2nd International Workshop on Mechanical Engineering Design of Synchrotron Radiation Equipment and Instrumentation (MEDSI02)
September 5-6, 2002 – Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois U.S.A.

Mitigation of Copper Corrosion and Agglomeration in APS Process Water Systems

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Abstract

Copper corrosion has been observed in process water (PW) systems at the Advanced Photon Source (APS) dating to the early postcommissioning phase of the project. In time, copper corrosion products agglomerated significantly in certain preferred locations. Significant agglomerations (or deposits) can occur in copper cooling passages such as magnet conductors and x-ray absorbers having relatively large length-to-diameter ratios and where heat is removed by water cooling. Such agglomerations also occur at restrictions found in noncopper system components such as valve seats, fixed orifices, pump seal faces, etc. Modifications to the APS process water system that significantly reduce the rate of copper corrosion are discussed. These modifications have not prevented corrosion altogether, however. Other means used to prevent component clogging and malfunction as a result of current copper corrosion rates are listed.

Keywords: copper, corrosion, water, oxygen, deaeration, agglomeration

1. Introduction

The first indications of copper agglomeration in APS deionized (DI) process water (PW) systems were noticed on various system components such as hoses, pipes and tubes, pump impellers, flow control valves, passive flow control devices as manufactured by Griswold, and small orifices used for flow control (typical diameter on the order of 0.06 in.) These indications did not appear threatening initially and their origin was unknown. Deposits consisted of varying ratios of black and reddish-brown residue.

Investigations of these deposits led to an awareness that oxides of copper were being formed in the water system, removed to other areas of the system, and deposited at certain preferred locations. It was not understood, however, why certain locations for deposits were preferred over others. However, it was noticed that deposits occurred primarily where high shear forces were occurring in the water system. Components having higher shear rates often seemed to exhibit larger amounts of deposits.

As time progressed, copper agglomeration became more pronounced. By the middle of 1997, there had been several instances of clogging of magnet conductors and insertion device absorbers at APS. These instances did not follow the pattern of the deposits that agglomerated in areas of high shear rates. Malfunctions of system flow components were occurring more and more regularly due to the apparent increase in the copper corrosion rate.

Since the frequency of copper agglomeration and clogging reached a peak in late 1997 and early 1998, much has been learned by personnel at APS concerning factors that influence the copper corrosion rate [1]. One important factor that has been addressed aggressively is the concentration of dissolved oxygen (DO) in the water. Other factors have since come to light [2]. However, these factors have not yet been addressed because efforts to date have resulted in mitigating to an acceptable degree the effect of agglomerations that continue to occur at the current (reduced) corrosion rate. Practices are now in place to reduce the ingress of DO, aggressively remove copper oxides in the water by filtration, and avoid the use of components in which copper can accumulate.

2. First Efforts at Mitigation

By September of 1997, it became clear that the concentration of DO was a key factor in the corrosion rate of copper in DI water [3]. This relationship was suspected qualitatively based on the apparent correlation between periods of relatively high DO in the water system and subsequent fouling of Griswold flow control devices in x-ray absorber water circuits. During this period of postcommissioning at APS, an aggressive program of water system upgrades was underway and periods of high DO were not unusual. The relationship with high DO was confirmed when Ref. 3 was obtained. We learned from engineers at the local power company that stator cooling water systems in electric power plants operate under similar conditions.

The most significant piece of information gleaned from the power industry reference document was the knowledge that copper corrosion rate was maximized when DO was in the neighborhood of 200 ppb. This information is indicated graphically in Fig. 1 [2]. This information led to the conclusion that existing DO sensing instrumentation at APS was inadequate. Further communication with those in the electric power industry led to procurement of DO instruments from Orbisphere, which can reliably measure DO to trace levels (down to 5 ppb or less).

With the installation of Orbisphere online sensors, it was learned that the APS system operated in the neighborhood of 100 ppb after long periods of time without the known introduction of oxygen to the system. Furthermore, it was observed that the installed deaeration system actually assisted in maintaining this level once DO had been reduced from initially higher levels. The deaerator did remove DO relatively quickly when levels were higher than 100 ppb. However, at approximately 100 ppb, the deaerator added DO to the water at a rate equal to the rate at which DO was being consumed by copper in the corrosion process. It should be noted that this was not due to any failure of the deaerator, but rather a consequence of the original set of design specifications.

It is important to understand that, for a closed system (assuming negligible oxygen ingress), the concentration of DO will approach zero because all DO will eventually be consumed by the corrosion process. This did not occur at APS because of the presence of the deaerator.

A deaerator, depending on its design, will operate at a certain pressure just above the boiling point of the water therein. Depending on the volume of noncondensable gas being removed by the vacuum pump, the pressure in the vessel will rise to a point where oxygen concentration in the vapor space and the liquid droplets reaches an equilibrium. For the original deaerator, this equilibrium occurred at around 100 ppb.

It was clear from the literature and DO data that an upgrade to the deaerator was required. This upgrade would have to address both the quality of treated water and the throughput quantity.

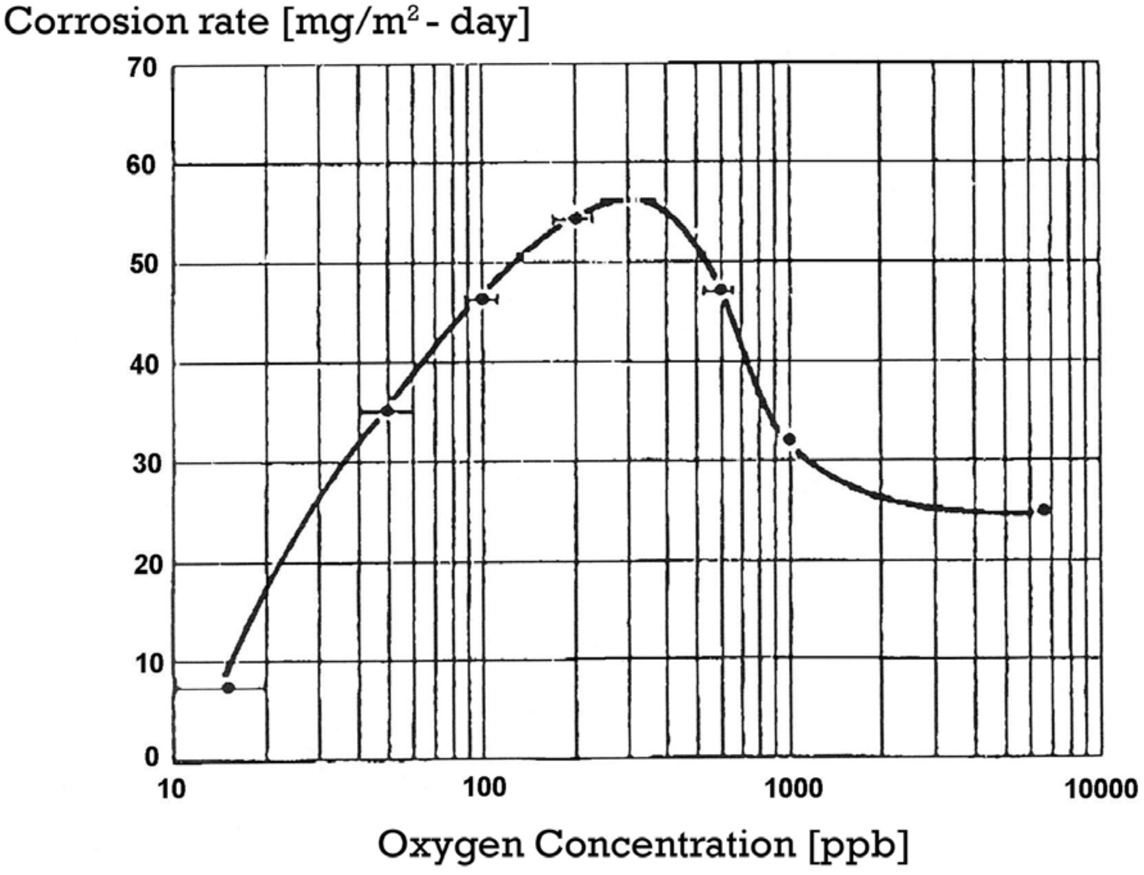

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Fig.1: Copper corrosion rate as a function of oxygen concentration.

3. Upgrade of Existing Vacuum Deaerator

Design specifications for the APS included a requirement for removal of DO from DI-PW to a concentration less than 500 ppb [4]. Specifications called for installation of a vacuum deaerator to continuously remove oxygen from the closed-loop PW system. The deaerator was designed by the Permutit Company, Inc. (now a part of U.S. Filter) and commissioned in late 1992 through early 1993.

As previously discussed, copper corrosion rates are maximized when DO concentration is in the range of 100-500 ppb, peaking around 200 ppb. Investigation of the APS deaeration system indicated that the deaerator actually exceeded design specifications and maintained the DI water system in the neighborhood of 100 ppb under "normal" circumstances. This figure would fluctuate significantly during maintenance periods depending the amount of makeup water required to refill lines drained during system upgrade work and the severity of leaks. Upsets frequently occurred in the range of hundreds of ppb and greater.

When the need for improvement of deaerator performance was indicated, the original designer of the deaerator provided design information which, after implementation, resulted in significant improvement in the performance of the deaeration system [5]. Table 1 summarizes these performance improvements.

Table 1: Performance of Original Deaerator System and Upgraded System.

	Original System	**Upgraded System**
Cooling system nominal flow (gpm)	10,000	10,000
Deaerator throughput (gpm)	150	450 (normal)
		550 (max)
Dissolved oxygen in effluent (ppb)	~80-150	<10
Pressure in vapor space (torr)	30-35	22-25
Number of vacuum pumps	1	2
Total vacuum throughput (cfm)	140-150	280-300
No. of ejector pumps and size (in)	one @ 1.5"	two @ 1.5"

The pressure envelope of the 4 ft-diameter vacuum vessel was not modified. Rather, modifications focused on lowering the pressure in the vapor space, improving the contact area and residence time between water droplets and the vacuum environment of the vapor space, and increasing the treatment flowrate.

The vapor space pressure was lowered by installing a second liquid ring vacuum pump. Larger ejectors were also installed. The ejectors provide for a vessel pressure very near the saturation pressure (boiling point) of the water while maintaining a higher pressure at the vacuum pump inlet. This prevents cavitation of water in the liquid ring pump.

Contact between water droplets and the vapor space was improved by removing the existing tower packing used in the deaerator and installing a more efficient packing (Maspac FN-1000-1").

Other modifications included a larger spray nozzle at the top of the vessel and a larger level control valve to match the increased throughput. Effluent pumps were increased in number from two to three and the corresponding pump suction line was increased from 4" to 8" in diameter to provide sufficient positive suction head to the pumps.

During the upgrade work for the deaerator, DO was minimized by the use of oxygen scavenger resin (60 cubic feet). The resin employed was a Type I strong base anion in the sulfite form.

After the deaerator was upgraded, it was found that lines in which no flow occurs can, if laden with DO, provide a source of oxygen contamination to water flowing past a branch "tee" in the DO-laden line. This was learned when the deaerator was initially commissioned. It was not possible to bring the deaerator effluent to trace levels of DO until an active flush of all three pump discharge lines was constantly maintained. Once this flush was installed and maintained, DO out of the deaerator was typically less than 5 ppb.

4. Other Steps Taken

During the deaerator upgrade, the point at which makeup water is introduced to the system was changed to a location in the treatment stream ahead of the deaerator. All makeup is now deaerated prior to introduction to the PW system.

Although modification of the deaerator was a very effective step taken in mitigating copper corrosion in the APS-PW system, copper corrosion continues to occur. Deposits of copper are still discovered, but far less often. Clogging of magnets and x-ray absorbers is no longer an issue of great concern. The most notable location for copper agglomeration is in the referenced Griswold flow control cartridges. Although copper corrosion continues, additional measures have been taken in order to mitigate the effects of agglomeration.

Filters (0.5 micron nominal, pleated polypropylene) are installed in all PW systems at the point of use. Prior to experiencing significant copper deposits, filter elements were changed on a regular basis (every six months). Since the strong link with oxygen is now understood, replacement of filter elements is currently performed only when indicated by differential pressure. Changing of filter elements results in an increase in DO throughout the system when the filter housing is refilled. As a further measure to reduce the amount of DO ingested during a filter change, filter housings are purged with nitrogen gas prior to refilling.

In addition to filtration at the point of use, water in the treatment system is filtered after passing through the deaerator (450 gpm). Particle size is 0.05 micron absolute.

For x-ray absorbers, parallel water circuits have been combined into series circuits. Griswold flow control cartridges have been replaced with coils of stainless steel (SS) tubing. For each installed Griswold, a pressure loss was measured across the cartridge. A coil of SS tubing (typically 1/4" to 3/8" in diameter) was then made to provide a similar amount of pressure loss in the circuit. These tubes do not exhibit the buildup of copper as do the Griswolds.

In general, Griswolds are avoided due to their potential for clogging (even though they are very successfully used when clean). Where Griswolds must be installed, a frequent preventative maintenance program is essential.

Copper deposits were noticed on pump mechanical seal faces. These deposits were the source of seal leaks in many instances. Mechanical seals with "hard" seal face surfaces (tungsten-silicon carbide) are now installed. Coupled with the reduced corrosion rate, seal life is upwards of 2-3 years or more, and seal leaks are now uncommon.

The water pumps at APS supplying PW for copper components are high-speed (3600 rpm) ANSI process pumps. Most of these pumps were provided by the manufacturer with a seal flush whereby a small portion of water from the pump discharge (~150-175 psig) was recirculated to the stuffing box. The pressure of the stuffing box is approximately 75 psig so one can expect very high turbulence in the area where the flush impinges. Since many copper deposits were noticed in areas of high shear rates, it was decided to reverse this flush so that water flows out from the stuffing box and back to the pump suction.

The use of flow measuring equipment having moving parts (such as paddle wheels) is avoided whenever possible. These wheels and their bearings can be a location where copper is deposited and cause early failure of the component.

As discussed above, a line in which there is no flow can be a source of DO to flowing water in branch lines. For this reason, it is important to ensure that water is flowing in all lines in a system. If there is no demand for water in a particular branch circuit, it is recommended to keep water flowing anyway so as to reduce the possibility of contamination.

5. Future Steps

It is now understood in the accelerator community that pH is another important parameter in the corrosion process and that agglomeration is the result of lower copper solubility as water temperature increases [1,2]. It is known that a pH of 8.5-9.0 will reduce corrosion rates significantly compared to when pH is 6.8-7.0. There are power plants that operate their stator cooling systems very satisfactorily in this manner [1,6]. However, because of lower limits on resistivity in accelerators to prevent leakage currents in high voltage equipment, it may not be possible to operate above a pH of 7.5. However, operating at pH 7.5 would be expected to reduce the corrosion rate significantly compared to a system operating at pH 6.8. There are power plants operating with mixed bed resins treated in the sodium form to provide an elevated pH without dosing with NaOH. Further documentation of such systems in power plants and application to an accelerator water system are the next logical steps in mitigating the effects of copper corrosion.

6. Acknowledgments

The authors would like to thank Mr. Phillip Egebrecht of GE-Betz who, while with the Commonwealth Edison Co. (now Exelon) in 1997, cited the EPRI document [3] as a source of valuable information on the subject of stator cooling systems for the electric power industry.

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

7. References

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