

Interpretation of Stator Cooling Water Chemistry Data

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ABSTRACT

Key parameters for chemistry monitoring of stator cooling water are conductivity, electrochemical potential (ECP), pH, and the concentrations of oxygen, copper, and of possible chemical additives (like NaOH for alkaline treatment). While conductivity, oxygen, and ECP merit continuous supervision, periodic analysis (e.g. once a month) may be sufficient for the other parameters.

The relation between the copper concentration and conductivity permits an assessment of the susceptibility of the system with regard to deposition and corrosion, as well as of possible impurity ingress. For alkaline treatment, measurement of conductivity and the sodium concentration indicates whether the alkalization is running properly. Oxygen concentration is a valuable indicator, but is ambiguous with low-oxygen regimes. Here, oxygen ingress may be detected by an elevated oxygen concentration in the water. However it is also possible that the oxygen is being consumed so rapidly that it does not show up in the water analysis.

BACKGROUND

As with any cooling water system in a power plant, a defined chemistry regime is required to avoid corrosion, deposition, and – in the case of electric systems – loss of electric insulation. These regimes and their monitoring parameters are specified in the International Council on Large Electric Systems (CIGRE) guide on stator water chemistry [1]; for generators with copper hollow conductors they comprise:

- Low-oxygen treatment, with an oxygen concentration as low as possible, in any case $< 20 \mu\text{g} \cdot \text{kg}^{-1}$ (ppb)
- High-oxygen treatment, with an oxygen concentration if possible close to saturation, in any case $> 2 \text{mg} \cdot \text{kg}^{-1}$ (ppm)
- Neutral (pH ~ 7) and alkaline (pH 8.5–9) treatment, both in combination with low- or high-oxygen treatment

Detailed specification values for chemistry parameters are given and discussed in an Electric Power Research Institute (EPRI) guide on stator cooling water systems [2].

This paper discusses the monitoring and interpretation of monitoring data in generators with copper hollow conductors. For generators with stainless steel hollow conductors, the requirements are simpler [3] and will therefore not be the subject of the present investigation.

MONITORING PARAMETERS

The key parameters for all mentioned treatment regimes are listed in [Table 1](#) [2].

In addition, other chemistry parameters are sometimes monitored, like for example the iron concentration. They however serve mainly to answer specific questions and usually do not require regular monitoring.

Conductivity Continuous on-line conductivity monitoring indicates whether water of sufficiently high purity is being used.

pH pH monitoring indicates whether the water is in the correct range for the chosen water treatment regime. Measuring pH in high-purity water is however difficult and may be unreliable. Conductivity is commonly used to indirectly monitor the pH.

Oxygen Oxygen monitoring helps to determine if the system is operating 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 possible oxygen ingress.

Parameter	Schedule	
	Continuous	Periodic
Conductivity	x	
Oxygen concentration	x	
pH		(x)
Copper concentration		x
Electrochemical Potential (ECP)	x	
Possible chemical additives (e.g. NaOH)		x

Table 1:

Key parameters and recommended schedule for monitoring water chemistry for stators with copper hollow conductors. A periodic schedule means once a month or more frequently if irregularities are observed or expected.

Copper Regular copper analyses in grab samples give reference spot 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 [2]. Comparison within a reference user group will indicate out-of-normal situations.

Electrochemical potential (ECP) This is a novel technique with promising results [4]. ECP may indicate risk conditions for stator bar plugging [5]. By its nature, it also responds to the system pH and oxygen concentration. Here also, comparison within a reference user group will indicate out-of-normal situations.

Chemical additives If such additives are used, they should also be regularly monitored. For example, with alkaline treatment periodic analysis of the sodium concentration is useful and a comparison to conductivity indicates whether the alkalization is performing correctly.

In addition to these chemistry-related parameters, the following plant parameters will give important information on the water flow conditions of the hollow conductors [2]:

- 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
- Individual slot temperatures, together with generator load
- Gas-to-water pressure
- Hydrogen leakage rate
- Make-up water consumption

These parameters have been discussed in more detail in a previous publication [6]. The present paper will give examples of the interpretation of common analytical data.

INTERPRETATION OF ANALYSES

The most common impurities in generator cooling water systems are copper (from oxidation of copper surfaces in the system) and carbon dioxide (from air ingress). Together with oxygen and NaOH (with alkaline treatment), their interrelation with the chemistry monitoring parameters will be discussed.

As these substances comprise the most common cases in stator cooling water, other substances will not be treated here for the sake of simplicity. If the proposed relations do not fit the observations, such other substances must however be taken into consideration.

In the following, all conductivity and pH values given refer to a reference temperature of 25 °C.

Conductivity, pH, and copper (with neutral treatment)

Suspended copper Suspended copper originates by spalling from an existing oxide layer or by precipitation from a supersaturated solution. In stator cooling water systems it is mostly CuO or Cu₂O, sometimes with a small fraction of metallic copper.

However, representative sampling for suspended particles requires special provisions [7], and therefore the average concentration of suspended copper is better determined by the total quantity of copper oxide found on spent mechanical filters, put into relation with the integrated water flow over the service time of the filter elements. Here it should also be considered that incidents with shutdown and inadequate lay-up may additionally contribute large quantities of oxides [8,9].

For example, 3 kg of copper on filters that have been in service for 16 000 h (approx. 2 years) with a stator water flow of 90 t · h⁻¹ (396 gpm) correspond to an average concentration of 3 000 g / (16 000 h × 90 t · h⁻¹) = 0.002 g · t⁻¹ or 2 µg · kg⁻¹.

A qualitative indicator for suspended particles is the actual service life of filter cartridges with regard to the expectation. But here, the suitability and quality of the filter elements are also of importance.

The evaluation of the data is best done by comparison within a reference group of similar generators. Typical values for suspended copper in stator cooling water are $< 5 \mu\text{g} \cdot \text{kg}^{-1}$.

Dissolved copper In generators, the copper oxides are always a mix of CuO and Cu₂O, the relative fraction depending on the water chemistry. These oxides dissolve in water, whereas in the area of interest Cu₂O has a significantly lower solubility [10], and with this also a lower dissolution rate. In consequence, dissolved copper in stator cooling water systems is mostly found as Cu²⁺.

Care has to be taken to distinguish between suspended and dissolved copper. For this, the sample is taken without acidification. In the laboratory, part of the sample is passed over a membrane filter and the other part of the sample is acidified. Analysis of the copper on the membrane filter provides the concentration of suspended copper, while analysis of the acidified sample gives the total copper. The concentration of dissolved copper is the difference. Measuring dissolved copper directly in the filtrate is problematic, as the filtering process is a source of contamination.

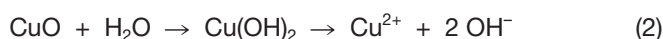
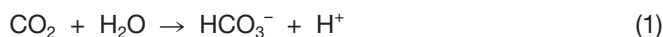
Usually, when the sample is taken after sufficient flushing of the sample line, the fraction of suspended copper will be minor.

If only total copper is analyzed, erratic values are frequently found. They are usually the result of irregular quantities of suspended copper originating from deposits in the sampling line.

The concentration of dissolved copper has proven to be a useful relative indicator when compared within a user group of similar generators. Typical values are ca. $5 \mu\text{g} \cdot \text{kg}^{-1}$ with neutral chemistry in low-oxygen systems, and $5\text{--}15 \mu\text{g} \cdot \text{kg}^{-1}$ in high-oxygen systems. With alkaline water treatment, copper concentrations are lower [2].

Interrelations of conductivity, pH, copper, and carbon dioxide In-plant observations have shown that increased levels of Cu²⁺ are usually coincident with increased conductivity. It will be shown that a true relation exists.

Both dissolved copper oxide and carbon dioxide (from air ingress) will contribute to conductivity and pH of the cooling water. The main overall reactions to be considered are shown in Eqs. (1) and (2):



Clearly, the presence of carbon dioxide will shift the pH value of the stator cooling water towards lower values (Eq. (1)), while dissolution of CuO will shift it towards higher values (Eq. (2)). The final pH will thus depend on both the bicarbonate and the copper concentration.

Eq. (1) is an established equilibrium reaction of the weak acid CO₂ and its hydrate H₂CO₃. Knowledge on the partition (between air and water) and dissociation of the dissolved CO₂ is state of the art. The resulting pH and conductivity of HCO₃⁻ (and CO₃²⁻) in combination with other electrolytes can be calculated with commercial software.

However, the behavior of copper oxide is more complex and the literature only provides information on its behavior in concentrated copper salt solutions. In order to be able to proceed, we will therefore make the following simplifications and assumptions in the interpretation of the data on conductivity and copper concentration:

- Due to their low solubility [10], copper(I) species will not be considered;
- Only the species listed in Eqs. (1) and (2) will be considered;
- The considerations will be limited to neutral water treatment;
- It will be assumed that the dissociation of Cu(OH)₂ will be as given by Eq. (2), and that the equilibrium lies completely on the right side. A reason to support this assumption is the fact that the concentrations are very low. This means that Cu(OH)₂ will be treated in the model calculations like a strong base of the alkaline earth hydroxides, e.g. Ca(OH)₂;
- A specific conductance of $53.6 (\mu\text{S} \cdot \text{cm}^{-1}) / (\text{mEq} \cdot \text{L}^{-1})^{\text{a}}$ for Cu²⁺ will be used [11];
- The experimental data on solubility limits as published in [10] and [12] will be used.

The most extensive work on the electrochemical equilibria of copper in aqueous solutions has been carried out and published by Pourbaix and co-workers [13]. Their stability diagrams for copper reveal complex anions like HCuO₂⁻ (bicuprite ion) and CuO₂²⁻ (cuprite ion) in the alkaline region, and not just OH⁻ as we propose assuming above in Eq. (2). These copper species are stable only at high pH values, typically above 9. At a pH value of 8.24 the ratio of

^a In this article, SI units are not used consistently since the old unit mEq · L⁻¹ (milliequivalent per liter) is still used in the literature on ion exchange and ion exchangers worldwide.

HCuO_2^- to Cu^{2+} is already 0.01. At pH values below 8 the prevailing copper species is therefore Cu^{2+} . This is our case of high-purity water, whereas Pourbaix and co-workers were considering concentrated solutions of copper salts.

It has to be acknowledged that this is a first approach that may be inaccurate and would need further development. For the moment, it is open to verification with field data, which up to now has given credible results.

Figure 1 shows the solubility that Cu^{2+} can achieve as a function of CO_2 . The dependence with an absence of CO_2 is given by the lowest curve to the right ($0 \mu\text{g} \cdot \text{kg}^{-1} \text{CO}_2$). With pure water, dissolution of copper oxide will start at pH 7 and $0 \mu\text{g} \cdot \text{kg}^{-1} \text{Cu}^{2+}$. Dissolution will then increase the Cu^{2+} concentration as well as the pH along the curve ($0 \mu\text{g} \cdot \text{kg}^{-1} \text{CO}_2$). Where the curve meets the solubility limit, the solution will be saturated and no further dissolution will take place (yellow triangle in the Figure). This means that in pure water at 50°C , Cu^{2+} will dissolve up to $22 \mu\text{g} \cdot \text{kg}^{-1}$ and yield a pH of 7.84 at 25°C . With the presence of CO_2 the solubility increases while the pH falls.

Figure 2 gives the pH as a function of conductivity and the concentration of Cu^{2+} . For example, $40 \mu\text{g} \cdot \text{kg}^{-1} \text{Cu}^{2+}$ with $0.2 \mu\text{S} \cdot \text{cm}^{-1}$ conductivity corresponds to a pH of 6.75. The graph also shows that about $80 \mu\text{g} \cdot \text{kg}^{-1} \text{CO}_2$ are

present (the measured point lies between the curves for 50 and $100 \mu\text{g} \cdot \text{kg}^{-1} \text{CO}_2$). In the following, the practical use of this diagram is demonstrated with the analysis of an incident.

Table 2 gives water analysis data from a plant that experienced periodic incidents of elevated conductivity necessitating non-scheduled or postponement of resin changes in the demineralizer mixed bed. It is noted that the demineralizer outlet conductivity is higher than in the main loop. These results can be inserted into Figure 3. For the moment, the pH data are ignored because reliable pH measurement in pure water requires instruments that are not compatible with the required closed-loop application in generator cooling systems (avoiding water losses). The following can be seen:

- Both points fit well on a curve for $300 \mu\text{g} \cdot \text{kg}^{-1} \text{CO}_2$. That means that while the mixed bed still retains Cu^{2+} , it does not retain CO_2 at all;
- The higher conductivity at the demineralizer outlet is a consequence of having pure acid here instead of an anion/cation mix with lower conductivity in the main loop;
- The Cu^{2+} concentration is – at the sample points – well below the solubility limit;
- The measured pH is about 0.2–0.3 units too high.

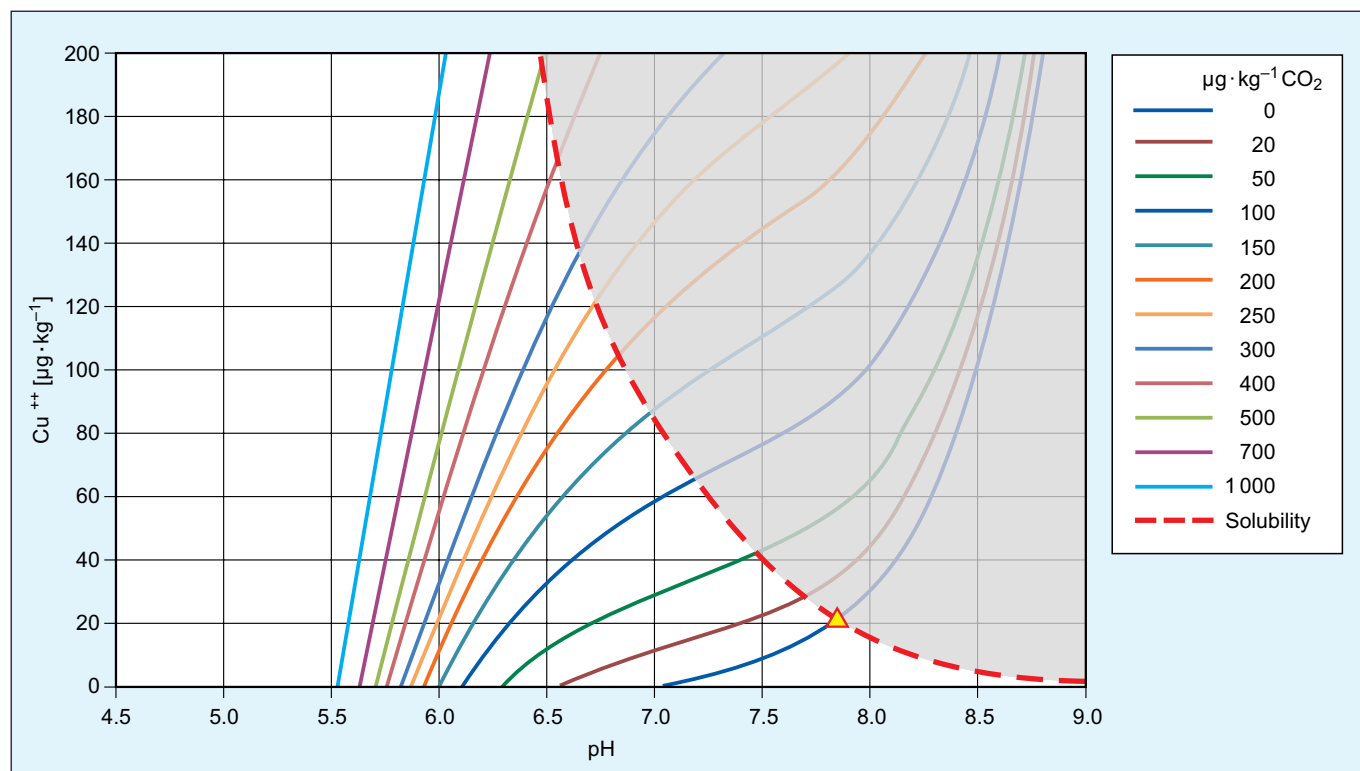


Figure 1:

Relation of Cu^{2+} and CO_2 to pH at 25°C . Tentative data. In addition, the solubility limit for Cu^{2+} (at 50°C) is shown; the yellow triangle point represents the solubility limit with no CO_2 . The grey shaded area indicates concentrations above the solubility limit.

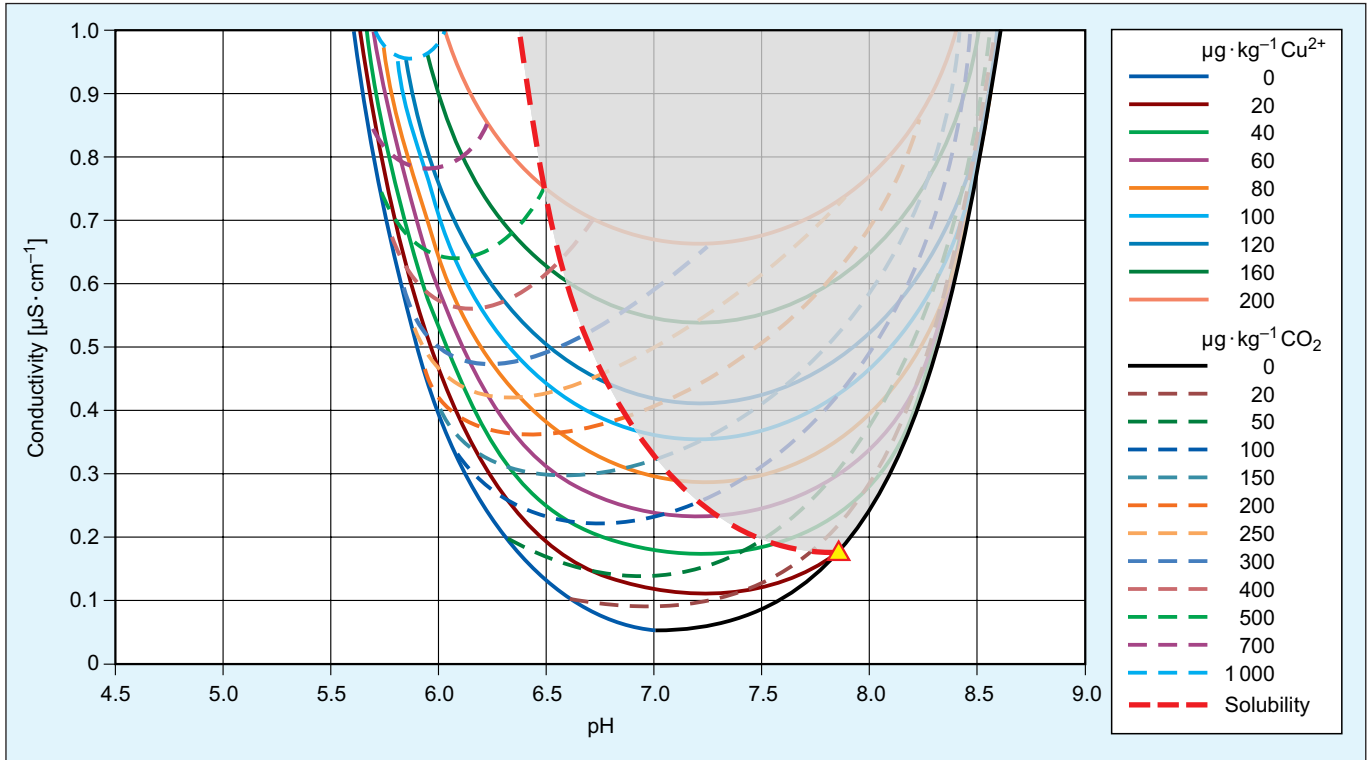


Figure 2: Conductivity at 25 °C as a function of pH at 25 °C, Cu^{2+} , and CO_2 . Tentative data. In addition, the solubility limit for Cu^{2+} (at 50 °C) is shown; the yellow triangle point represents the solubility limit with no CO_2 . The grey shaded area indicates concentrations above the solubility limit.

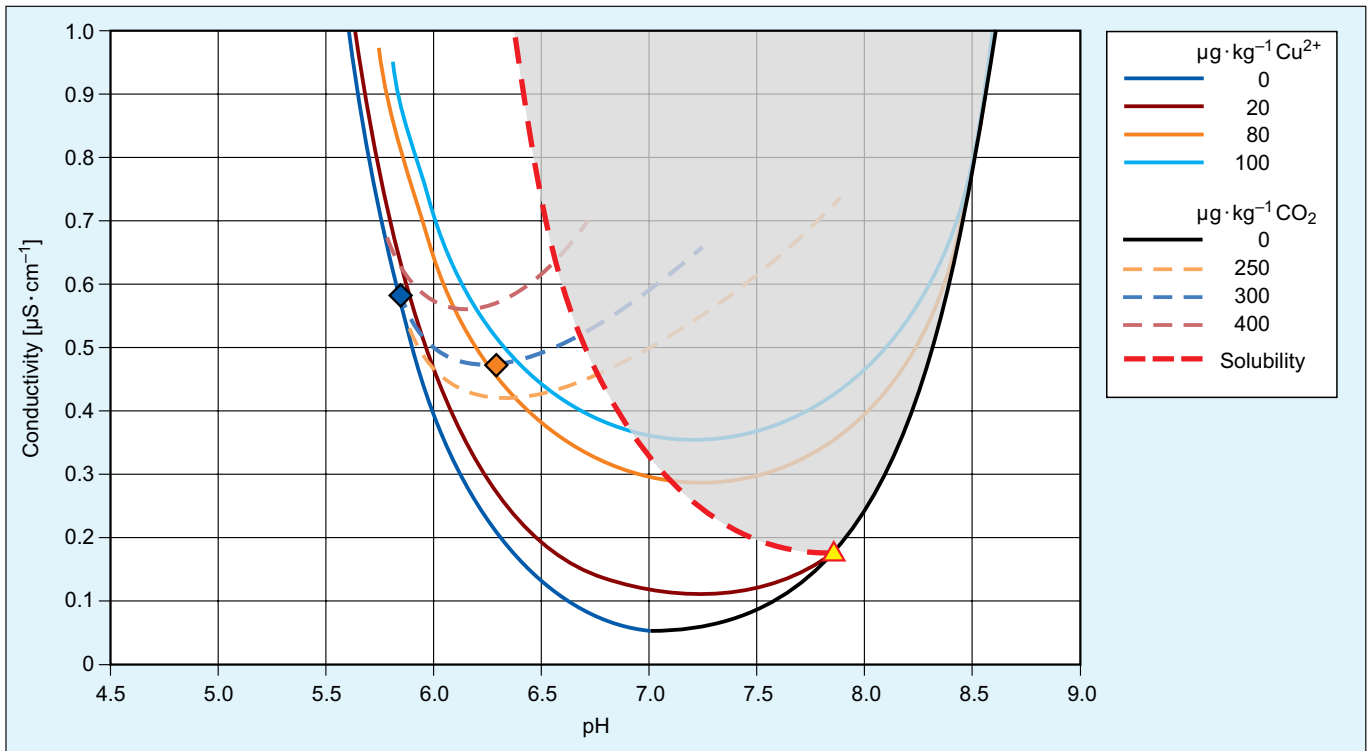


Figure 3: Extract from Figure 2; for clarity, only selected curves are displayed. Measured data for Cu^{2+} concentration and conductivity in the stator water/main loop (orange diamond) and at the mixed-bed outlet (blue diamond). It is seen that these two points also fit on the curve for $300 \mu\text{g} \cdot \text{kg}^{-1} \text{CO}_2$.

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Sample	Conductivity [$\mu\text{S} \cdot \text{cm}^{-1}$]	Cu^{2+} Concentration [$\mu\text{g} \cdot \text{kg}^{-1}$]	pH
Stator water main loop	0.469	85	6.59
Demineralizer outlet	0.586	5	6.05

Table 2:
Stator water analysis from a power plant with an incident of elevated conductivity [14].

The situation can thus be interpreted as follows: due to ingress of carbon dioxide the anion resin of the mixed bed becomes exhausted. Therefore the stator water accumulates CO_2 and the pH decreases. In consequence, copper becomes more soluble, and the Cu^{2+} concentration rises. This indicates an elevated copper release that has the potential to corrode copper and brazing above normal levels. Although the concentration in this incident has stayed below solubility, there is a risk of re-deposition when parameters change, for example when the mixed bed starts to leak copper significantly or even becomes fully exhausted.

Conductivity, pH, and sodium (with alkaline treatment)

The measurement of pH in high purity water requires elaborate equipment and procedures which are usually not available for stator cooling water systems. Therefore, conductivity is used as an indirect measure of pH, using the known correlation for NaOH.

However, stator cooling water systems may also contain some carbon dioxide from air ingress, and this will jeopardize the simple correlation with NaOH. Cu^{2+} will be of no importance here because of the very low concentrations with alkaline treatment, especially when related to the sodium concentration.

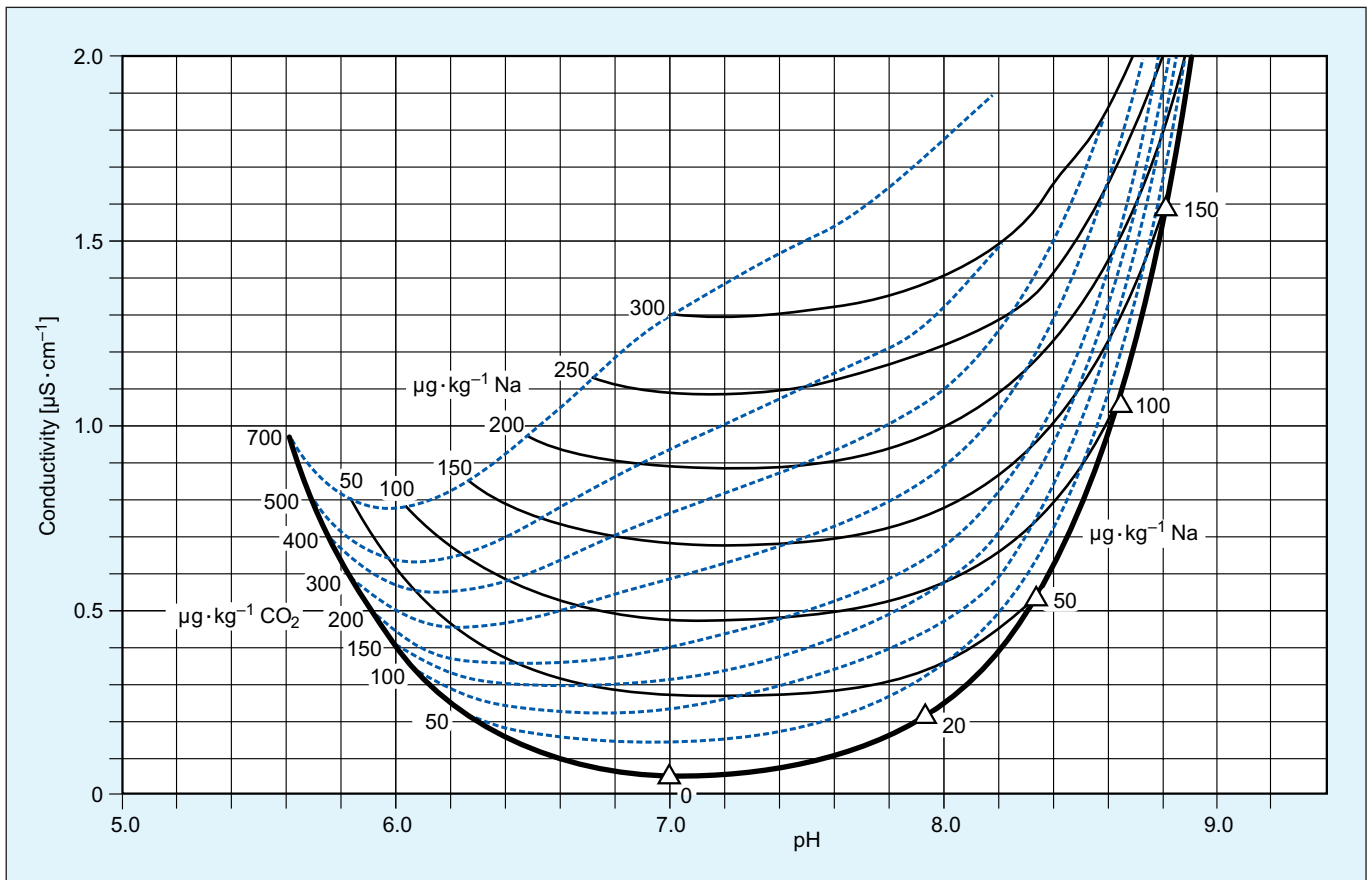


Figure 4:
Relation of conductivity to pH as a function of the concentrations of sodium and CO_2 at a reference temperature of 25 °C (CO_2 will partition into HCO_3^- and CO_3^{2-} , which are the anions in this figure). The marker triangles identify the points with pure NaOH and no CO_2 .

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Figure 4 shows the theoretical correlation between conductivity, pH, sodium, and CO₂. With conductivity and sodium concentration known, the associated pH can be read from the figure. The border curve with pH ≥ 7 represents the relation for pure NaOH, without CO₂.

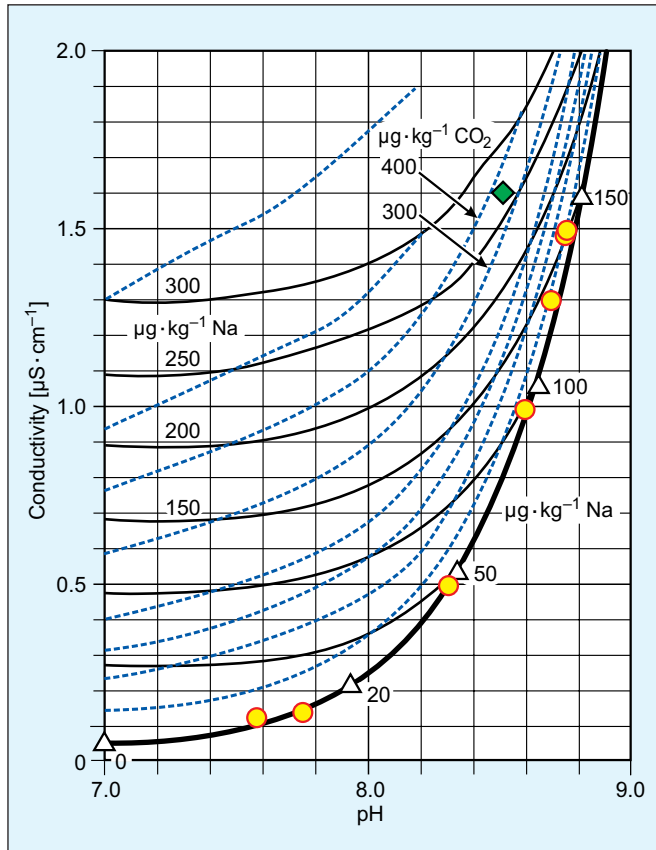


Figure 5:
Measured data for conductivity and sodium concentration, plotted in the pH/conductivity graph. Case 1: red/yellow circles. Case 2: green diamond.

Figure 5 gives a detail of Figure 4 for the illustration of two case studies on the interpretation of analytical data.

Case 1: Quality control of alkalization Measurements of conductivity and sodium concentration were made during start-up of the NaOH injection and included in Figure 5.

The points very closely follow the ideal relation for pure NaOH; they are slightly to the left, indicating a minor presence of CO₂.

It can be concluded that alkalization started up properly and the pH can with sufficient accuracy be directly derived from conductivity using its relation to pure NaOH. For later operation, it is however recommended to verify the situation by periodic analysis of the sodium concentration.

Case 2: Reliability check for improvised field measurements Measurements of conductivity (1.61 µS · cm⁻¹), pH (8.51), and sodium concentration (132 µg · kg⁻¹) were taken. Before alkalization, conductivity had been low (< 0.1 µS · cm⁻¹).

Figure 4 indicates that with a conductivity of 0.1 µS · cm⁻¹, the CO₂ concentration in the system must be < 20 µg · kg⁻¹ (for clarity, the 20 µg · kg⁻¹ CO₂ curve has not been drawn but it can be estimated from the 50 µg · kg⁻¹ curve).

The point in Figure 5 represents the field measurements for conductivity and pH. It lies between the curves for 300 and 400 µg · kg⁻¹ CO₂, corresponding to a CO₂ concentration of ca. 360 µg · kg⁻¹. Assuming that the conductivity measurement of 1.61 µS · cm⁻¹ is reliable and that CO₂ was in fact only < 20 µg · kg⁻¹, the measured pH is too low by 0.3 units.

It also can be seen in Figure 5 that a conductivity of 1.6 µS · cm⁻¹ cannot be achieved with the measured concentration of 132 µg · kg⁻¹ sodium.

It can be concluded that these measured values are not consistent and indicate unreliable data.

Oxygen

High-oxygen chemistry With high-oxygen chemistry, measurement of the oxygen concentration gives direct information about whether the oxygen level of the system is sufficient. Concentrations below the minimum required concentration unambiguously indicate a detrimental situation.

Low-oxygen chemistry With low-oxygen chemistry, matters are a bit more complex. A measured low oxygen concentration may indicate the absence of oxygen and with this, the absence of abnormal oxidation. It may however also mean that there is significant oxygen ingress and oxidation, but the oxygen is consumed so rapidly that it does not show up in the water analysis.

Therefore, with measurements in systems with low-oxygen chemistry, high oxygen concentrations indicate a detrimental condition. A low oxygen concentration however indicates an ambiguous situation, being either good or detrimental. Low oxygen levels here cannot be considered an indication of the absence of oxidation.

Such a situation can be clarified by measuring the consumption rate of oxygen in the system. This will be illustrated by the following example.

For this test, 9.5 kg (2.5 gal) of air-saturated water at 6.5 mg · L⁻¹ O₂ were injected into a system with 2 120 kg (560 gal) water. Before the test, the oxygen concentration

was at a background level of $3 \mu\text{g} \cdot \text{kg}^{-1}$, which may be due to slight oxygen ingress but also to measuring accuracy. The injection raised the oxygen level from $3 \mu\text{g} \cdot \text{kg}^{-1}$ to $32 \mu\text{g} \cdot \text{kg}^{-1}$ (net $29 \mu\text{g} \cdot \text{kg}^{-1}$). The net oxygen concentration then decreased approximately in an exponential manner; see Figure 6.

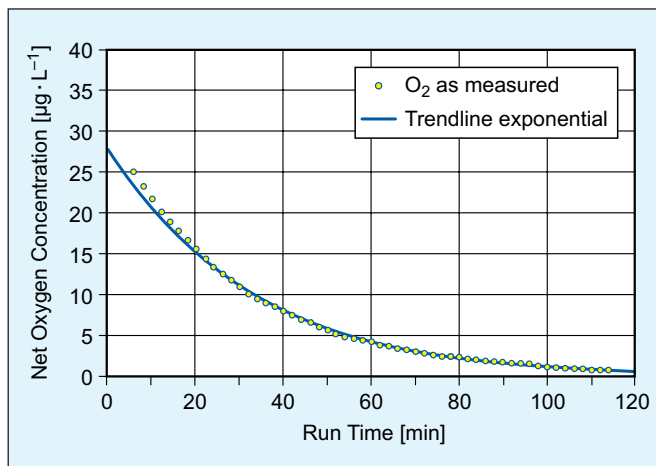


Figure 6:
Oxygen injection test in a stator cooling water system:
Oxygen concentration after a single oxygen injection at $t = 0$.
Data collection started after sufficient time (4 min) for even mixing throughout the whole system.

Exponential decrease indicates a constant consumption rate for oxygen. It can be formalized by Eq. (3):

$$\Delta(M \times C)/\Delta t = -\lambda \times (M \times C) \quad (3)$$

or when integrated, one arrives at the exponential decrease rate (Eq. (4)):

$$C(t) = C_0 \times e^{-\lambda t} \quad (4)$$

where

- M is the total water quantity in the system [kg],
- C oxygen concentration in the system [$\mu\text{g} \cdot \text{kg}^{-1}$],
- $M \times C$ oxygen inventory in the system [μg],
- C_0 C at time $t = 0$,
- λ consumption rate ("decay constant") [h^{-1}],
- t time [h].

Analysis of the data in Figure 6 can be most simply done using the formula of the trendline that the software may provide. In the present case, the formula is $28.1 \times e^{-0.0307t}$, therefore the consumption rate is 0.0307 min^{-1} or 1.84 h^{-1} , corresponding to a "half-life" of 23 min.

Applying this consumption rate, the effect of a continuous entry of oxygenated water can be calculated as follows:

$$\Delta(M \times C)/\Delta t = c \times m - \lambda \times (M \times C) \quad (5)$$

or at equilibrium with $\Delta(M \times C)/\Delta t = 0$:

$$C_{eq} = c \times m / (\lambda \times M) \quad (6)$$

where

- C_{eq} is the concentration at equilibrium,
- c concentration in the entering water [$\mu\text{g} \cdot \text{kg}^{-1}$],
- m entry rate of water [$\text{kg} \cdot \text{h}^{-1}$].

Let us now look at the consequences of a continuous entry of $1 \text{ kg} \cdot \text{h}^{-1}$ of air-saturated water with $6.5 \text{ mg} \cdot \text{kg}^{-1}$ dissolved O_2 . Eq. (5) shows that the oxygen concentration in the stator cooling water rises by $6.5 \text{ mg} \cdot \text{kg}^{-1} \times 1 \text{ kg} \cdot \text{h}^{-1} / (1.84 \text{ h}^{-1} \times 2120 \text{ kg}) = 1.7 \mu\text{g} \cdot \text{kg}^{-1}$, that is from originally $3 \mu\text{g} \cdot \text{kg}^{-1}$ to $4.7 \mu\text{g} \cdot \text{kg}^{-1}$.

Although such an increase in the oxygen concentration is hardly noticeable and still well within specifications ($< 20 \mu\text{g} \cdot \text{kg}^{-1}$ [1] or $< 10 \mu\text{g} \cdot \text{kg}^{-1}$ [2] above normal), the consequences can be quite detrimental. This ingress of $1 \text{ kg} \cdot \text{h}^{-1}$ of air-saturated water with $6.5 \text{ mg} \cdot \text{kg}^{-1}$ of oxygen can produce 509 g Cu_2O in 365 days. That means, in a few years, the generator can have accumulated enough oxide to plug up [15].

Using the same calculation, it is possible to estimate the total Cu_2O production over an extended period of time. Assuming a constant oxygen consumption rate and a precise oxygen measurement, a background level of $3 \mu\text{g} \cdot \text{kg}^{-1}$ oxygen indicates a Cu_2O production of 916 g in 365 days. In this specific case, data were available for the quantity removed by chemical cleaning, by the mechanical filter, and by the mixed bed. The total quantity Cu_2O removed compared well to the calculated production. Such good correspondence can however not be expected for every case.

It may be possible that the oxygen consumption rate will slow down with time, in consequence resulting in a higher and thus better visible oxygen concentration, giving a clearer alarm signal. On the other hand, the steadily formed oxides may start to flake off, either ending up in the filter or in restricted areas in the hollow conductors.

This test demonstrates that even when staying within the oxygen specification, excessive oxidation may not necessarily be avoided. Remember that this applies for low-oxygen chemistry only.

CONCLUSIONS

The diagrams of conductivity versus pH, either with the concentration of dissolved copper and CO_2 as parameters for neutral treatment or with sodium and CO_2 as parameters for alkaline treatment, are useful for the interpretation of chemical analyses in stator cooling water.

Measuring the oxygen concentration is useful for detecting irregular situations. Low oxygen concentrations with low-oxygen chemistry may however not necessarily indicate the absence of excessive oxidation.

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