

Chemistry-Related Monitoring of Generator Cooling Water Systems

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ABSTRACT

The generator is a key component of an electric power plant, and if the generator is not functioning, the rest of the power plant cannot fulfill its proper purpose. Therefore, adequate generator water chemistry and its monitoring are essential to avoiding component damage and loss of availability. Automatic monitoring parameters are conductivity and in some cases also oxygen. Measuring pH is not recommended. A novel technique provides the electrochemical potential, which research indicates may be more meaningful than oxygen and pH. Laboratory analyses of the quantity of copper in the spent mixed-bed resin are also a useful indicator of long-term abnormal situations.

INTRODUCTION

Generator cooling water systems are closed systems with corrosion resistant materials and no generic sources of impurity ingress. It is therefore relatively easy to keep high water purity by means of main stream filtration as well as by a side-stream mixed bed.

The aim of generator water chemistry is therefore rather limited, but nevertheless important for avoiding problems. It must be remembered that the generator is a key component of an electric power plant, and if the generator is not functioning the rest of the power plant cannot fulfill its proper purpose.

From worldwide experience with some 2 000 water-cooled generators from various OEMs, some dating back as far as 1956, the following chemistry-related problems have emerged as more general issues [1].

Plugging of Copper Hollow Conductors by Copper Oxides

This subject is described extensively in the literature, summarized in [1–4]. Under the conditions typically found in pure water systems, copper does not react with water in the absence of oxygen. However, in many cases, oxygen is introduced into a generator stator cooling water system, resulting in oxidation of copper 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.

The quantities of oxides are small in relation to the thickness of the strands. As a result, there are no significant corrosion effects on the hollow conductors, as long as no corrosive additives or acidic pH is used. Water quality, as determined by electrical requirements, is sufficient for avoiding corrosion.

Small cross sections and bends make the hollow conductors however susceptible to plugging by copper oxides. Plugging of the stator hollow copper conductors has affected practically all designs and manufacturers, and also all water chemistry regimes. Consequences have ranged from a benign increase in stator pressure drop, to overheating and deterioration of the electrical insulation, and in a few cases even to the destruction of the coil because of partial meltdown of stator bars.

Attack on Brazing Material

The brazing materials used for attaching the hollow conductor to its water chamber are not completely inert in water but will dissolve slowly. This is considered in the component design, but some brazes dissolve in water into phosphoric acid, which will attack the hollow conductor in the contact area. Although this is a specific materials issue, it can be influenced by water chemistry, low oxygen content being beneficial [1].

Leaks in the Secondary Coolers by Cooling-Side Corrosion or Vibration

Such leaks do not originate in stator water chemistry. As the water pressure in the generator water system should be kept higher than in the cooling system, there will be no

cooling water in-leakage, but a loss of stator water. This will require the addition of make-up water, which frequently does not meet the requirements for generator operation (e.g., oxygen content), and may lead to the problems listed above.

CHEMISTRY REQUIREMENTS FOR GENERATOR WATER COOLING

Besides the scope of generator water chemistry listed in [Table 1](#), it must be mentioned that adequate provisions for

conservation during shutdown (lay-up) are equally important [3,5].

The ensuing water chemistry requirements are formulated in water chemistry specifications, [Tables 2–4](#). For generators with copper hollow conductors, the EPRI specifications are given, as they summarize their research as well as industry consensus. Of course, individual OEM specifications may have some variations. The specifications for stainless steel hollow conductors are taken from a major OEM as no neutral body has yet issued such specifications.

Target	Water Chemistry Parameters
Ensure electrical insulation across the water-filled insulation hoses	Electric conductivity
Avoid hollow conductor plugging	Oxygen content, pH, ECP, dissolved metals, particles and debris
Avoid general corrosion issues	Electric conductivity

Table 1:
Main targets of generator water chemistry.

Parameter	Normal Operating Value	Short-Term Action Level	
Conductivity (25 °C) [$\mu\text{S} \cdot \text{cm}^{-1}$]	≤ 0.5	> 10	neutral water treatment
	≤ 2	> 10	alkaline water treatment *
Oxygen [$\mu\text{g} \cdot \text{L}^{-1}$]	≤ 20	> 50	
		> 10 above normal	"start troubleshooting"
ECP ** [mV (SHE)]	< 223	> 266	

Table 2:
EPRI specifications for low-oxygen stator water chemistry with copper hollow conductors (abridged) [5]. A low-oxygen system is defined as a system normally operating with $20 \mu\text{g} \cdot \text{L}^{-1}$ of dissolved oxygen or less. The target is a stable oxygen level as low as possible, ideally zero.

* $8 < \text{pH} < 9$

** electrochemical potential (ECP): tentative specifications [6].

Parameter	Normal Operating Value	Short-Term Action Level	
Conductivity (25 °C) [$\mu\text{S} \cdot \text{cm}^{-1}$]	≤ 0.5	> 10	neutral water treatment
	≤ 2	> 10	alkaline water treatment *
Oxygen [$\text{mg} \cdot \text{L}^{-1}$]	≥ 2	< 1	
ECP ** [mV (SHE)]	> 315	< 305	

Table 3:
EPRI specifications for high-oxygen stator water chemistry with copper hollow conductors (abridged) [5]. A high-oxygen system is defined as a system normally operating with $2 \text{mg} \cdot \text{L}^{-1}$ of dissolved oxygen or more. The target is a stable oxygen level corresponding to the saturation of water with air.

* $8 < \text{pH} < 9$

** electrochemical potential: tentative specifications [6].

Parameter		Normal Operating Value	Short-Term Action Level
Conductivity (25 °C)	$[\mu\text{S} \cdot \text{cm}^{-1}]$	≤ 0.3	> 10
Copper	$[\mu\text{g} \cdot \text{L}^{-1}]$	≤ 10	—
Iron	$[\mu\text{g} \cdot \text{L}^{-1}]$	< 20	—

Table 4:

OEM specifications for generators with stainless steel hollow conductors [7].

No significant levels of copper and iron are encountered in a generator cooling water system made of stainless steel, even with coolers of copper-alloyed tubing. In order to cover a wide range of possible cooling water system configurations, copper and iron are nevertheless specified in order to prevent fouling of the hollow conductors. A limitation of oxygen is not required because under the given conditions oxygen does not significantly reduce the margin of the material against corrosion.

CHEMISTRY-RELATED MONITORING

Table 5 lists the recommended monitoring parameters. Some of these parameters go beyond the purely chemical ones; they are nevertheless mentioned here because they give a better context to the chemist's data. The whole cooling water system has to be considered with a more holistic approach to take into consideration interdependent relationships between many parameters. This should be understood as an invitation for the plant chemist and the generator engineer to share their thoughts. In the following, only the chemical parameters are discussed in detail.

In case of specific problems, it may be useful to add appropriate parameters.

It is important to remember that any withdrawal of water from the system is undesired or even detrimental. The make-up water that has to be added in such a case may upset stator water chemistry, for example by adding air-saturated water into low-oxygen chemistry systems. Monitors must therefore be in-line, with the effluent recycled back into the system. The best situation would be for the monitors to be in a separate slip stream to enable probe maintenance during operation.

Parameter	Importance	Monitoring Frequency
Instruments		
Conductivity	most important chemical parameter	continuous
pH	no good in high-purity water	—
Oxygen	useful	continuous
Electrochemical potential	most promising novel technology	continuous
Coil/bar temperatures *	critical parameter	continuous
Coil flow *	critical parameter	continuous
Δp coil inlet/outlet *	important indicative information	continuous
Δp gas/water *	important parameter	continuous
Hydrogen leakage *	important parameter	daily
Make-up consumption	good indicative information	daily
Laboratory Analysis		
Copper concentration	limited usefulness	4 weeks or as needed
Copper in ion exchanger and filter	good indicative information	at each resin change

Table 5

Recommended monitoring parameters for a generator cooling water system [4].

* these parameters refer to the water-cooled stator

Δp pressure difference

Conductivity

Electric conductivity is the key parameter of the generator water specifications.

The electric conductivity of water is dependent on temperature. Conductivity data are usually referred to a temperature of 25 °C.

It has to be taken into account that the conductivity probes are usually inserted directly into the generator cooling water system. The sample may have a temperature of 40–60 °C. While the conductivity of pure water at 25 °C is $0.054 \mu\text{S} \cdot \text{cm}^{-1}$, it is $0.25 \mu\text{S} \cdot \text{cm}^{-1}$ at 60 °C. Pure water has a larger temperature coefficient than its impurities, which complicates temperature compensation. Instruments with appropriate temperature compensation have to be used.

Built-in conductivity probes are subject to the flow conditions in the pipe they are inserted in. If the location is inappropriate (e.g., strong turbulence in a bend), then the results may be unstable or incorrect. This is a generic problem in some designs that can be avoided by installing the probe in a slip stream.

All OEMs have 2 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 the OEM, values between 0.3 and $2 \mu\text{S} \cdot \text{cm}^{-1}$ are common.

Systems operating with alkaline water treatment will have a higher normal conductivity limit, because the alkalizing agent will provide a background conductivity; see [Figures 1 and 2](#).

- **Maximum conductivity limit**
The maximum conductivity limit usually refers to the risk of water boiling in the insulating water hoses. Depending on OEM and design, values between 6 and $20 \mu\text{S} \cdot \text{cm}^{-1}$ are common.

The required action depends on the OEM. In some designs, the generator is tripped automatically with no delay, or with some delay. Other designs call for manual generator trip within a limited time. And other designs link this shutdown with the simultaneous loss of cooling water flow.

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

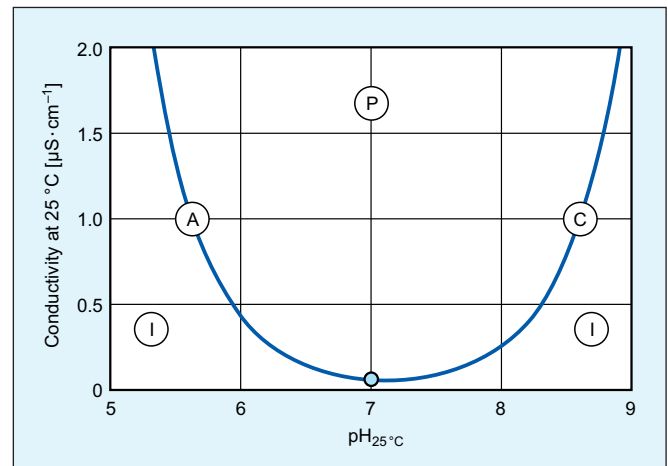


Figure 1: Conductivity versus pH.

- A relation for strong acids
- C relation for strong caustic
- I impossible region
- P region for all possible electrolytes

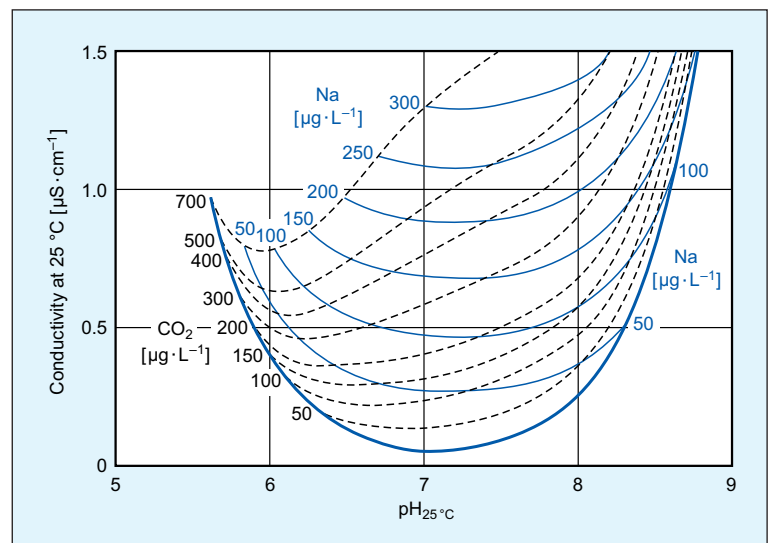


Figure 2:

Conductivity and pH of mixtures of NaOH with CO_2 – solutions in high-purity water.

Pure NaOH is represented by the right-hand border curve; the dotted curves are for various concentrations of CO_2 (courtesy Alstom).

In many designs there is also a conductivity measurement at the mixed-bed outlet, monitoring its performance. The mixed bed, however, depletes normally due to the copper that it absorbs with time.

pH

Direct pH measurement in high-purity water is delicate and prone to errors. Special instruments would be required with such low conductivity as in generator cooling water. The electrode membranes of such commercial instruments would either let sample backflow pass into

the electrolyte, or let electrolyte pass into the stator water, depending on pressure conditions.

The efforts required for a suitable instrument are, however, not necessary as pH can easily be indirectly controlled by measurement of conductivity; Figure 1. Thus, with a conductivity of $0.15 \mu\text{S} \cdot \text{cm}^{-1}$, pH will automatically be within 6.5–7.8, which is considerably more reliable than the data from a pH meter.

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 alkali (sodium). Here the conductivity is compared to the theoretical conductivity of NaOH. Lower conductivity indicates the presence of an anion, thus lower pH; Figure 2.

It is better to have no pH meter than an unreliable one that opens up more questions than it answers. Conductivity is a good substitute parameter.

Oxygen

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

- With high-oxygen water chemistry, oxygen measurements are unquestionably of direct use in keeping oxygen sufficiently high.
- With low-oxygen systems, the information may, however, be inconclusive.

Ingress of oxygen into a low-oxygen system will cause a rise in oxygen concentration, which is counteracted by removal of oxygen by consumption on the copper surfaces or by de-aeration. If there were no such oxygen removal, the system would go into oxygen saturation ($5\text{--}8 \text{ mg} \cdot \text{L}^{-1}$, depending on temperature). An oxygen concentration below saturation always represents the equilibrium between ingress and removal. Let us 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.
- Or the copper may be very reactive, consuming oxygen rapidly. In such a case, oxygen ingress is not seen at all, even though it may produce enough oxides, oxide migration and localized copper oxide deposits.

Oxygen level should therefore always be seen in correlation with the speed of oxygen consumption within the system. Thus high oxygen values may not necessarily be bad

if at the same time the consumption rate is low; on the other hand, a rapid consumption rate may be detrimental.

The oxygen consumption rate can be measured, when for example some air-saturated water is brought into the system (e.g., addition of make-up water).

Electrochemical Potential (ECP)

Phenomena like corrosion and deposition are governed by the ECP. The ECP is a complex parameter, being determined by oxidizing and reducing agents in the water, pH, temperature, impurities, materials, etc. The ECP is therefore a summary parameter that describes the chemical reactivity better than any single parameter, better even than oxygen.

Laboratory investigations by EPRI have indicated a correlation between copper release, oxide deposition and ECP. Suitable ECP sensors have been developed and their use in generators with high oxygen as well as with low oxygen has been demonstrated [6].

Tentative ECP specification values have been developed ($< 223 \text{ mV (SHE)}$ for low-oxygen systems, or $> 315 \text{ mV (SHE)}$ for high-oxygen systems). Future application will lead to a refinement of the technology.

It is sufficient for plant monitoring to compare the instrument values with the specifications. For a detailed analysis it is, however, practical to view such data in the Pourbaix diagram.

Figure 3 shows results of laboratory tests with freshly pickled and with passivated copper specimens, in low-oxygen and in high-oxygen water. It can be seen that the surface condition has a greater influence on the ECP than the oxygen concentration in the water.

Figure 4 gives a practical example from tests in a power plant with low-oxygen stator water chemistry. It can be seen that this plant operated above Alarm Level 1. It should be mentioned that this generator suffered from oxide deposits.

In one test, 10 L of air-saturated water were added to the system. The pH dropped to 6.3 (as determined by the conductivity increase), oxygen rose temporarily to $30 \mu\text{g} \cdot \text{L}^{-1}$ and disappeared within 1 h, and the ECP rose by 36 mV (SHE) and stayed elevated for several hours. The rise in ECP was mainly caused by the drop in pH; the increase in oxygen evidently did not influence ECP significantly. This insensitivity to the oxygen ingress should not be interpreted as a shortcoming of the ECP data; the interpretation is that this oxygen ingress did not cause a detrimental situation (it is rather the drop in pH which was detrimental).

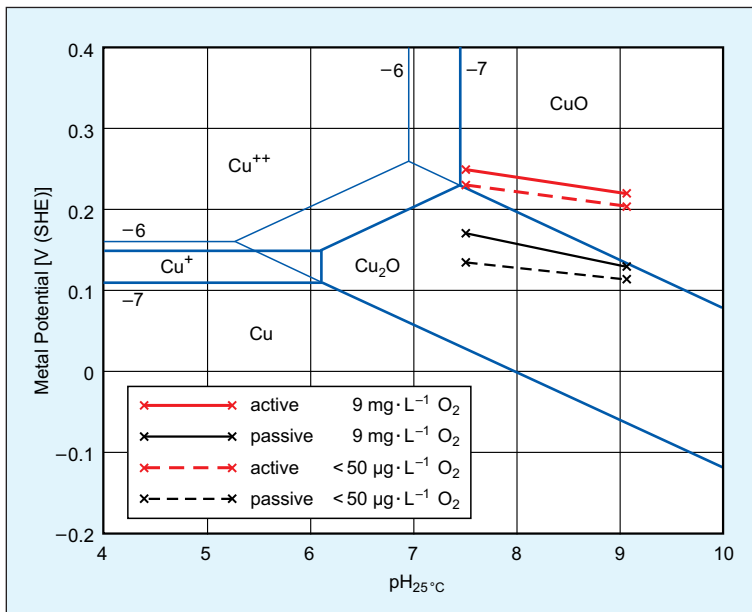


Figure 3:

Pourbaix diagram of Cu at 25 °C.

The solid blue lines indicate the domains of the various Cu species. "-6" and "-7" represent the respective molar concentration of the ionic species ("-7" therefore means $6.4 \mu\text{g}\cdot\text{L}^{-1}$).

The figure also includes results from laboratory tests on active (freshly pickled) and passive (black CuO layer) copper specimens, under low-oxygen and high-oxygen water chemistry.

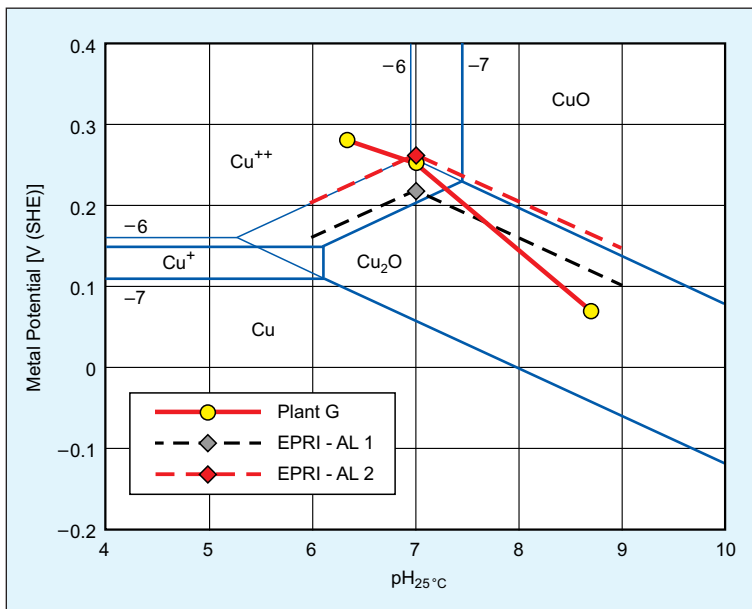


Figure 4:

Pourbaix diagram of Cu at 25 °C.

The diamond points indicate the EPRI specifications for low-oxygen systems and the semi-dotted lines their extension into alkaline and acidic media.

The yellow dots/red line indicate the values before (pH 7) the tests, during the test with ingress of 10 L of air-saturated water (pH 6.33), and during the test with alkalization by injecting NaOH (pH 8.7).

AL action level

In another test, the water was alkalized by addition of NaOH. The pH rose to 8.7, and ECP dropped by 180 mV (SHE), which is clearly more than the pure effect of pH.

Even though ECP monitoring seems more like a scientific tool, it is nevertheless strongly recommended to consider this technique for routine monitoring. With more widespread use, a broader database for the evaluation of these data will become available. The price of an ECP monitor is probably less than the cost of some other less useful analyzers sometimes used in generator cooling water systems.

Copper Concentration

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

Here again, the copper concentration is governed by the release of copper counteracted by the removal of copper in the filters and ion exchangers, as well as by deposition in the coil. As a result, copper concentration values also do not conclusively indicate the actual copper release.

However, copper has proven to be a useful relative indicator, when compared within a user group of similar generators. Typical values are ca. $5 \mu\text{g}\cdot\text{L}^{-1}$ with neutral chemistry in low-oxygen systems, and $5\text{--}10 \mu\text{g}\cdot\text{L}^{-1}$ in high-oxygen systems. With alkaline water treatment, copper concentrations are lower.

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 that there is a sufficient continuous sampling flow. This is, however, not possible in closed generator cooling systems. In addition, the low levels make analysis difficult and possibly even unreliable.

Analyses of grab samples may also give only a short-term picture. The copper release of the system is best measured by taking a representative sample of the mixed bed resin at the same occasion each year. The total amount of copper in the resin bed has to be determined. It should be presented as $\text{g}\cdot\text{m}^{-2}$ copper per "hot" copper surface per year. A comparative empirical value may indicate whether oxide deposits are less likely to become a problem. It is therefore recommended to perform such an analysis on a regular basis and to observe the trend. It would also be

useful if the OEM, or a user group, were to keep a comparative database for the specific type of generator.

In addition to the integrated copper analysis in the ion exchange resin, the quantity of oxides removed in the filter should also be measured or at least be estimated (including the material settled on the vessel bottom).

The result of such measurements will be the release rate as grams ionic copper and grams particulate copper per square meter of system "hot" copper surface per year. Comparative trending is an important tool.

Other

Iron is frequently measured in generator cooling water systems. 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 present in such a system with no purification device capable of removing any released organic matter. Thus, with time, organics may accumulate in generator cooling water. Often, a foam carpet floats on the water level of the compensation tank. However, no damage has been related to organics in this system. Very seldom, chemical analyses are made for specific troubleshooting, e.g., in case of increased conductivity. Organics are certainly not a routine parameter.

Sometimes exotics in a generator are also analyzed. Unless they serve to solve a very specific problem, such analyses are questionable.

CONCLUSIONS

Automatic monitoring parameters in generator cooling water systems are conductivity, and in some cases oxygen. Measuring pH is not recommended. A novel technique provides the ECP, which according to research may be more meaningful than oxygen and pH. Laboratory analyses of the quantity of copper in the spent mixed-bed resin are also a useful indicator of long-term abnormal situations.

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