

THE CHEMISTRY OF COPPER IN WATER AND RELATED STUDIES PLANNED AT THE ADVANCED PHOTON SOURCE*

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forms at the metal surface, which, in the absence of other

Abstract

Interactions between water and copper are a critical issue at most accelerators. The release rate of copper and oxides in water is affected by several variables: dissolved oxygen concentration, pH, and temperature. Relative corrosion rate, solubility data, and operating regimes are summarized based on previous work by others. Mechanisms for oxide release are discussed, and a means of pH control employing an ion exchange process is described.

1 INTRODUCTION

Accelerator components made of copper are routinely cooled by deionized (DI), low-conductivity water. Release of copper oxides from the parent surface is common. Releases comprise reddish-brown residue (Cu_2O) and, depending on the concentration of dissolved oxygen (DO), black residue (CuO). In extreme cases, releases can accumulate such that flow through system components is significantly restricted or blocked altogether.

During operations at the Advanced Photon Source (APS) up to 1998, release of copper oxides became a significant issue. These issues were addressed by improving the performance of an existing vacuum deaeration system. Deaeration DO quality is routinely less than 5 ppb; the bulk system operates between 5-10 ppb. Throughput of the deaeration system is 450 gpm (approximately 4.5% of bulk throughput). Combined with improved filtration, oxide accumulation has been reduced to manageable rates. Filtration at point of use is nominally 0.5 micron; treatment system filtration is 0.05 micron absolute.

DI water systems for accelerators have much in common with those for cooling the stators of electrical generators. Specifications for DO at the Advanced Photon Source (APS) are based on those utilized in the electric power industry [1]. A significant bibliography exists concerning the chemistry of copper-water systems [2-8]. From this work, it is clear that the hydrogen ion plays a significant role in the copper corrosion mechanism.

2 CORROSION MECHANISM [9]

Oxygen (O_2) and carbon dioxide (CO_2) are present in water due to interactions with the atmosphere. An oxide

influences, is stable. The presence of CO_2 in the water results in the formation of carbonic acid (H_2CO_3), which dissociates into HCO_3^- and hydrogen ions (H^+). H^+ , which has an affinity for the oxygen component of the oxide, readily forms water. The copper at the surface is now left in its ionic form and readily dissolves. The metal surface, now unprotected by the oxide, is again exposed to water, DO, and H^+ – allowing the process to recur.

3 DISSOLVED OXYGEN CONCENTRATION

The corrosion rate of copper in water (at neutral pH) as a function of DO is indicated in Fig. 1 [10]. The maximum rate occurs in the range of 200-300 ppb. “Low oxygen” and “high oxygen” operating regimes are defined relative to this maximum. Stator cooling systems can be designed to operate successfully in either regime. The choice is usually specified by the manufacturer but can be changed by the owner if operating experience indicates a benefit [8,13].

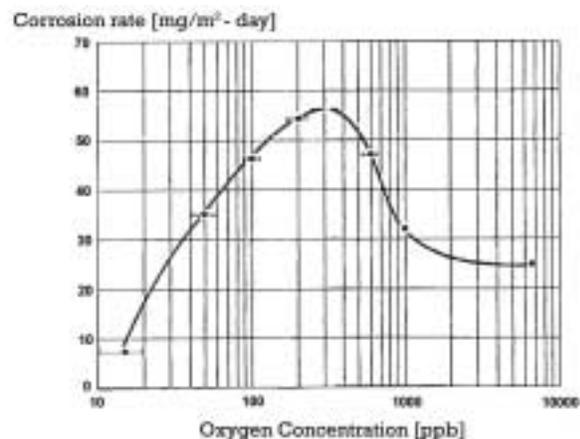


Figure 1: Corrosion rate vs. DO.

4 INFLUENCE OF PH

$[\text{H}^+]$ also influences the corrosion rate, as indicated in Fig. 2 [10]. The rate is minimized at pH values approaching 8.5 and greater. The Pourbaix diagram in Fig. 3 [11] indicates stable forms of copper in aqueous

*Work supported by the U.S. Department of Energy, Office of Basic Energy Sciences under contract No. W-31-109-ENG-38

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solution as a function of pH and metal potential. For pH values below 7.0, the copper ion is stable in solution. Formation of the ion occurs from the oxide state when pH is just below 7.0. Replacement of the oxygen component of the oxide occurs readily under these conditions.

For pH values above 7.0, the preferred form of the metal is the oxide. Replacement of the oxygen component of the oxide does not occur and slows the corrosion mechanism. This is consistent with Fig. 2 and provides an understanding of reduced corrosion rates when the solution is alkaline.

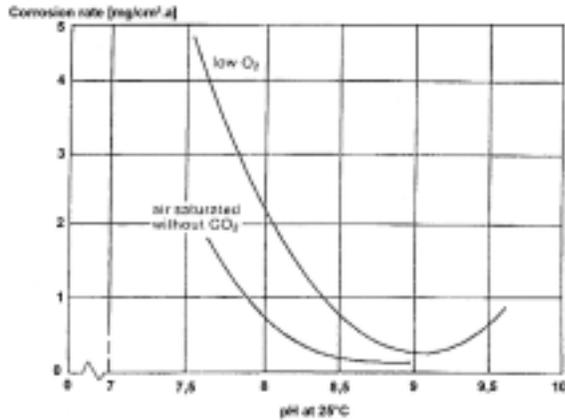


Figure 2: Corrosion rate vs. pH.

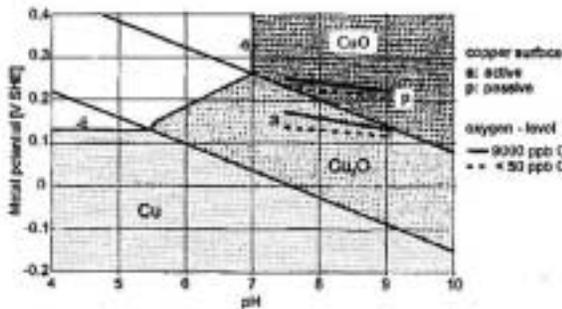


Figure 3: Pourbaix diagram for copper.

5 INFLUENCE OF TEMPERATURE

Temperature plays a significant role in the solubility of copper in water, particularly at neutral to acidic pH. Figure 4 [12,13] indicates the relationship of copper solubility as a function of temperature for various values of pH. Figure 5 [12,13] indicates the relationship of solubility in terms of pH for various temperatures. When pH is lower than 7.0, the influence of temperature is more noticeable and provides an explanation for water flow restrictions that occur at the outlet ends of copper components where heat transfer takes place along the length of the component.

6 OPERATING REGIMES

Several options exist for choosing an operating regime for a copper-water system. These are:

- Neutral pH, low oxygen,
- Neutral pH, high oxygen,

- Elevated pH, low oxygen, and
- Elevated pH, high oxygen,

Figure 6 shows corrosion rate data for various operating regimes [13].

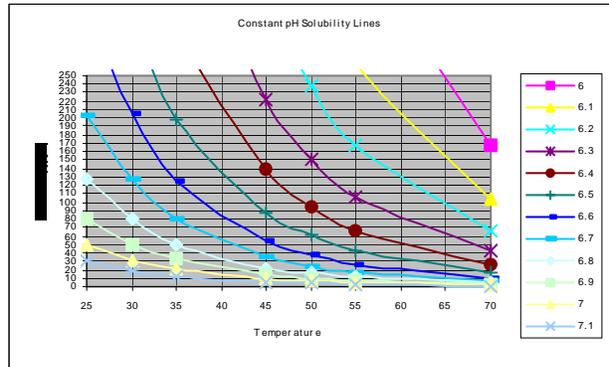


Figure 4: Copper solubility vs. temperature.

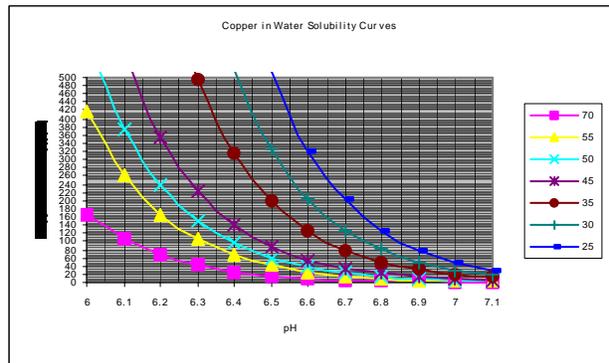


Figure 5: Copper solubility vs. pH.

Because of the relatively high heat fluxes experienced at APS, the decision to operate at low oxygen has been in place for some time. At this time, it is believed that the pH of the DI water for copper components is, at best, neutral or slightly acidic (see Fig. 7). This is likely due to the fact that the makeup tank is open to the atmosphere and that the cation resins in use for treatment are in the hydrogen form.

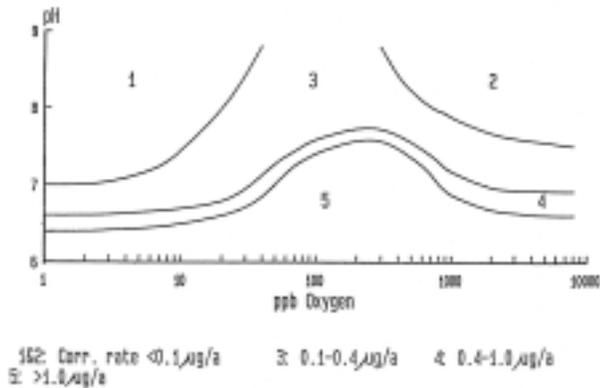


Figure 6: Corrosion rate at various operating regimes.

7 LIMITATIONS ON OPERATING REGIME

The relationship between pH and resistivity of DI water is shown in Fig. 7. Operation of a water system at 8.5 pH would require a resistivity of 1 Mohm-cm or lower. Currently, the APS water system operates at between 8-10 Mohm-cm. A resistivity value below 3.0 is not acceptable from the point of view of leakage currents. A more realistic minimum for resistivity is around 5.0. The corresponding maximum pH that would be feasible is about 7.5. Adjustment of pH to 7.5 could be expected to reduce the already-manageable corrosion rate by as much as a factor of 5-10 based on Fig. 6.

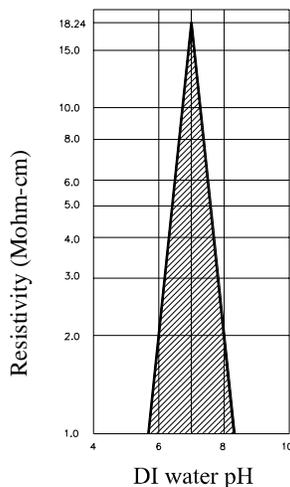


Figure 7: Resistivity limits of DI water.

8 MEANS OF CONTROLLING PH

It is common for resistivity to be maintained by the use of ion exchange resins. Positively charged ions are typically removed from the system by the cation resin and replaced with hydrogen ions. When this process occurs, the hydrogen ion content of the water system is increased (i.e., pH decreases). If cation resin is processed in the

sodium form, however, positively charged ions are replaced with a sodium ion, and the pH value increases.

Such a means is being employed in a stator cooling system at an Eskom generating facility in South Africa [13]. When pH falls to a low limit, the treatment stream is transferred to cation resin in the sodium form. When pH rises again to a high limit, the flow is returned to resin in the hydrogen form. Although pH control is achieved, the conductivity of the water is sampled as the diagnostic because there is a direct relationship between conductivity and pH (see Fig. 7).

9 PLANS FOR INVESTIGATION AT APS

Plans for investigation at APS include learning to control pH through the means described above using resin treated in the sodium form. The investigation should verify that corrosion rates change as expected in a quantitative way. Learning reliable measurement and calibration techniques for pH and conductivity is also imperative.

10 ACKNOWLEDGMENTS

The authors would like to acknowledge Scientech, Inc. (formerly NUS Information Services) for its efforts in facilitating the transfer of this valuable information through its pre-seminar workshop entitled "The Basics of Stator Coolant Water Chemistry," presented by E.V. Maughan at the 2000 International Chemistry On-Line Process Instrumentation Workshops in Clearwater, Florida (Nov. 14-17, 2000).

11 REFERENCES

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- [10] E.V. Maughan, "The Basics of Stator Coolant Water Chemistry," pre-seminar workshop presented at the 2000 International Chemistry On-Line Process Instrumentation Workshops in Clearwater, Florida (Nov. 14-17, 2000).
- [11] Work performed by Alstom, Switzerland (R. Svoboda), private communication with E. Maughan.
- [12] Work performed by Electricite de France, private communication with E. Maughan.
- [13] Work performed by Eskom (J.D. Aspden), private communication with E. Maughan.