

Behaviour of Copper in Generator Stator Cooling-Water Systems

Robert Svoboda ^a and Donald A. Palmer ^b

^a Alstom Power, Brown Boveri Str.7, CH-5401 Baden, Switzerland

^b Oak Ridge National Laboratory, Box 2008, Building 4500S, Oak Ridge, TN 37831-6110, USA
Email: robert.svoboda@alstom.power.com

Water-cooled generators with hollow copper strands frequently suffer from deposition of copper oxides that clog them and thus impair cooling water flow. Solubility is one of the factors governing the release and the re-deposition of copper oxides. Results presented in this paper indicate that under generator cooling water conditions the solubility of copper oxides is dependent on pH and also, to a lesser degree, on temperature. At neutral pH, the solubility of copper oxides increases with increasing temperature. The dependence is stronger for Cu₂O and small for CuO. With acidic pH, the solubility of CuO may even slightly decrease with temperature. The apparently contradictory information in the literature - whether the solubility decreases or increases with increasing temperature - is probably a result of differing test conditions, or a differing mix of copper oxides, or to experimental differences.

Introduction

Water-cooled generators with hollow copper strands ("hollow conductors") frequently suffer from deposition of copper oxides that clog them and thus impair cooling water flow, Figure 1. Various water treatment regimes have been developed in order to mitigate this problem [1]. The aim of these water treatment regimes is to control formation, release, migration, and re-deposition of copper oxides, either individually or in combination, Figure 2 and reference [2].



Figure 1: Copper oxide deposits at the hollow conductor inlet

Copper itself is stable in pure water. If oxygen is added, copper(I) oxide and / or copper(II) oxide are formed, depending on the electrochemical potential (ECP) [2][3]. Laboratory-scale experiments at ORNL have shown that ingress of oxygenated water to a column of clean copper beads at 100 °C, can lead to copper release well in excess of that solubility limits of either oxide so that presumably the kinetics of copper metal oxidation and release can exceed that of copper oxide film formation [4]. Nevertheless, the release and re-deposition of these oxides play a pivotal role in the clogging of hollow conductors.

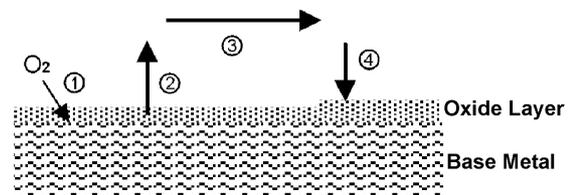


Figure 2: Model for copper oxide deposits
1 formation (oxidation)
2 release
3 migration
4 re-deposition

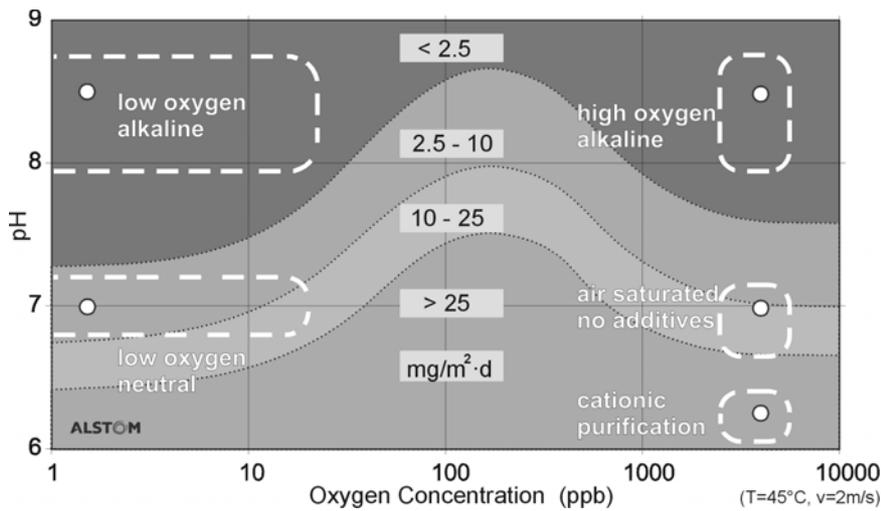


Figure 3: Summary of copper release rates in function of oxygen level and pH. Operating areas of various chemistry regimes [2]

There is a wealth of information published on parameters influencing release and deposition [1] to [13], some of which will be discussed more closely in this paper. Figure 3 summarizes the influence of pH and oxygen concentration, and also shows their relation to the current water treatment regimes.

This paper is following up reference [2], which noted that international literature presented conflicting information on the temperature dependence of the solubility of copper oxides.

Morphology of hollow conductor deposits

Laboratory tests with clean copper surfaces under simulated stator operating conditions yielded crystalline oxide layers.

The morphology of the oxides was influenced by the system water chemistry. Figure 4 gives examples of a specimen with dense polyhedral oxides, typical for high-oxygen or alkaline water chemistry, and another one with flower-shaped needles, typical for low-oxygen or neutral water chemistry. Coupon samples in a generator stator cooling system verified these results.

With long-term generator operation, the picture becomes more complex. Deposits can be of either predominantly crystallized growth, Figure 1, or an agglomeration of broken-off particles, or a combination of both, Figures 4 and 5.

The oxides from a generator stator are always a mixture between Cu_2O and CuO , with Cu_2O dominating in low-oxygen systems, and CuO dominating in high-oxygen systems.

There is evidence that an accumulation of deposit growth occurs preferentially in areas of increased turbulence, that is: at the inlets, outlets of hollow conductors and inside its length also on bends and Roebel transpositions. Very often, the

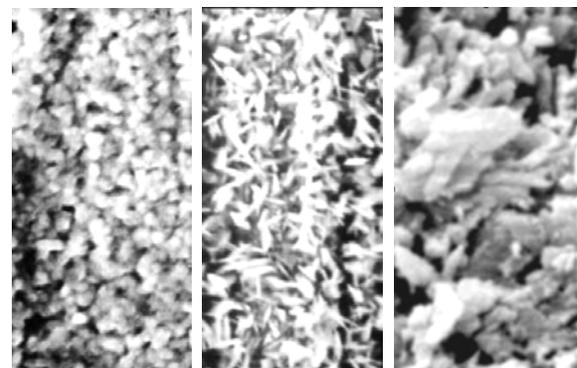


Figure 4: Oxides from oxidation of a fresh copper surface in laboratory loop: at pH=8 (left) and pH=7 (center). Pile of oxide flakes found in a generator stator (right). Scale: the horizontal width of each picture corresponds to 5 μm .

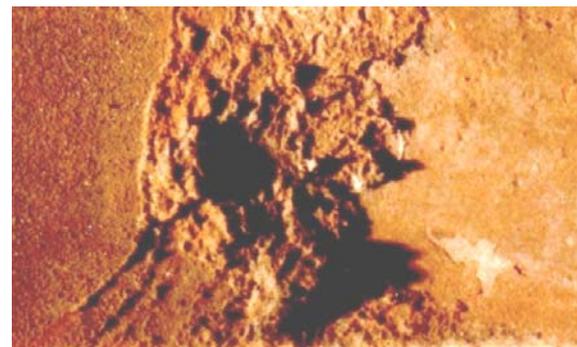


Figure 5: Oxide deposit in a used hollow conductor taken from a generator. Flow is from right to left.

first step of excessive deposition is ripple-like growth, Figure 5. An explanation of this dependence on hydrodynamics could be the increased mass transport from the bulk liquid to the copper surface, enhancing crystallographic growth.

As the water velocity in hollow conductors is moderate (usually 0.5 - 2 m/s), Flow Accelerated



Figure 6: Compact oxide plug in a used hollow conductor taken from a generator.

Corrosion is improbable under neutral and alkaline conditions. This is supported by field experience.

With aging, the oxides become more compact, Figure 6, possibly by crystallographic deposition in porous deposits. Often, the aged deposits also contain important fractions of metallic copper and become hard to remove. The occurrence of metallic copper may be the result of deposition of possible colloidal Cu particles. It is also possible that copper oxides are reduced to metallic copper. The dissolved hydrogen in stator water alone however does not provide sufficient electrochemical driving force, Figure 7 [12]. Possibly, disproportionation of Cu_2O into Cu and CuO may take place. It should be mentioned that metallic copper deposits are also found in generator cooling systems outside of the generator, like on stainless steel pump wheels or hard metal pump seals.

Effect of temperature on copper oxide deposits

Research by Hwang, Park, and Rhee asserts that hollow conductor plugging is mainly caused by the excessive release of CuO and Cu_2O particles. This release was found to be dependent on the ECP [3].

Other researchers consider that variations in the solubility of copper oxides in water cause local deposition and plugging. Here, the temperature dependence of the solubility is of relevance, because the copper strands are subject to a temperature increase along the water path through the generator. If, for example, solubility decreases with increasing temperature, copper oxide is dissolved at the colder inlet and re-deposited towards the warmer outlet of the hollow conductor [13]. Literature data however give apparently contradictory information on such a trend of temperature dependence. This shall be explored in some detail.

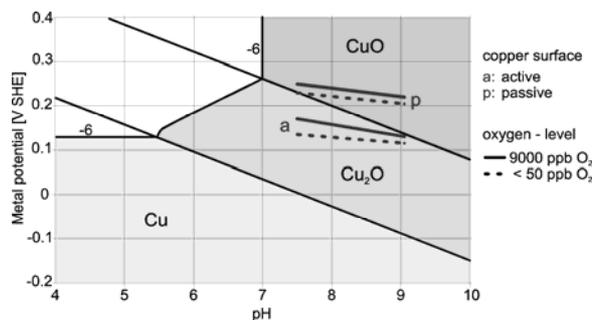


Figure 7: Pourbaix diagram and potential of passivated (black CuO layer) and active (freshly pickled) copper specimens [12]

Temperature effect on the copper release rate

Literature data

It is a well known experience from fossil plant chemistry that copper-alloy tubed feedwater heaters release copper, and the higher the temperature level is, the higher is the copper release [14]. It has however to be taken into account that these plants usually operate with ammonia and possibly also with hydrazine which makes copper chemistry more complex than it is in a water cooled generator. It is therefore of special interest to follow the investigations done by Brush and Pearl in the late 1960's for BWR cycle chemistry with neutral feedwater, Figure 8 [15][16]. The findings are similar to those from fossil plants: copper release increases with rising temperature.

These results are however only indicative, because these investigations related to various copper alloys, but in generators pure copper is used.

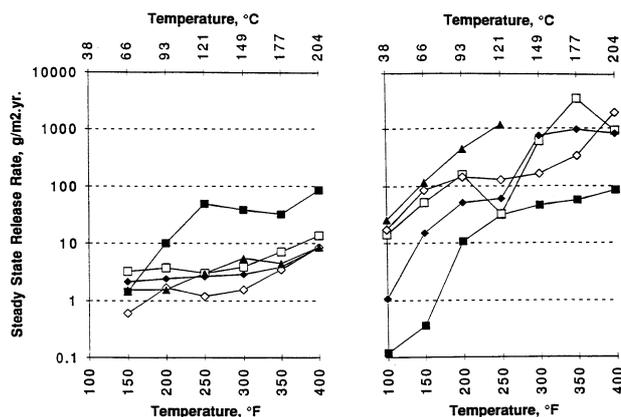


Figure 8: Steady state copper release in neutral feedwater at 5 ft/s containing (left) low oxygen ($3 \mu\text{g}/\text{kg}$ O_2 and $100\text{-}200 \mu\text{g}/\text{kg}$ H_2), and (right) elevated oxygen ($200 \mu\text{g}/\text{kg}$ O_2 and $25 \mu\text{g}/\text{kg}$ H_2) [15][16].

- Alloy 400, ▲ Admiralty brass,
- CuNi 70/30, ◆ CuNiFe 70/30, ◇ CuNi 90/10,

Laboratory tests on copper release rate

Laboratory investigations were made on the parameters for copper release rates in BBC technology generators. Some data have been previously published [2][12]. The laboratory test loop was equipped with features that allowed control of the water velocity, temperature, oxygen, pH, and chemical additives. The tests were made on pure copper.

It is however problematic to measure pH directly in a closed test loop with high purity water. It was therefore measured indirectly via conductivity. Spot checks were made with a single-electrode device that had been conditioned in a neutral salt solution. Giving allowance for these uncertainties, a pH range of 6.5-7.0 is given for the absolute value of pH. The actual pH was then kept constant throughout the tests. The results, Figure 9, indicate that the release rate increases with increasing temperature.

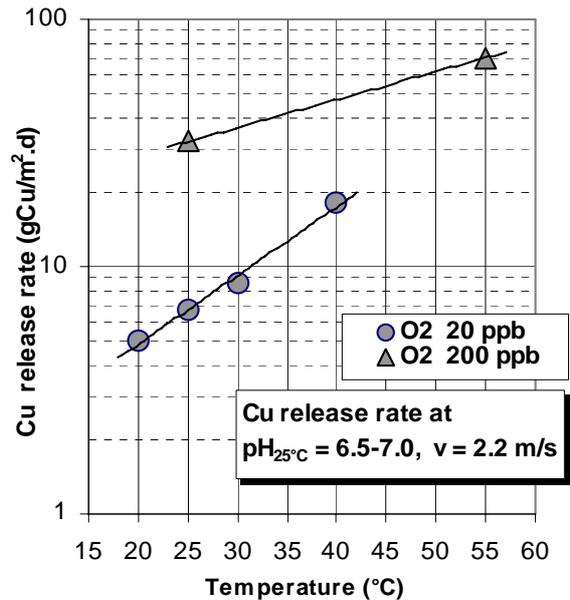


Figure 9: Copper release rate in a laboratory test loop.

Significance of the copper release rate

The drawback of these considerations however is that the release rate is only one contributing factor to oxide deposits. Once the copper is released it may re-deposit (and that may depend on the existence of previous deposits that act as nucleation seeds), but it may also be properly removed by the stator water mixed bed.

Temperature effect on copper oxide solubility

The solubility of copper oxides has been extensively studied in order to understand copper transport in the thermal cycle of power plants. Reference [14] gives an overview. The majority of work focuses on cycles treated with alkalinizing agents like ammonia and hydrazine that may also react with copper oxides. Data from such complex chemistries are however not readily applicable to generator stator systems. On the other hand, data from investigations in neutral, high purity water are here of direct interest [4] and [14] to [22].

While most research indicates that oxide solubility increases with temperature, other research point to a reverse relationship [13]. Different test conditions and the influence of stronger parameters like the pH may account for this discrepancy.

Laboratory tests on copper oxide solubility

The laboratory tests at ORNL are described in earlier publications [4][17]. A selection of these results was made with regard to conditions in stator water systems. Figure 10 presents the solubility of

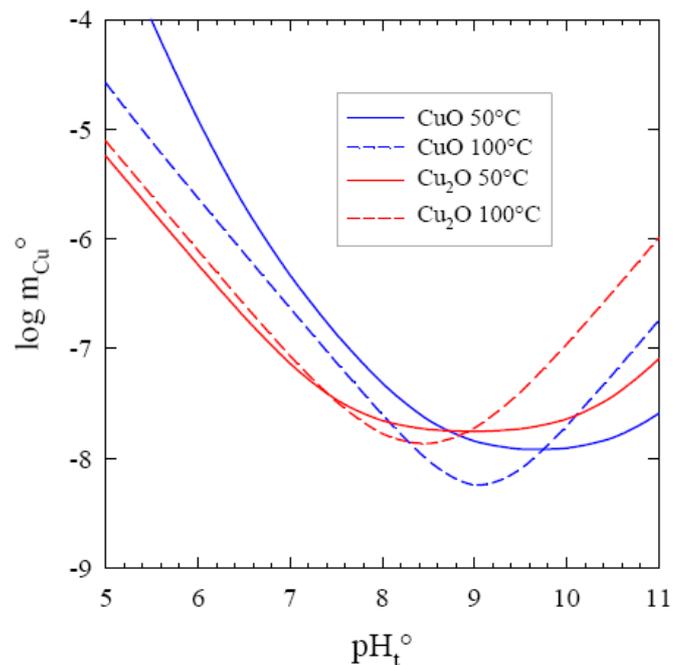


Figure 10: Experimental data for the solubility of copper oxides, in dependence of pH (at temperature) and of temperature.

Cu_2O and of CuO in dependence of pH and for temperatures of 50°C and 100°C [4]. Although 100°C is not attained at normal generator cooling conditions, this temperature nevertheless serves as an anchor-point for the temperature trend. For reasons of clarity, other temperatures, like 25°C have not been included in the graph.

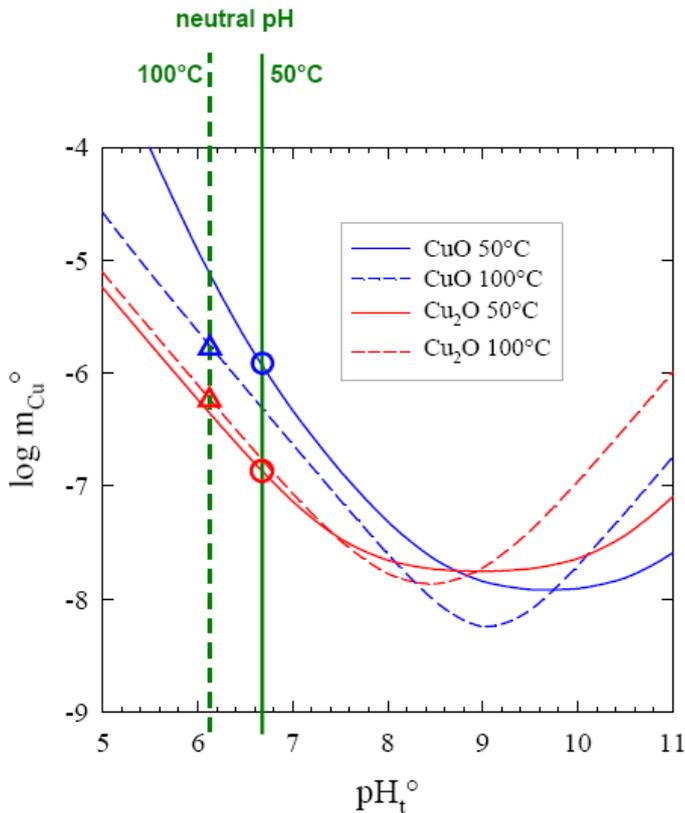


Figure 11: Solubility of Cu_2O and of CuO at neutral pH. The vertical lines indicate the neutral pH at 50°C and 100°C , resp. Their intersection points with the respective solubility curves give the solubilities at pH_N . Full lines and round intersection points \circ are for 50°C , dotted lines and triangular intersection points Δ for 100°C .

Analysis of the test data

Figure 11 analyzes the conditions at neutral pH, which is 6.64 at 50°C , and 6.13 at 100°C . It is seen that at a constant neutral pH, the solubility of both CuO and Cu_2O at 100°C are higher than at 50°C , but the change is less pronounced for CuO .

This positive dependence of solubility on temperature is also seen at very slightly acidic and at slightly alkaline pH values, such as encountered with neutral or alkaline generator water treatment.

The trend can however be reversed and solubility at 100°C may be smaller than at 50°C in the following cases:

- at acidic pH, which is within the range of some stator water treatment regimes
- at intermediate alkaline pH (for example with NaOH , $\text{pH}_{25^\circ\text{C}}$ ca. 10-11), which is however not any more relevant for generator water chemistry

Summary and Conclusions

Results presented in this paper indicate that the solubility of copper oxides are dependent on pH and also, to a lesser degree, on temperature.

At neutral pH, the solubility of copper oxides increases with increasing temperature. The dependence is stronger for Cu_2O and small for CuO .

With acidic pH, the solubility of CuO may even slightly decrease with temperature.

The apparently contradictory information in the literature - whether the solubility decreases or increases with increasing temperature - is probably a result of differing test conditions, or a differing mix of copper oxides, or due to experimental differences such as: the control and measurement of pH; the characterization of the copper oxide before and after the experimental sequence; continuous control of the redox state of the system; the attainment of a true equilibrium condition.

The model that oxide deposits take place because their solubility decreases at the higher temperature of a stator bar outlet could not be confirmed: the solubility increases with temperature. Further, oxide deposits do not only occur at the warm conductor outlets, but also at the colder conductor inlets, Figure 1 and reference [8], which contradicts this model.

Reference [3] indicates that hollow conductor plugging may be related to the excessive release of CuO and Cu_2O particles, in dependence on the ECP.

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