Monitoring Generator Cooling Water System Chemistry by the Electrochemical Potential

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ABSTRACT

The electrochemical potential (ECP) is a factor that governs corrosion processes. Research work has indicated that the ECP may be a good parameter for monitoring oxide deposition in stator cooling water systems. This publication reports on field experience with such a device.

The effects of a sudden air ingress, of chemical cleaning, and of alkalization could be clearly seen by ECP monitoring. This qualifies ECP measurement as a valid diagnostic tool.

During normal operation, however, the ECP was above the normal operation specification level, near the immediate action level, indicating the presence of an abnormal situation with stator water chemistry. In fact, during this period, the stator suffered hollow conductor plugging by oxides.

Even though ECP monitoring seems more like a scientific tool, it is nevertheless strongly recommended to consider this technique for routine monitoring.

INTRODUCTION

Generator cooling water systems are closed systems with corrosion-resistant materials and no generic sources of impurity ingress. With worldwide experience of some 2000 water-cooled generators by various OEMs, some dating back as far as 1956, only few chemistry-related problems have emerged as more general issues [1], plugging of copper hollow conductors by copper oxides being the most frequent one.

Chemistry requirements for generator cooling water systems and recommendations for monitoring parameters are given in [2–4]. Oxygen concentration and pH are considered to be the key chemical parameters for the avoidance of hollow conductor plugging [5,6]. For practical reasons, conductivity is monitored as a surrogate for pH [4].

A research project initiated by the Electric Power Research Institute (EPRI) indicated the electrochemical potential (ECP) as a significant parameter for copper release and re-deposition. The study identified the ECP range in which the copper oxidation state changed and concluded that stresses induced by this change were the principal cause of particulate release and the resulting plugging or clogging. Experimental results supported the recommendation that copper strand ECP should be monitored and not be allowed to reach the dangerous range associated with a change in copper oxidation state [7].

In consequence a technique to monitor the ECP in generator cooling water systems has been developed and its use in generators with high oxygen as well as with low oxygen has been demonstrated [8]. Tentative specifications have been established (Table 1).

Parameter	ECP Normal Operating Value	ECP Short-Term Action Level
Low-oxygen chemistry	< 223 mV (SHE)	> 266 mV (SHE)
High-oxygen chemistry	> 315 mV (SHE)	< 305 mV (SHE)

Table 1:
Tentative EPRI specifications for electrochemical potential (ECP) in neutral water [8]. Future experience may lead to a refinement of these values.
A low-oxygen system is defined as a system normally operating with 20 $\mu g \cdot L^{-1}$ (ppb) of dissolved oxygen or less, and a high-oxygen system is one normally operating with 2 $mg \cdot L^{-1}$ (ppm) of dissolved oxygen or more.
Note: At 50 °C, the Ag/AgCl electrode will indicate an ECP lower by 219 mV relative to the standard hydrogen electrode (SHE).

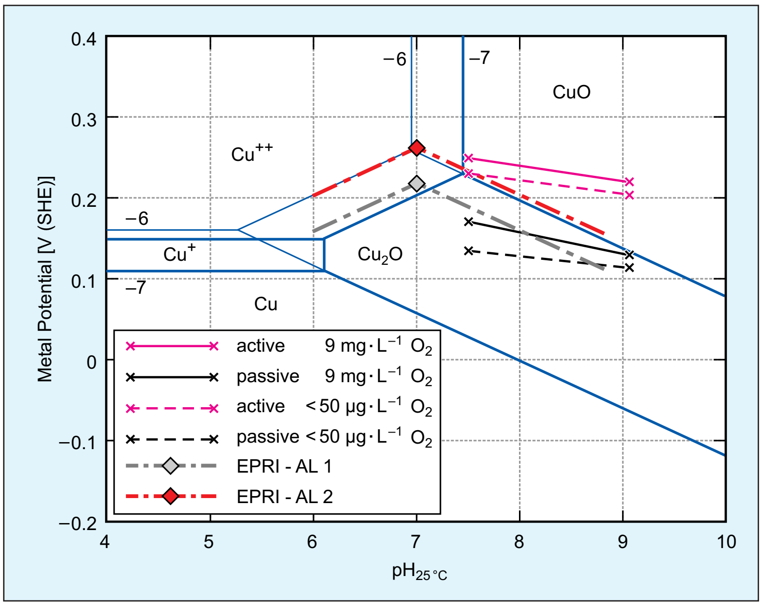

Figure 1:

Pourbaix diagram of Cu at 25 °C [9].

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 µg · L^{-1} (ppb). The diagram can of course be expanded to even lower ionic concentrations if needed. Dotted lines indicate results from laboratory tests on active (freshly pickled) and passive (oxidized) Cu specimens, in low-oxygen and in high-oxygen water [10]. It can be seen that the surface condition has more influence on the ECP than the oxygen concentration in the water.
The diamond points indicate the EPRI specifications for low-oxygen systems and the semi-dotted lines their proposed extension into alkaline and acidic media.

AL action level

It is interesting to note that the EPRI project found that particle (or colloid) release and re-deposition is the governing mechanism for hollow conductor plugging. Other researchers consider the release and re-deposition of dissolved copper to be the governing mechanism [6]. As can be seen in the Pourbaix diagram (Figure 1), the solubility of copper is also governed by the ECP. That means that whatever the basic theory on hollow conductor plugging is, the ECP is a significant parameter.

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, even oxygen.

BACKGROUND

The Gerald Gentleman Power Station, near Sutherland, Nebraska, USA, is owned and operated by NPPD (Nebraska Public Power District). The plant consists of two coal-fired units of 757 MW capacity each. Unit 1 was supplied with a Brown Boveri generator and commissioned in 1979. Since then, it has operated an average of ca. 7 800 h per year.

The generator stator is water cooled and still has its original coil with copper hollow conductors. The stator coil has 42 bottom bars, each hydraulically in series with 42 top bars. The rotor is gas cooled by hydrogen. The water treatment regime is low oxygen/neutral. By diffusion and small leaks from the gas side, the water is saturated with hydrogen at a partial pressure of ca. 1.5 bar.

In 1990, 2007 and 2010 the generator developed a rise in stator water pressure drop, indicative of plugging of the hollow conductors. Each time, the conditions were brought back to normal by Cuproplex™ chemical cleaning [11]. In order to help identify the situations that caused the plugging, in 2008 it was decided to implement ECP monitoring after the model of the EPRI investigations.

ECP MONITORING EQUIPMENT

Two different types of sensors were used in the EPRI project. One is a Yokogawa sensor, using a copper ECP electrode and a Ag/AgCl reference electrode, with 1 M KCl electrolyte. The other sensor is from FNC Technology Ltd and incorporates an immobilized chloride electrolyte (solid state electrolyte) instead of the 1M KCl internal electrolyte [8].

The Yokogawa sensor was used in Gerald Gentleman power plant, Figure 2.

Besides the ECP equipment, conductivity and oxygen concentration are measured continuously, and laboratory analyses are regularly made on Cu and Na (when using alkaline treatment).

For the interpretation of data, the Pourbaix diagram is useful (Figure 1). This figure includes results from laboratory tests to indicate the expected approximate placement of the generator data.

The tentative EPRI specifications for ECP (Table 1) were made for neutral water treatment. The question arises of how to extend these specifications into alkaline and acidic water. The intent of the EPRI specifications was to avoid transition from one oxide phase into another. Figure 1 includes a proposal for such an extension. In the alkaline region, it follows in parallel to the CuO/Cu_2O borderline. In the acidic region there is a high solubility for the oxides and keeping the phase transition therefore does not make much sense. It is herewith suggested to follow a line of constant solubility.

Figure 2:
The ECP sensor (center) in a side-stream of the stator cooling water system.
Also seen are the sensors for oxygen (bottom left corner) and conductivity (top right side). This arrangement permits precise control of sample flow and synchronization of the sample time, as well as the possibility of temporary removal for service and calibration.

EXPERIENCE

Figure 3 compiles data over a period of 18 months. There are two periods where oxygen and ECP increased, and some time later the stator coil pressure drop also increased. The question arises of whether this sequence is related or only coincidence. But a fact is that plugging took place during periods of increased ECP. In both periods the ECP was above the "normal operating value," and only slightly below the "short-term action level" as defined in Table 1. The ECP seems to have indicated the abnormal situation.

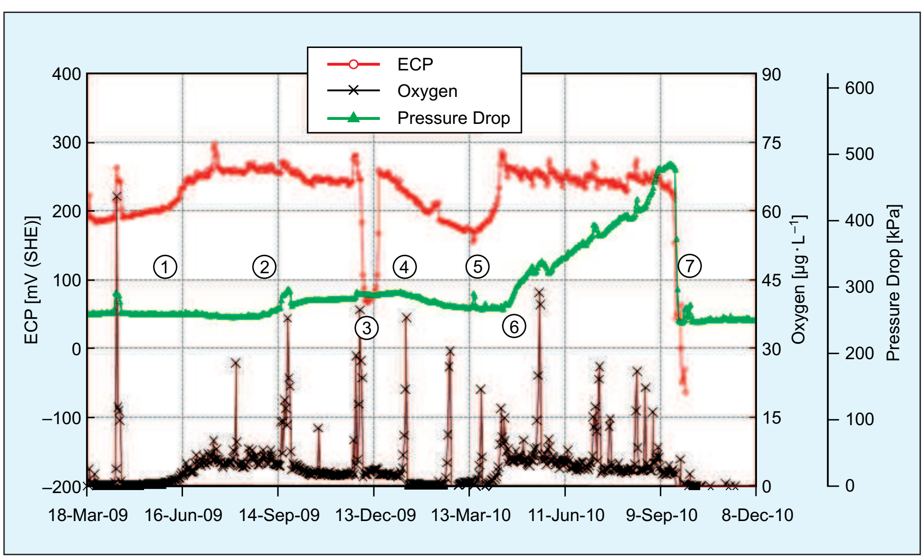

Figure 3:
ECP, oxygen concentration in stator water, and stator coil pressure drop over a period of 18 months.

① ECP and oxygen start to increase, but the pressure drop (Δp) stays stable
② Δp starts to increase
③ test with alkalization of stator water: ECP drops during the test
④ Δp starts to decrease, ECP also decreases
⑤ ECP and oxygen start to increase, but Δp stays stable
⑥ steady increase of Δp to a value that necessitates chemical cleaning
⑦ on-line Cuproplex cleaning brings down Δp to its normal value; after cleaning the stator water is alkalized, and ECP is down at a low level

The oxygen spikes originate in part from the addition of water to the system and in part from irrelevant numbers during sensor maintenance work. The absence of ECP values after Cuproplex cleaning is due to sensor malfunction.

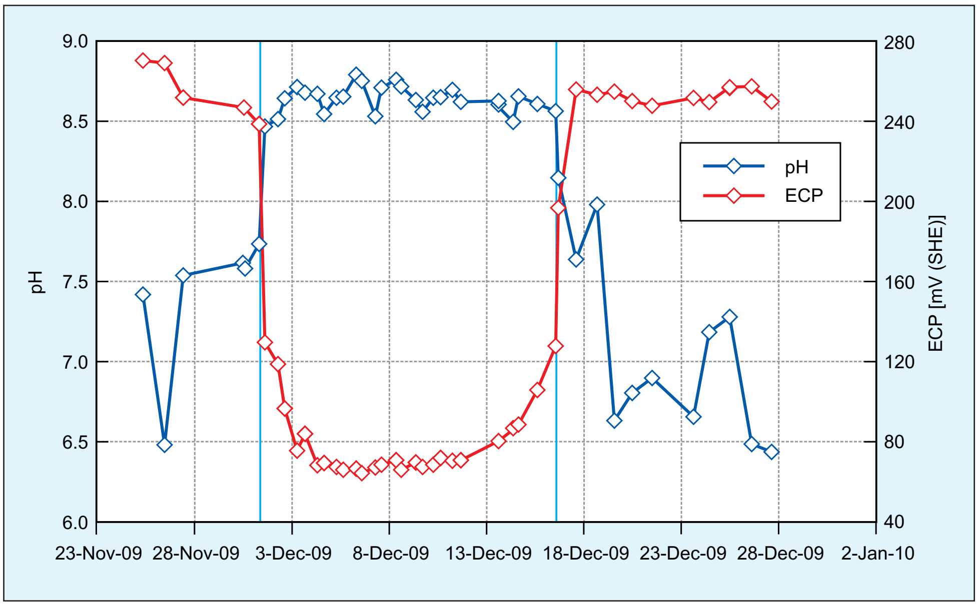

Figure 4:
ECP and pH during the 16-day alkalization test. Towards the end, the ECP trends upward despite constant pH.

The second rise in pressure drop was so strong that a Cuproplex on-line chemical cleaning was carried out to restore normal conditions. Following this cleaning, the stator water was converted to alkaline treatment for a period of 8 months. After this, the plant was able to locate and eliminate the source of air inleakage so the water was again converted back to neutral treatment.

These data lend themselves to a closer look at specific events. It should be mentioned that the pH data might have some inaccuracies (0.1–0.3 pH units) due to the difficulty of measuring in low-conductivity water.

Stator Water Alkalization

Alkalization Test, Duration 16 Days For a test period of 16 days, the stator water was alkalized with NaOH to pH = 8.7. This period is represented in Figure 3 (item "③"), in Figure 4, and in Figure 5 (item "Test 1").

It is seen (Figure 4) that the ECP dropped from 252 mV to 69 mV for the first 10 days, and then it drifted slowly upward. At the end of alkalization it increased to 128 mV within 6 days.

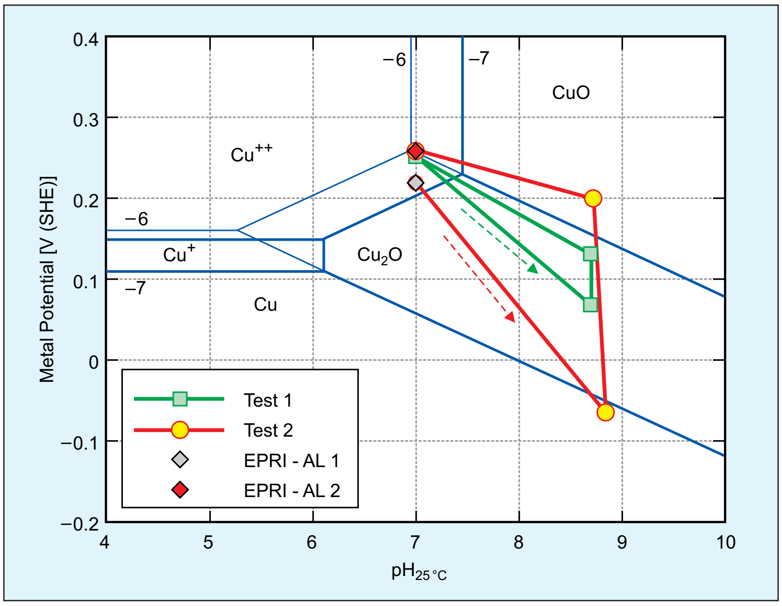

Figure 5:
Pourbaix diagram of Cu at 25 °C.
The diamond points indicate the EPRI specifications for low-oxygen systems.
The green squares / green line indicate the values before (pH 7), during (pH 8.7) and after (pH 7 again) the alkalization test (Test 1).
The yellow dots / red line indicate the values before (pH 7), during (pH 8.7) and after (pH 7 again) the 8-month alkalization period (Test 2).
The dotted arrow indicates the time sequence in the tests.

Figure 5 shows that the slope of ECP decrease with increasing pH is (252–69)/(7.0–8.7) = –108 mV per pH unit and thus stronger than the theoretical slope of the CuO/Cu_2O borderline (–59 mV per pH unit). This indicates that the ECP change is not only related to the associated change in pH, but also to a change in copper behavior, e.g., the formation of a more passive oxide layer.

Figure 5 also shows that alkalization at first brought the system well into the Cu_2O domain, and towards the end of the test it had drifted up towards CuO. It would be interesting whether such electrochemical findings can be substantiated by crystallographic analysis of the oxide layers.

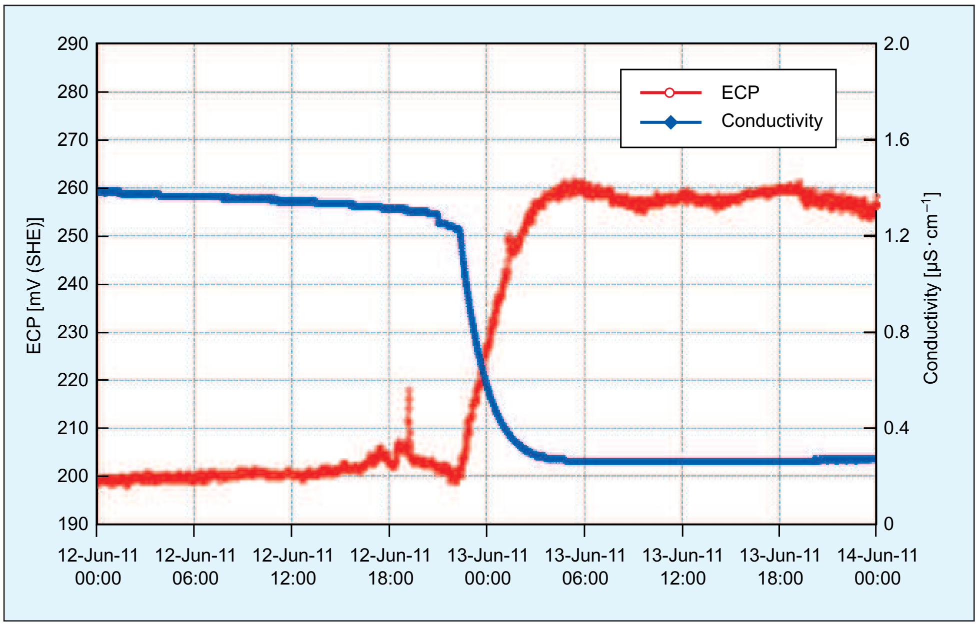

Figure 6:

ECP and conductivity at termination of the 8-month alkalization period. Both parameters react simultaneously to the termination of NaOH injection.

Alkalization Test, Duration 249 Days For 8 months, the stator water was alkalized with NaOH to pH = 8.7. This period is represented in Figure 3 (item "⑦"), in Figure 5 (item "Test 2"), and in Figure 6.

At the start of the period, the stator coil had been chemically cleaned by the Cuproplex method. It is therefore no surprise that the ECP went down into the domain of metallic copper, represented by the freshly cleaned coil. With time, the system drifted across the Cu_2O domain into CuO (Figure 5).

When alkalization was terminated, the ECP instantaneously started to rise back to approximately its original level (Figures 5 and 6).

Air Inleakage Test

9.5 L (2.5 gallons) of air-saturated water were drawn into the system via the depressurized standby system filter. Evenly distributed and not consumed, this would mean a calculated average oxygen concentration of ca. 31 µg · L^{-1} (ppb) and ingress of carbon dioxide from both the water and the contact with air. The results are seen in Figure 7.

- The oxygen increased from 2–3 µg · L^{-1} (ppb) and stabilized shortly at 31 µg · L^{-1} (ppb) after 3 min, then decayed with a "half-life" of 24 min. The stabilization value corresponds very well to the expected one.

The half-life indicates a moderate consumption rate for oxygen. From this, it can be calculated that a continuous ingress of 0.02 liter (20 mL) of air per hour would cause an increase in oxygen concentration of 3.3 µg · L^{-1} (ppb), which would probably still go unnoticed, but would produce enough oxides (400 g per year) to cause a potential problem in the long run.

- Conductivity had a slow increase from 0.08 µS · cm^{-1} to a maximum of 0.185µS · cm^{-1} to a after 27 minutes, and a half-life of 68 min. 0.185µS · cm^{-1} to a by CO_2 correspond to a pH = 6.34.

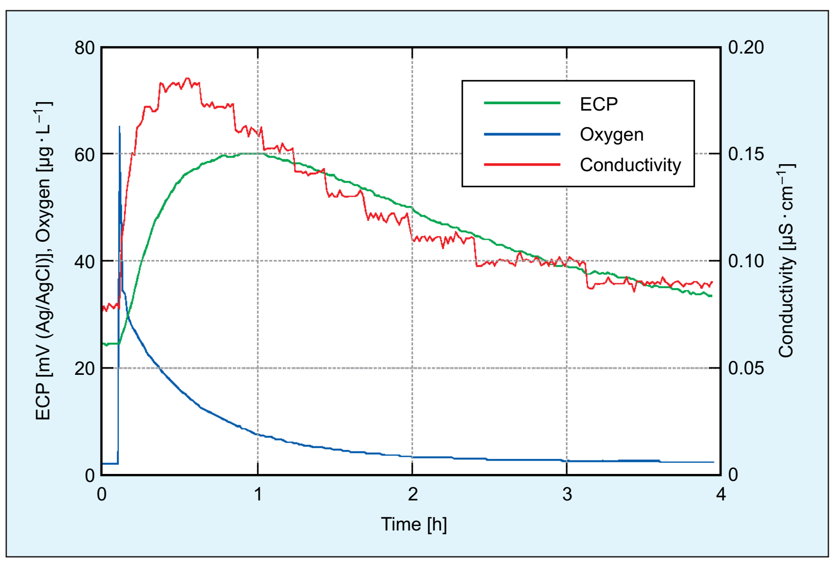

Figure 7

ECP, conductivity and oxygen concentration during the test with intentional ingress of 9.5 liters of air-saturated water.

Note: The ECP is given here in mV (Ag/AgCl). Converting these values to mV (SHE), one must add 219 mV to these values.

- ECP (SHE) also had a slow increase from + 244 mV to a maximum of + 280 mV after 53 minutes, and a similar decrease rate to conductivity.

  The ECP is influenced by the increased oxygen concentration as well as by the change in pH. The dissimilar behavior relative to oxygen but similar behavior to conductivity suggests that the influence of pH may be the dominant parameter. The delayed response of the ECP may however also be caused by surface conditions that may take some time to develop.

  Figure 8 shows that the ECP increased with lower pH at a rate of (280–244)/(6.34–7.0) = –55 mV per pH unit. This is quite close to the slope of the CuO/Cu_2O borderline (–59 mV per pH unit) and indicates that the ECP change during this test is only related to the associated change in pH.

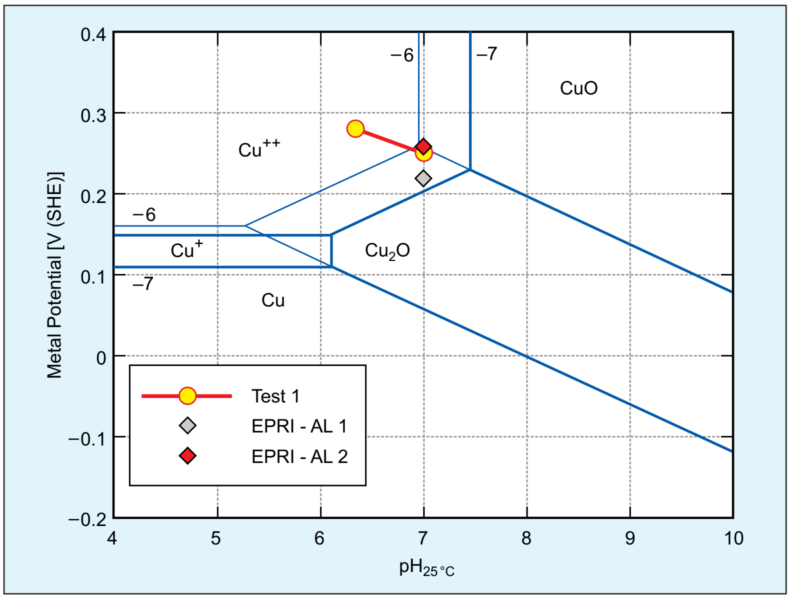

Figure 8:
Pourbaix diagram of Cu at 25 °C.
The diamond points indicate the EPRI specifications for low-oxygen systems.
The yellow dots / red line indicate the values before the test (pH 7), and at the test with ingress of 9.5 L of air-saturated water (pH 6.33).

CONCLUSIONS

The effects of a sudden air ingress, of chemical cleaning, and of alkalization could be clearly seen by ECP monitoring. This qualifies ECP measurement as a valid diagnostic tool.

During normal operation, however, the ECP was above the normal operation specification level, near the immediate action level, indicating the presence of an abnormal situation with stator water chemistry. In fact, during this period, the stator suffered hollow conductor plugging by oxides. A source of very small, steady oxygen ingress was thought to have caused this situation. It is however not yet known what the baseline ECP will be once the system has been brought to a trouble-free condition. This can only be seen in the long range over some 3 to 5 years.

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. Its price is probably less than that of some other less useful analyzers sometimes used in generator cooling water systems.

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