and type of water treatment. For low-oxygen systems a water flow of 0.5 to 5% is sufficient, while with high oxygen systems a flow >10% is required because, as experience shows, larger quantities of released copper have to be removed and the mixed bed also may have to remove some carbon dioxide from air.

The resin volume should be chosen such that the running time of the mixed is at least one year, or more depending on plant specific maintenance philosophies. Mixed bed sizes may range from 25 to 600 litres of resin.

Usually, there is only one mixed bed vessel. Some designs have 2 vessels in parallel. For replacing the resin, even during plant operation, it is not necessary to have a spare ion exchanger vessel available. It is perfectly acceptable to run a few hours without a mixed bed filter, because a clean system hold good water quality a while without deterioration. If the system is not sufficiently clean, then this is a situation that may be beyond the tasks of the mixed bed itself.

When modifying the mixed bed water flow, the implications for the overall hydraulic performance of the stator cooling water system have to be considered.

Make-up water

If available, make-up water with the oxygen content corresponding to the respective water treatment is used. However, practice shows that this is achievable only in a minority of the power plants. In such case, the use of make-up water has to be minimized.

For low-oxygen treatment, sometimes the de-aerated turbine condensate is used. This condensate has to be demineralised (to remove ammonia and alike) before entering the stator cooling water system. Provisions have to be made for the case of plant shutdown, as in this case there will be no deaerated condensate available

An integrating water volume counter is useful in order to keep track of the quantities of make-up water used.

Cooling water temperature

If a stator coil becomes plugged the bar temperatures will increase. In such case it may be tempting to lower the stator water inlet temperature. This will then reduce the monitored bar outlet temperatures and therefore give more margin in relation to the temperature limits. The temperatures of possible hot spots within the bar will however not be significantly affected and therefore the risk for damage is not improved.

Materials

Piping, vessels, valves, etc of the stator cooling water systems are typically made of stainless steel, but other materials are also used.

Components made of low-alloyed or carbon steel would corrode, producing iron hydroxides and magnetite. Magnetite deposits are magnetic and slightly conductive, and could therefore cause damage inside the generator windings.

Frequently, copper and copper-based alloys are also used in the stator cooling water system, e.g. cooler tubes, valves, even piping. Normally they do not cause any problems.

Plastic materials, like Teflon hoses, filter cartridges etc. have their specific use. Inappropriate materials may decompose and pollute the stator water, or end up in debris that may plug the stator coil.

Stator water pumps usually have sliding ring seals, with one hard-faced ring against a softer counter-ring, for example tungsten carbide impregnated nickel against an impregnated graphite ring. There are no general corrosion related problems with these materials in stator water systems.

It is natural that brazing alloys dissolve slowly in generator cooling water. The corrosion rate should, however, be such that no leaks develop before the end of design lifetime.

Hollow conductors made of stainless steel do not suffer plugging by copper oxides, even if there are copper based components in the stator water system. The chemistry requirements are similar to those for any other similar stainless steel heat exchanger at elevated temperature, like feedwater heaters, low salinity water and no constraints regarding dissolved oxygen.

3.5 Generator Cleaning

If a generator winding does become plugged, the first step would be to perform a mechanical or a chemical cleaning. Cleaning however does not eliminate the root cause. The water chemistry control should then be reviewed in an effort to reduce or eliminate plugging in the future [2][16].

4 CHANGING WATER TREATMENT REGIME OR SYSTEM DESIGN

This guide has pointed out various options on stator water chemistry, design and materials. It should however not be left without a disclaimer and a warning.

Any change from an existing condition to another option should not be undertaken without an in-depth analysis of the implications to the rest of the cooling water system. The risks associated with such changes may be higher than just simply missing the actual targets; they may affect the integrity and reliability of other components in the cooling water system.

The guide is not intended to provide instructions for the implementation of such modifications. The advice of an institution that has practical experience or expertise on this implementation is strongly recommended.

5 CONCLUSION

Our purpose, in this guide, was to give information on the common options to manage stator water chemistry, as well as on their advantages and drawbacks. Depending on manufacturers or on utilities, several solutions are possible and have been described in detail above.

6 TWO CASE STUDIES

In the following case studies, two major utilities have modified the original water chemistry in order to improve their performance. In both cases, the original water chemistry was related to problems that prompted the utility to search for another solution. The first example is based on alkaline, and the second one on temporarily acidic water treatment. However, it should be noted that these two examples represent solutions that are quite different from the majority of all other pure water chemistry regimes. Presenting these cases is not an endorsement of either, but rather demonstrates how two large national utilities have separately addressed their individual situations.

6.1 Eskom solution: Changing to alkaline treatment regimes

Eskom presently has 66 water cooled generators, from 5 different original manufacturers. 48 of them were provided to operate under low-oxygen / neutral water chemistry, and 18 under high-oxygen / neutral water chemistry.

Operating experience with both low and high oxygen under neutral pH water treatment has been found to be unsatisfactory, in some cases led to plugging of the hollow conductors, necessitating mechanical and chemical cleaning and to two cases of catastrophic failure. In order to improve the situation, Eskom has converted up to date all 66 water cooled generators from neutral to alkaline treatment. Both low-oxygen as well as high-oxygen systems have been converted with entirely satisfactory results.

Earlier recommendations were to install a small dosing pump to introduce a dilute sodium hydroxide solution into the cooling water circuit. However, an alternative, to avoid the potential control problems when utilizing an injection tank and a dosing pump was chosen. The required level of alkalizing is done by the use of two mixed bed ion exchange columns, both of which are continuously in service under selected different flow rates installed in a parallel flow configuration.

The two vessels are utilized as mixed bed ion exchangers with the strongly acidic cation exchange resin in hydrogen form in one bed and in sodium form in the other. The mixed bed ion exchanger in sodium form treats approximately 90% of the side-stream flow whilst the conventional mixed bed with hydrogen form cation resin treats the remaining 10% of the flow. Adjustments to keep within the specified limits for this mode of treatment are very infrequent so very little operator intervention is required. In order to maintain the desired level of alkalization, it may be necessary to inject from time to time a minor quantity of NaOH into the water but usually only after a complete drain and refill of the system and therefore no dosing systems have been provided. The sodium hydroxide which is needed in this case is usually applied either through the buffer tank during filling or with a syringe through a convenient access point in the stator water loop. It is stressed that this would be a very rare occurrence indeed.

Eskom experience has shown that, elevated pH delivers the most consistent results and this experience over more than 20 years has not resulted in a single case of plugging with either high or low oxygen systems.

Only top quality new pre-regenerated resin is used. In the past, for single mixed bed systems as required for neutral pH conditioning the resin ratio were normally 1:1 equivalents with strongly acidic cation in the hydrogen form, and strongly basic anion, in the hydroxyl form.

For dual mixed bed systems as required for the elevated pH conditioning, one vessel contains strongly acidic cation exchange resin in the hydrogen form and the other strongly acidic cation resin in the sodium form. The strongly basic anion exchange resin for both mixed beds is in the hydroxyl form. In all cases the resin is replaced after 18 months of operation or earlier if chemical conditions cannot be maintained.

Experience has shown that a higher ratio of anion resin to cation resin in the sodium form mixed bed offers distinct advantages in terms of achieving and maintaining the required elevated pH conditions. A

ratio of 2:1 equivalents of anion to cation resin is favored. The resin ratios for the second mixed bed with the conventional hydrogen form cation resin are retained at 1:1 equivalents.

When replacing the resins, co-current rinsing is made before the ion exchanger is returned to service. This is necessary to remove any manufacturing residuals from the resins, thus preventing them from contaminating the generator cooling water system.

Although it is a mechanical maintenance function to replace the mechanical filter cartridges, the chemical services department is involved as well. This way the extent of corrosion product fouling may be assessed. Since the conversion to alkaline treatment, virtually no corrosion products are ever found in the filters.

6.2 EDF solution for aerated systems: cationic purification

Since the early 1980's and up to 1995, EDF has faced several plugging problems on its aerated water cooled generators causing significant production losses due to reduced load operation and unscheduled outages for off-line cleaning.

Before the late 1980's, all EDF nuclear plants generators were operated under "low oxygen/neutral" conditions which were high-purity water without any additives and under low oxygen. But recurrent problems of hollow conductor plugging lead EDF to change operating conditions from low to high oxygen.

Experience with hollow conductor plugging in de-aerated water/neutral treatment cooling system proved that any period of change from low to intermediate oxygen concentrations was particularly damaging. The stringent requirement on low O₂ content (< 50 ppb) to stay away from high corrosion rate of copper was, on a maintenance point of view, a heavy constraint. Indeed, keeping a circuit air-tight is rather difficult: on several de-aerated water cooling systems, air-leak at pump intake increased the speed of copper oxide precipitation leading to severe strand plugging in an irreversible process. Such cases caused, in the late 1980's, to choose the aerated water/neutral treatment cooling system for its ease of maintenance and better behavior.

However, operating under these new conditions showed very quickly that switching from a de-aerated regime to an aerated one was not sufficient to prevent the generator water cooling system from plugging phenomena: several cases of plugging occurred in the early 1990's on aerated water/neutral treatment systems proving that the chemical parameters were not fully mastered at that time.

In 1995, research and metallurgical investigations showed that the bullet-shaped plugs located in the copper hollow conductors were due to CuO (tenorite) precipitation. This information allowed EDF to design and implement a soft on-line curative process named cationic purification on a total of 54 generators of 1080 - 1710 MVA output [17][18].

This patented process is based on:

- reducing the operating pH of the cooling water. Indeed with a pH between 6 and 7, the solubility of CuO is increased within a factor 100, thus the protective Cu₂O layer remains uncorroded.
- Increasing the retention capacity of the Cu²⁺ ions released by the dissolution of CuO plugs with the addition of an extra demineralizer loaded with a cationic ion-exchange resin.

It is worth noticing that this process is effective only if the hollow conductors are not totally plugged. The cooling water must be able to flush across each conductor for effective cleaning, otherwise a prior mechanical flushing is necessary.

The cationic purification operating parameters are specific for each machine i.e. the cationic demineraliser size and resin volume as well as the purification rate must be calculated according to the design of the water circuit, the copper surface in contact with the cooling water, the flow rates in different areas of the system (water tank, demineralizer) and, of course, the chemical data under normal operation (O_2 , dissolved copper concentration).

Chemical parameters for the water such as O_2 , pH, Cu^{2+} concentration and water conductivity must be carefully monitored. So, a too low cooling pH can lead to large amount of Cu^{2+} released in water, causing re-precipitation of CuO and perturbing moving of copper oxide plugs. Thereby, cationic purification must never be considered as a normal operating mode but really as a temporary curative treatment.

Last but not least, the use of cationic purification doesn't require a machine shutdown. It can be conducted on-line without any load restriction if the stator plugged strand temperature allows it. It only requires an extra deioniser installation loaded with the appropriate cationic resin. The treatment lasts about 4 to 12 months, the copper loss is less than 5 $\mu\text{m}/\text{year}$ and the water conductivity remains under 0,4 $\mu\text{S}/\text{cm}$.

Based on EDF operating experience and on the information available from research on copper oxide formation, extra specifications have been added to the design of stator water cooling system:

- Deioniser must be sized according to the surface area of copper in contact with water.
- Two deionisers are necessary to implement cationic purification as soon as required.
- Main filter mesh must be about 1 μm to remove all copper oxide particles.

7 REFERENCES

- [1] EPRI Report 1015669, Dec 2008. Turbine Generator Auxiliary System Maintenance Guides - Volume 4: Generator Stator Cooling System.
- [2] EPRI Report 1004704, July 2002. Guidelines for Detecting and Removing Flow Restrictions of Water-Cooled Stator Windings.
- [3] R.Svoboda, O.Jonas. Corrosion in Electric Generators. Chapter 16 of "Low Temperature Corrosion Problems in Fossil Power Plants--State of Knowledge Report". EPRI Report Nr. 1004924, Dec 2003.
- [4] K.Schleithoff, H.W.Emshoff. Optimierung der Konditionierung von Generatorkühlwasser. (Optimization of Generator Cooling Water Conditioning). VGB conference on Chemie im Kraftwerk 1989, VGB Kraftwerkstechnik 70(1990)9, pg 794-798.
- [5] R.Svoboda, H.Sandmann, H.G.Seipp, and C.Liehr. Water Chemistry in Generator Water Cooling Systems. International VGB/EPRI-Conference on Interaction of Non-Iron Based Materials with Water and Steam, Piacenza / IT, June 1996. TR-108236.
- [6] D.A.Palmer, B.Bénézeth, J.M.Simonson: The Solubility of Copper Oxides around the Water-Steam Cycle. 7th International EPRI Conference on Cycle Chemistry in Fossil Plants. Houston / USA, June 2003.

- [7] R.Svoboda, D.A.Palmer. Behaviour of Copper in Generator Stator Cooling-Water Systems. 15th International Conference on the Properties of Water and Steam, Berlin / DE, Sep 8 - 11, 2008. Power Plant Chemistry 11(2009)2, pg 70-76.
- [8] M.Pourbaix. Atlas of Electrochemical Equilibria in Aqueous Solutions. Pergamon Press, Brussels, 1966.
- [9] R.Svoboda, H.G.Seipp. Flow restrictions in water cooled generator stator coils - prevention, diagnosis and removal. Part 1: Behaviour of copper in water cooled generator coils. Power Plant Chemistry, 6 (2004) 1, pg 7-14.
- [10] P.H.Effertz and W.Fichte. Beeinflussung der Kupferkorrosion in hochreinem Wasser (Influencing Copper Corrosion in High Purity Water). Jahrbuch vom Wasser, 1974.
- [11] W.Oschmann. Probleme in Kühlsystemen wassergekühlter Generatoren (Problems Encountered in Generator Water Cooling Systems). VGB Conference on Power Plant Chemistry, Essen / DE, Oct 1979.
- [12] EPRI Report 1006684, Feb 2002. Prevention of Flow Restrictions in Generator Stator Water Cooling Circuits.
- [13] EPRI Report 1004004, Dec 2001. Generator Cooling System Operating Guidelines. (Cooling System Maintenance and Performance Guidelines During Startup, Operation, and Shutdown).
- [14] J.D.Aspden and E.Maughan. Maintaining the Flow of Revenue from the Production of Electrical Power: Optimization of the Chemistry of Generator Cooling Water Systems – One Utility's Experience over More than 20 Years of Operation. EPRI's Seventh International Conference on Cycle Chemistry in Fossil Plants. Houston / USA. June 3-5, 2003.
- [15] R.Svoboda, R.Chetwynd: "Flow restrictions in water cooled generator stator coils - prevention, diagnosis and removal. Part 2: Detection of flow restrictions in water-cooled generator stator coils. Power Plant Chemistry", 6 (2004) 2, pg 71-79.
- [16] R.Svoboda, C.Liehr, H.G.Seipp: "Flow restrictions in water cooled generator stator coils - prevention, diagnosis and removal. Part 3: Removal of flow restrictions in water-cooled generator stator coils". Power Plant Chemistry, 6 (2004) 3, pg 135-144.
- [17] D.Vermeeren, J.C. Gabriel, J.L. Drommi. *On-Line flushing of plugged hollow conductors in stator bars". EPRI 1997 - April 14-16 1997 - Florence / IT.
- [18] J.L.Drommi, F.Mesnage. "How to prevent hollow conductor plugging : EDF solution for aerated systems". IRMC (Iris Rotating Machine Conference) 2002 - June 10-13, 2002 - San Antonio / USA, also: PPChem 5 (2003) 4, pg 203-205.