

Review of Alkaline Treatment for Generator Stator Cooling Water Systems

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ABSTRACT

Alkaline treatment is a proven tool for reducing the occurrence of flow restrictions in copper hollow conductors caused by oxide deposits. Its action is based on the reduced solubility of Cu^{++} in alkaline water. Hydrodynamic parameters like water flow velocity, turbulences, temperature etc. also play a role. Therefore alkaline treatment is beneficial but is not the only decisive parameter for avoiding flow restrictions.

However, there are indications that alkaline treatment produces thicker oxide layers than with neutral water. These oxide layers are nevertheless very thin and are of no concern as long as they do not migrate, e.g. by variations in the oxygen concentration or by fluctuations of pH. It is therefore very important to always keep alkaline treatment under good control. This also includes during shutdown periods.

Alkalization with an injection pump is the simplest and most reliable method. Parallel dual beds are also used for alkalization, but they need careful expert supervision and follow some often overlooked rules, especially in regard to proper priming of the alkalization and a very restricted use of the neutral mixed bed.

INTRODUCTION

There are only few chemistry-related issues in water-cooled generators, but if they appear they can cause severe damage and affect plant availability. The main issues are corrosion and plugging of hollow conductors, and corrosion in the brazing joints connecting the stator bars to the cooling water system ("clip to strand leakage"). In order to minimize their occurrence and effects, several types of water treatment have been introduced. They comprise low-oxygen chemistry and high-oxygen chemistry, in combination with neutral or alkaline water treatment. This publication explores the alkaline water treatment.

HISTORY

In 1956 the first generator (30 MW) with directly water-cooled stator bars was put into power plant operation by AEI (BOLD power plant, UK). Also in 1956, a prototype machine (12 MW, 6.3 kV and 3 000 revolutions per minute) with water cooling of both the stator and rotor windings was manufactured and tested in China [1]. Large-scale commercial use of water cooling started in 1960 in the USA [2], 1961 in England [3] and 1964 in Germany [4]. The idea of water cooling is however older [5].

It was not until the early 1970s that the first publications appeared on chemistry-related problems in water-cooled generators. In 1974 researchers from the Allianz Insurance laboratories reported flow restrictions in water-cooled stator coils by deposition of copper oxides [6]. The researchers found that copper release is dependent on the oxygen concentration and that upon alkalization to pH 8 the release rate changes to very low values (Figure 1). In 1979, Biblis power plant reported positive results from testing alkaline treatment under low- as well as high-oxygen conditions [7].

Subsequently, one major OEM (Siemens) further developed alkaline treatment and applied it as its standard chemistry in generator cooling systems [8] (Figure 2). Both injection by an injection pump and release from a Na^+ -loaded mixed bed were applied [8,9]. In the following years a few power plant operators converted their generator cooling water systems on their own. Most notably, Eskom (South Africa) converted its fleet of 66 water-cooled generators from neutral to alkaline chemistry, in both low- and high-oxygen systems [10,11]. However, no other OEM has followed up with alkaline treatment for their generators. This may be partly due to company traditions, but is also partly due to a generally good performance of their established solutions.

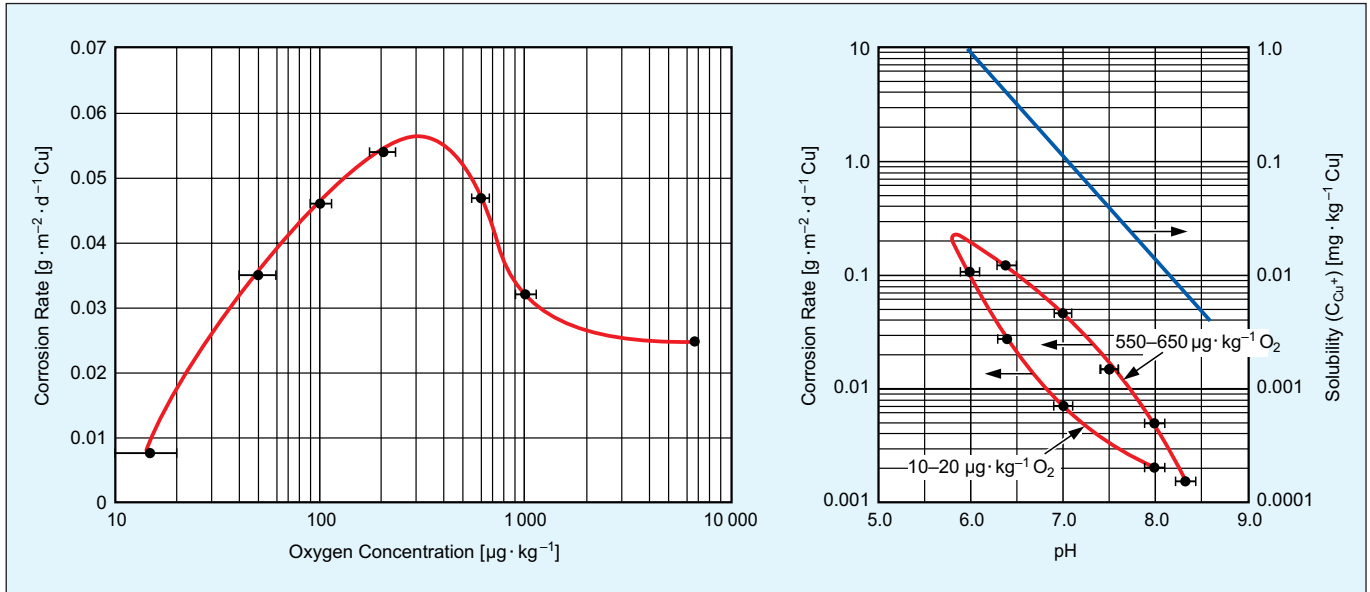


Figure 1: Copper release rates under various water chemistry conditions, by Effertz and Fichte [6] (courtesy of Wiley VCH/Jahrbuch vom Wasser).

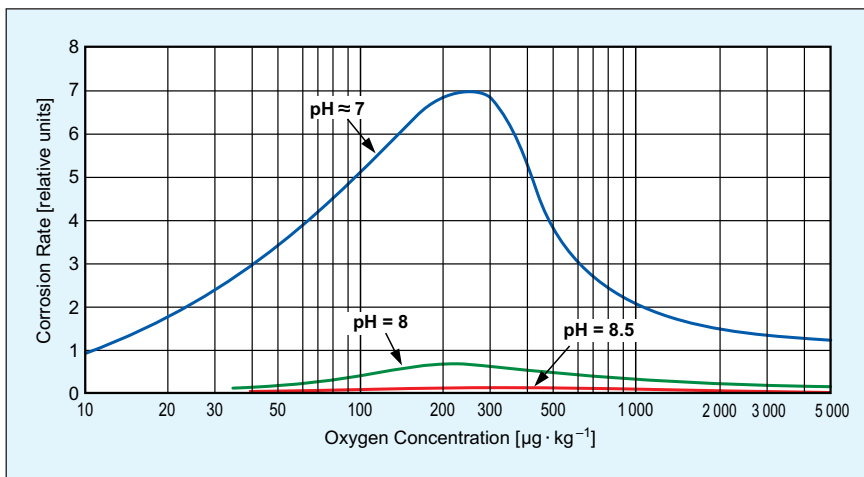


Figure 2: Copper oxidation rate as a function of oxygen concentration and pH, by Schleithoff and Emshoff [8] (courtesy of VGB PowerTech).

Presently, there are about 2 000 water-cooled generator stators operating worldwide, not including Russia and China (Table 1). Some of the generators have reached more than 250 000 successful operating hours [12]. It is estimated that about 10 to 20 % of the generators suffer from flow restrictions sooner or later within the first 25 years of operation.

Of these 2 000 generators, about 260 presently operate under alkaline treatment, with an increasing tendency.

BASICS

The main purpose of alkaline treatment is to prevent or to reduce the occurrence of flow restrictions in copper hollow conductors caused by oxide deposits. It will be

shown that this effect is based on the reduced solubility of copper ions with moderately alkaline pH.

Mechanism of Flow Restriction by Copper Oxides

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

The mechanism of growth of flow restrictions can be separated into four steps [13]:

- (1) Oxidation of the copper

Part of the world	Stators	Rotors	Stator Water Chemistry		
			High Oxygen	Low Oxygen	Of These Alkaline
World ex Russia & China	2 000	80	1 100	900	260
Russia	800	60	0	800	0
China	1 200	many	0	1 200	0

Table 1:

Number of water-cooled generators worldwide and type of stator water chemistry. These figures are approximate [12].

- (2) Release of the oxidized copper
- (3) Migration of the released copper
- (4) Re-deposition of the migrating copper

The effect of alkaline treatment is linked to step (2), by decreasing the release rate of Cu ions. The less copper that is released, the less migrates and re-deposits.

Relation between corrosion rate and release rate

It is important to remember that the release (dissolution) rate does not reflect the actual oxidation (corrosion) rate (Eq. (1)).

$$[\text{Oxidation rate}] = [\text{Release rate}] + [\text{Build-up rate of oxide and hydroxide in place}] \quad (1)$$

Oxidation of the copper Under low-oxygen conditions, all oxygen entering the system is fully consumed. Otherwise, the incoming oxygen would add up in the system and the oxygen concentration in the water would increase towards saturation, which is not the case in low-oxygen systems. This is completely independent of any water chemistry regime. In such a case, alkaline treatment does not reduce the oxidation ("corrosion") rate. Because the release rate is lower with alkaline treatment, the oxide build-up in place will be higher. These considerations are supported by the amount of oxides found during chemical cleanings.

Under high-oxygen conditions, a copper oxide layer forms which hinders the access of oxygen to the copper and thus slows down the rate of further oxidation. This oxide layer is steadily dissolved in the water. The thickness of the oxide layer is then determined by the balance between oxidation rate and dissolution rate. If the dissolution rate is decreased by alkalization of the water, the oxide layer will grow and slow down oxidation until the oxidation rate is again in balance with the lower dissolution rate. It is therefore probable that with high-oxygen chemistry the oxide layers with alkaline treatment will also be thicker than with neutral water chemistry; however no experimental data on this have been published yet.

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

Particle release is usually related to spalling of deposits, for example by phase changes ($\text{Cu}^+ \rightarrow \text{Cu}^{++}$) during transient operation like inadequate layup, or by mechanical stresses caused by high water velocity or turbulence. Water chemistry has a secondary influence on these effects via the release rate of copper ions (see below), which governs the maintaining or dissolving of the crystallized Cu-oxides and -hydroxides that bond these particles together.

Copper ion release can be modelled as a mass transfer phenomenon as used for the dissolution of iron in feed-water [14,15] (Figure 3).

In water and in the presence of oxygen, Cu dissolves by the formation of Cu^{++} ions. Depending on solubility limits, the Cu^{++} ions are transformed into precipitated Cu-oxides and -hydroxides. A more detailed description with all the involved reactions and species is given in the literature [16]. The dissolution progresses until the solubility limit is reached. Then a covering layer of precipitated Cu^{++} -oxide/hydroxide is formed.

The release rate of copper, as symbolized by step (B) in Figure 3, will then depend on how much dissolved Cu^{++} is removed from the boundary layer and replenished by the oxidation (step (A)). The release rate can then be described by mass transfer kinetics (Eq.(2)).

$$dm/dt = k \cdot (C_S - C_B) \quad (2)$$

where dm/dt mass transferred per unit of time (release rate)

k mass transfer coefficient

C_S copper concentration in the oxide/water boundary layer

C_B copper concentration in the bulk liquid

The mass transfer coefficient is determined by the mechanical transport with the flowing water and by diffusion. It includes the effect of various parameters, such as

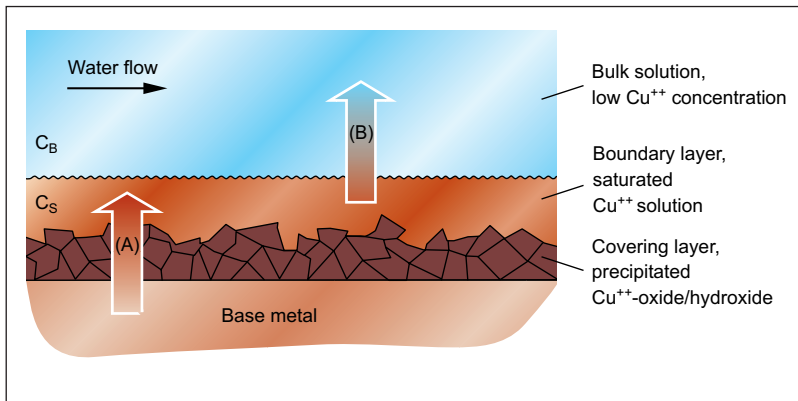


Figure 3:
Mechanism for the dissolution of copper in water.

C_S, C_B concentration of Cu^{++}

- (A) oxidation $\text{Cu} + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Cu}^{++}\text{-oxide/hydroxide}$
 (B) mass transfer from the saturated boundary layer into the water flow $dm/dt = k(C_S - C_B)$

the water velocity and turbulence, flow geometry and temperature.

It is therefore useful to remember that other parameters besides water chemistry also have an influence on the release rate. Not all can be blamed on bad chemistry; good chemistry may not bring a cure for everything.

The same considerations also apply for Cu^+ .

The copper concentration in the boundary layer (C_S) will be the saturation concentration, which is approximately equal to the solubility limit. Figure 4 gives the solubility of Cu^{++} and Cu^+ in dependence on pH. It can be seen that copper solubility is at a minimum at a pH between 9 and 10.

The effect of alkaline treatment is based on the reduced release rate for Cu^{++} and Cu^+ ions, which is due to the reduced solubility with alkaline pH < 10.

For practical reasons, however, alkaline treatment in generator cooling water systems is limited to pH 8.5 to 9.0. pH higher than 9.0 would cause a conductivity of the water of $> 2.5 \mu\text{S} \cdot \text{cm}^{-1}$, which is not desirable for generator operation as a high conductivity would challenge the electrical insulation of the coil to ground (the actual conductivity limit is generator-specific and considerably higher). Below pH 8.5, the solubility is sensitive to pH variations.

Effect of Adverse Water Chemistry Situations

Abnormal water chemistry or inadequate layup can destabilize the oxide layer and cause it to flake off. These particles then can plug hollow conductors, up to catastrophic failure [13]. As mentioned, with alkaline treatment the oxide layers are thicker than with neutral water chemistry. Thus, the consequences of a destabilization of the oxide layer will be more severe with alkaline treatment. It is therefore important to strictly adhere to the selected oxygen regime, to a constant pH (variation smaller than ± 0.1 units), and to appropriate layup [12].

Influence of Alkaline Treatment on the Stator Cooling Water System

The increased conductivity of the water interferes to a certain extent with the phase-to-ground insulation of the stator coil across the insulating water supply hoses. A conductivity of $1\text{--}2 \mu\text{S} \cdot \text{cm}^{-1}$, however, is acceptable for continuous service conditions with all known designs.

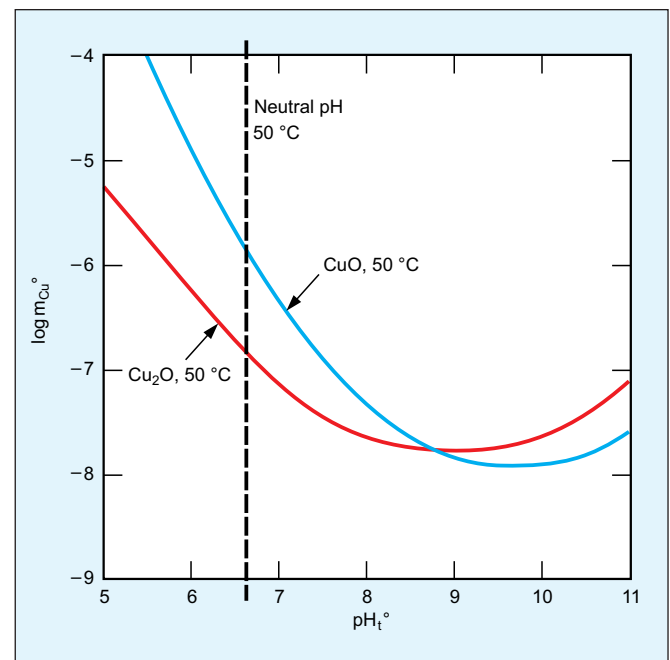


Figure 4:
Solubility of copper oxides at 50 °C in dependence of pH [15]. $\log m_{\text{Cu}^o}$ is the solubility in $\text{mol} \cdot \text{kg}^{-1}$, and pH_t^o is the pH at the respective temperature. Note that the dissolved $\text{Cu}^{+}/^{++}$ will increase pH slightly, e.g. with $20 \mu\text{g} \cdot \text{kg}^{-1} \text{Cu}^{++}$ at 50 °C in the order of 0.5 units. 1 mol Cu is 63.6 grams; the $\log m_{\text{Cu}^o} = -6$ corresponds to $63.5 \mu\text{g} \cdot \text{kg}^{-1}$.

There is the question of whether alkaline water might have an effect on system materials. Alkaline treatment raises the electrochemical corrosion potential at copper/braze interfaces [18], but actual corrosion cases have not yet been reported. Generally, the slightly alkaline medium should be of no concern, as it conforms very well to the good industrial experience of water treatment in closed cooling systems.

Monitoring of Alkaline Water Treatment

The scope of alkaline treatment is the adjustment of the water into a defined pH range of 8.5–9.0 [11]. As pH measurement in high-purity water is difficult and prone to errors, it is common practice to use conductivity as a surrogate parameter. The relation between conductivity and pH is shown in Figure 5. It can be seen that there is an unambiguous relationship only in the absence of anionic impurities like carbon dioxide from air ingress. In such a case, supplemental analyses of Na are required for correct interpretation of the conductivity measurement. Correct interpretation of the measured data will therefore require expert knowledge or additional instrumentation.

METHODS FOR IMPLEMENTATION

There are several options to achieve alkalization of the stator cooling water (Figure 6). All have in common that a premeditated concentration of NaOH is maintained in the water, and that the concentration is controlled via water conductivity as an indirectly indicating parameter.

The mixed-bed water flow can be kept smaller with alkaline treatment because the release rate and copper concentration in the water will be smaller. Consequently fewer ions have to be removed by the mixed bed. However, removal of carbon dioxide that may enter the system still requires a certain mixed-bed flow. A flow rate in the order of $1 \text{ m}^3 \cdot \text{h}^{-1}$ for low-oxygen systems and $5 \text{ m}^3 \cdot \text{h}^{-1}$ in a high-oxygen system may be sufficient, depending on verification of adequate water quality by chemical analyses.

Injection Pump

This is the classic way for injecting chemicals into a system. The NaOH injection is balanced by the continuous removal with the mixed bed, resulting in a controlled concentration in the water.

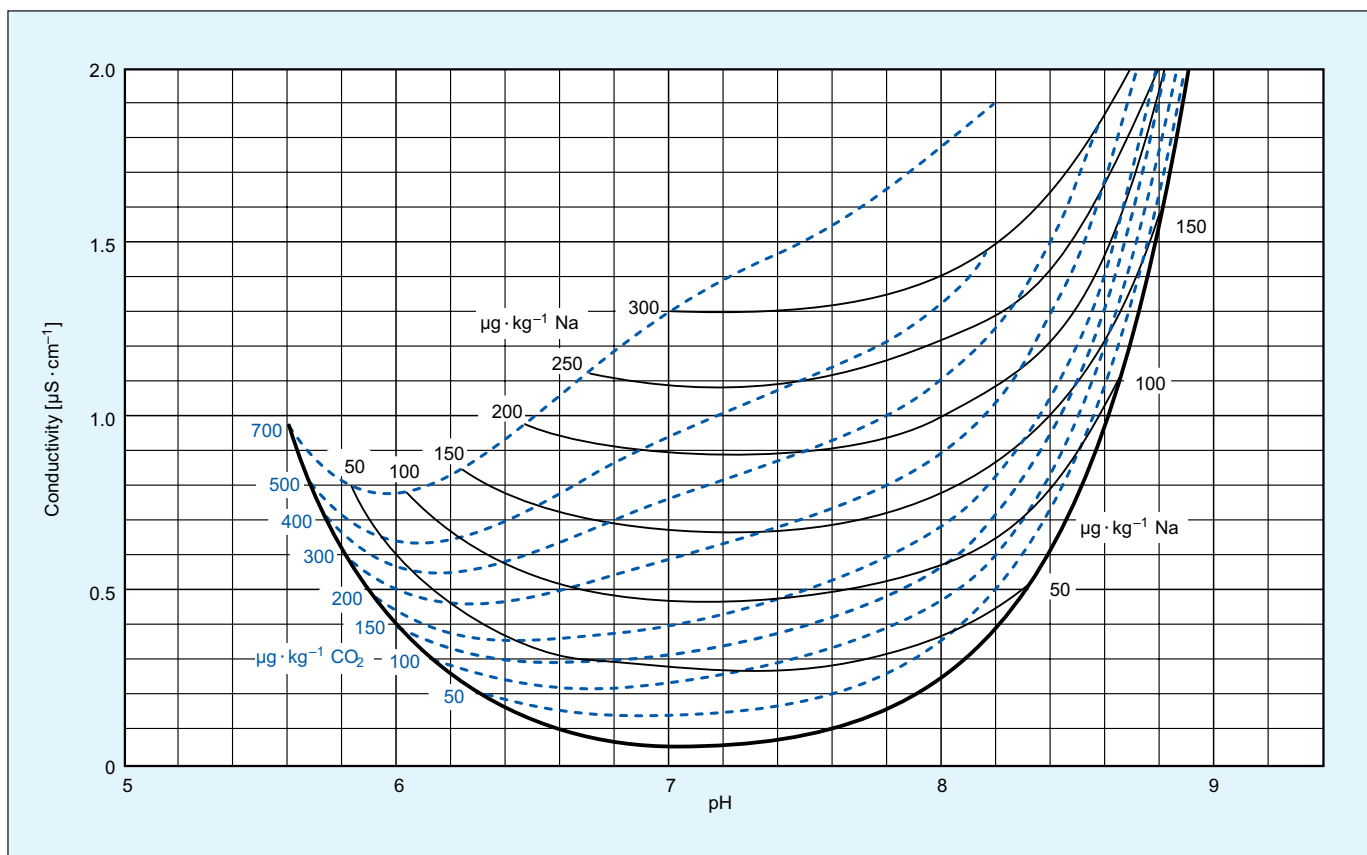


Figure 5:

Conductivity and pH of mixtures of NaOH with CO_2 . Solutions in high-purity water at 25 °C. Pure NaOH is represented on the right-hand border curve; the dotted curves are for various concentrations of CO_2 .

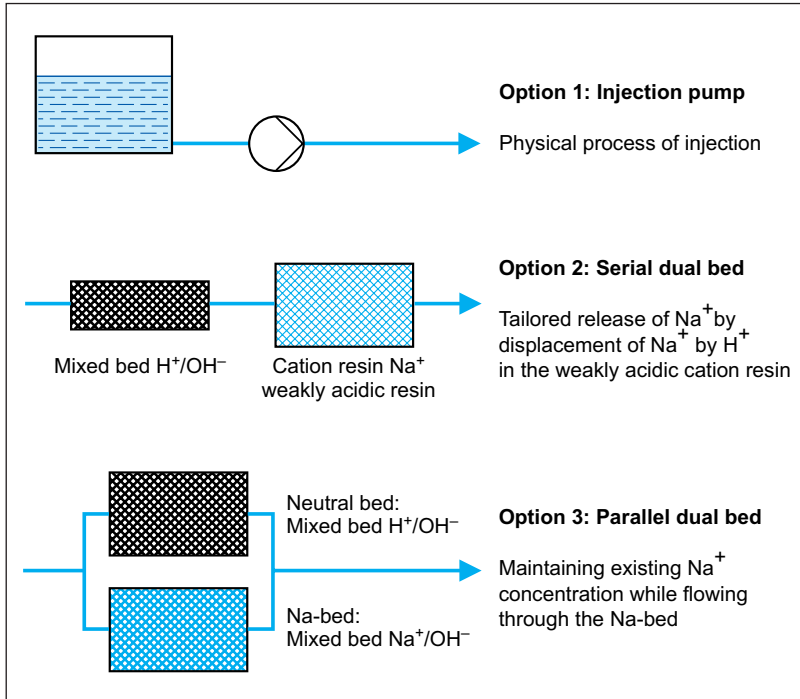


Figure 6:
Current options for alkalinizing the stator cooling water system. All mixed-bed resins are strongly acidic cation/strongly basic anion resin.

In the range of interest, pH has a logarithmic correlation to conductivity. Therefore, two-point conductivity control in a narrow band can be used to keep the pH within tight limits (e.g. variations < 0.1 pH). Additional controls are required to meet various operating conditions, e.g. loss of mixed-bed water flow, shutdown of the system etc.

The injection works reliably and does not require regular expert supervision. However, periodic makeup of the NaOH stock solution is necessary, as well as replacement of the mixed-bed resin, which will eventually be loaded with NaOH. With a fitting design, the frequency of these actions can be kept to once per year. A mixed bed loaded with NaOH is not necessarily exhausted and may be kept in operation if the other chemical parameters are kept under control.

Serial Ion Exchange Beds

A mixed bed with strongly acidic H^+ cation exchange/strongly basic OH^- anion resin is followed downstream, in series, by a selected weakly acidic cation exchange resin with a customized loading of Na^+ . The mixed bed releases ultrapure water, and the serial cation bed a predetermined constant concentration of Na^+ ions. These two resin beds may be layered into a single vessel.

As long as the mixed bed is not exhausted and kept at full efficiency, the Na^+ release of the cation resin is stable and

influenced only slightly by variations in temperature.

Apart from preparing the resin and putting it into service this system does not require expert supervision.

This system was developed and used by Siemens in the 1980s, but preference later shifted towards the injection pump system because it is simpler.

Parallel Ion Exchange Beds

Two mixed beds are used. One mixed bed is filled with strongly acidic H^+ cation exchange/strongly basic OH^- anion resin ("neutral bed"), the other one with strongly acidic Na^+ cation exchange/strongly basic OH^- anion resin ("Na-bed") in parallel.

The process Strongly acidic cation resin cannot be regenerated with pure water. Therefore, with pure water, the strongly acidic Na^+ resin does not release Na^+ ions, it releases just pure water. Thus, the Na-bed is per se not useful for alkalinizing the system.

The idea is that impurities in the water, e.g. the dissolved Cu^{++} ions, will replace the Na^+ in the resin, so that the resin bed receives Cu^{++} at the inlet and expels 2Na^+ at the outlet. As good as it sounds, stoichiometry, however, does not permit a useful alkalinization of the system. Alkaline treatment requires in the order of $100 \mu\text{g} \cdot \text{L}^{-1} \text{Na}^+$; at the corresponding pH, however, Cu^{++} solubility is in the order of $2 \mu\text{g} \cdot \text{L}^{-1}$. So the Cu^{++} (or other trace impurities) cannot be the driver for a sufficient alkalinization of the system.

However if the system has, let us say for example, $100 \mu\text{g} \cdot \text{L}^{-1} \text{Na}^+$ in the water, the Na-bed will not retain this quantity of Na^+ ; the outlet concentration will be equal to the inlet concentration and the pH of the water will remain unchanged. When now a few $\mu\text{g} \cdot \text{L}^{-1}$ of Cu^{++} enter the Na-bed, a few $\mu\text{g} \cdot \text{L}^{-1}$ of Na^+ will be released from the bed, so the Na concentration in the system will rise very slowly. This is where the neutral bed comes into action to remove the excess of Na^+ .

To summarize, once the system is sufficiently alkalinized, the Na^+ is not removed by the Na-bed, so alkalinization will stay constant. Trace cationic impurities like Cu^{++} will cause a slow increase in Na^+ concentration, which has to be corrected with the neutral bed. It is evident that only a very small and infrequent flow of the neutral bed is required. If this flow is too large, the alkalinization will be lost [19].

Note: It is also possible to place the neutral bed in series downstream of the Na-bed [9]. A sufficiently large bypass is required for limiting the water flow through the neutral bed.

Kinetics The kinetics of the parallel dual bed is illustrated in the following example.

The following operating parameters are stipulated:

- Na-bed flow: $1 \text{ m}^3 \cdot \text{h}^{-1}$
- Neutral bed flow: closed off to begin with
- System water volume: 5 m^3
- Na^+ concentration in the system: $100 \mu\text{g} \cdot \text{L}^{-1}$
- Cu^{++} concentration in the system: $2 \mu\text{g} \cdot \text{L}^{-1}$

At the beginning, $100 \mu\text{g} \cdot \text{L}^{-1} \text{Na}^+$ circulate through the system as well as through the Na-bed. The $2 \mu\text{g} \cdot \text{L}^{-1} \text{Cu}^{++}$ will displace $2 \cdot (23/32.5) = 1.42 \mu\text{g} \cdot \text{L}^{-1} \text{Na}^+$ from the Na-bed. This adds $1.42 \mu\text{g} \cdot \text{L}^{-1} \cdot 1 \text{ m}^3 \cdot \text{h}^{-1} = 1.42 \text{ mg} \cdot \text{h}^{-1} \text{Na}^+$ to the system.

$1.42 \text{ mg} \cdot \text{h}^{-1} \text{Na}^+$ influx will mean a rise of $(1.42 \text{ mg} \cdot \text{h}^{-1}) / (5 \text{ m}^3) = 0.28 \mu\text{g} \cdot \text{L}^{-1}$ per hour in the main system. With this, it will take 35 hours until the system Na^+ concentration increases by 10 % to $110 \mu\text{g} \cdot \text{L}^{-1}$.

If the neutral bed is now taken into operation with $1 \text{ m}^3 \cdot \text{h}^{-1}$, it can be shown that it will take about 0.48 hours or 29 minutes to bring the Na^+ in the system back again to $100 \mu\text{g} \cdot \text{L}^{-1}$.

Alternatively, the neutral bed may be left in constant operation all the time. In this case, the Na^+ influx ($1.42 \text{ mg} \cdot \text{h}^{-1}$) must be balanced by the removal rate of the neutral bed ($[\text{bed flow } \text{m}^3 \cdot \text{h}^{-1}] \cdot 100 \mu\text{g} \cdot \text{L}^{-1}$). From this, it can be derived that a mixed-bed flow of only $14.2 \text{ L} \cdot \text{h}^{-1}$ will be required to keep the Na^+ concentration in the system at $100 \mu\text{g} \cdot \text{L}^{-1}$. Larger neutral bed flow will cause the Na^+ concentration to collapse.

These considerations indicate that the neutral bed is needed only infrequently to correct the rise in Na^+ concentration in the system. Frequent use or more than trickle flow will compromise the level of alkalization. Any automatic control of the neutral bed flow has to be very subtle.

Practicalities The key point is how to start up this self-sustaining chain. It is not self-priming, or if so, is very slow and depends on "dirt effects". The proper way to start is to temporarily inject a NaOH solution [9,20]. Less controlled alternatives are to add a few pellets of NaOH to the system [11,21], to start with incompletely rinsed Na^+ resin [20], or to rely on various trace impurities [22].

The literature does not yet contain a reminder that proper start-up of the alkalization as well as a very limited use of the neutral bed are essential for getting the parallel dual bed working properly. This has caused severe inadequacies in stator water chemistry in some power plants where this alkalizer system was built just from literature information.

One feature of alkaline water is that it absorbs carbon dioxide from air more readily than neutral water. In addition, the Na-bed, operating in an alkaline medium, has poor retention efficiency for carbon dioxide. Therefore, the system is sensitive to lowering of the pH by air leakage. Besides compromising the alkalization, conductivity no longer gives a correct indication of pH. In such a case, supplemental analyses of Na are required for correct interpretation of the conductivity measurement (Figure 5). These effects are especially important for high-oxygen systems, where air is injected in order to maintain the high oxygen level. The injected air should here be free of carbon dioxide.

The advantage of the serial dual bed method is the longevity of the resin and the NaOH inventory (several years), and the absence of chemicals on site. It is, however, evident that this system requires expert supervision for starting up and also for further operation.

EXPERIENCE

Alkaline treatment is the standard used by Siemens and associated companies with more than 200 applications (low-oxygen systems), and by the large utilities Eskom with 60 and ENEL with 12 alkalized generator cooling water systems (low-oxygen as well as high-oxygen systems) [2,21,22]. All report distinctly improved performance with regard to the elimination of hollow conductor plugging.

The author's experience is limited to direct insight into about 2 dozen alkalized systems, however with all of the three alkalizing options described earlier.

Injection Pump System

Simple and trouble-free operation. All cases were preventative applications, where no statement is possible with regard to hollow conductor plugging.

Serial Dual Bed

This case concerns 9 generators by one manufacturer (4 with 824 MVA and 5 with 766 MVA), plus 9 with identical basic design by another manufacturer, all equipped with

identical cooling water and alkalizer systems. Measurements indicated pH fluctuations up to 0.5 units within one week. The first group of 9 generators mentioned above suffered substantial oxide deposits and needed chemical cleaning, while the generators of the other manufacturer were reported to be significantly less affected.

Parallel Dual Bed

The first case was a generator with a history of repeated plugging. In order to "survive" the time until the planned rewind, parallel dual bed alkalization was started. Insufficient alkalization was observed and in order to correct the situation, it was followed up by gradually lowering the mixed-bed flows to the point where both beds had no more flow. After a few weeks, the stator started to plug up rapidly. Following the rewind, the parallel dual bed could be brought into proper functioning.

In the second case, the dual bed did not bring sufficient alkalization. Injection of a few pellets of NaOH caused a conductivity spike which prompted the operators to suspend further operation of the dual bed indefinitely.

In two more cases, on the occasion of a chemical cleaning to lower stator pressure drop, the pH was found to be only 7.8.

Other cases: A generator with high-oxygen alkaline chemistry had proper stator pressure drop and no indications of oxide deposits. Finally, a generator with poor control of high-oxygen chemistry and of alkalization still had proper stator pressure drop, but inspections showed some deposits in the stator bar water chambers ("clips").

CONCLUSIONS

The main purpose of alkaline treatment is to prevent or to reduce the occurrence of flow restrictions in copper hollow conductors caused by oxide deposits. Its action is based on the reduced solubility of Cu^{++} in alkaline water. Hydrodynamic parameters like water flow velocity, turbulences, temperature etc. also play a role. Therefore alkaline treatment is beneficial, but it is not the only decisive parameter for avoiding flow restrictions.

However, there are indications that alkaline treatment produces thicker oxide layers than with neutral water. These oxide layers are nevertheless very thin (in the order of a few micrometres) and do not restrict flow as long as they stay in place. When these oxides however migrate, e.g. by variations in the oxygen concentration or by fluctuations of pH, there is a risk of local accumulation and flow restrictions. It is therefore very important to always keep alkaline treatment under good control. This is especially important during generator shutdown periods.

The increased conductivity of the alkaline stator cooling water does not have known adverse effects on generator operation and on system materials.

Alkalization with an injection pump is the simplest and most reliable method. Parallel dual beds are also used for alkalization, but they need careful expert supervision, and follow some often overlooked rules, especially regarding proper priming of the alkalization of the system water and a very restricted use of the neutral bed.

A side benefit of alkaline treatment is that stator water chemistry is not a side issue any more and will get increased attention.

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