

## Alleviation of Copper Problems in Fossil Plants

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Research sponsored by EPRI has now led to a clear understanding of both the science of copper corrosion, transport and deposition, and also of the processes through the feedwater, boiler water and steam in a fossil plant.

### 1. Introduction

**1.1 Background.** For fossil plant units with mixed-metallurgy feedwater systems, copper has a major influence on availability and performance at a number of cycle locations – feedwater, boiler, and high pressure turbine. Utility experiences in the mid 1990s with severe copper turbine fouling and other related problems illustrate the need to improve the understanding of copper around the fossil plant and to develop a set of guidelines for copper control. At this time EPRI initiated five major research projects within “Program Copper” to address: a) the corrosion of copper-based materials in low pressure (LP) and high pressure (HP) feedwater environments, b) the solubility of copper and its oxides and hydroxides in boiler water and steam, c) the volatility of copper and its oxides and hydroxides between water and steam, d) high temperature pH-potential diagrams, and e) the deposition of copper compounds in the HP turbine.

The results of all these studies are now complete and a final set of “guiding principles” has been developed and incorporated within a comprehensive “Guideline for Copper”. [1]

The primary purposes of this current paper are three-fold: a) to briefly outline the fossil plant problem areas (1.2), b) to outline the key research results (1.3), and c) to provide the latest understanding of copper around a fossil plant (2.0). The last is an updated version which was originally presented in an abbreviated form [2].

**1.2 Copper in the Fossil Plant.** Copper alloys have been used in the low and high pressure feedwater

heaters and condensers of fossil plants for well over 50 years. Serious problems did not emerge until the late 1950s when copper fouling of the steam turbine of once-through and supercritical units occurred. This prompted some initial research, with the paper by Pocock and Stewart<sup>(3)</sup> being a pinnacle milestone. Essentially only drum units now operate with mixed-metallurgy feedwater systems; estimates in the U.S. indicate that about two thirds of the total drum units contain copper alloys in the feedwater.

Basically the same technical issues for copper remain as they were 40 years ago, but the higher temperatures and pressures of today’s plants have changed the priority of the problems. Figure 1 illustrates a typical fossil plant and identifies the following copper corrosion and transport processes:

- corrosion of copper alloys in the low pressure feedwater heaters
- corrosion of copper alloys in the high pressure feedwater heaters
- deposition of copper onto high pressure feedwater heater tubes
- transport of copper to the boiler
- deposition of copper onto boiler water walls
- solubility of copper and oxides in boiler water
- partitioning of copper oxides into steam
- deposition of copper in the superheater
- transport of copper to the turbine and subsequent deposition on high pressure surfaces.

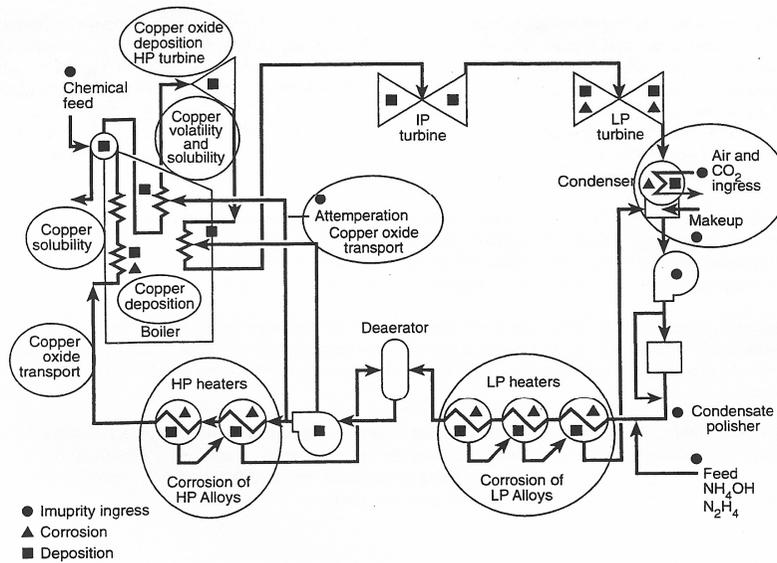


Fig. 1. Cycle diagram showing copper transport processes

It was clear in the mid-1990s that the entire cycle and all operating conditions must be addressed to optimize control of copper. The next part of the paper delineates some key research results and the final part relates this understanding to the optimum plant conditions to control and minimize copper problems.

**1.3 Overview of Research Results from Program Copper.** To upgrade the deficiencies in understanding of the copper corrosion and transport processes delineated in 1.2, the following provides an overview of the key results.

**1.3.1 Corrosion of Copper Alloys in Low Pressure Feedwater Heater Environments.** Work was conducted on admiralty brass, aluminum brass, and 90/10 copper/nickel alloys up to 95°C across a range of pH (7-11) and oxidizing-reducing potentials (ORP).[4-6] The following are the key results:

- ORP is most important in determining the surface oxide and morphology on copper alloys at temperatures below 100°C.
- Under reducing conditions (ORP-350mV), the surface oxide is cuprous oxide (Cu<sub>2</sub>O) and its formation results in a compact even layer on the surface.

- Under oxidizing conditions (ORP +100 mV) the surface oxide contains increasing amounts of cupric oxide (CuO). The copper release rate under these conditions is about three times higher than under the reducing conditions.
- When a reducing condition (-350 mV) is changed to an oxidizing condition (+100 mV) at an operating temperature of 95°C, the surface layers start to change quickly (within 10 hours) from Cu<sub>2</sub>O to CuO.
- When the temperature is reduced (as during shutdown) from 95 to 25°C, if the ORP is kept reducing at -350 mV at a constant pH, the surface oxide (Cu<sub>2</sub>O) remains on the surface.
- During a non-protected shutdown, when conditions change from 95°C and an ORP of -350 mV to 25°C and an ORP of +100 mV, the surface oxide layers start to change quickly (within 10 hours) from Cu<sub>2</sub>O to CuO again with a marked increase in surface roughness.
- Under conditions of transition between oxidizing and reducing conditions, approximately between 0.1 and 1 ppm O<sub>2</sub> or -50 to +50 mV ORP, very high corrosion and release rates are found.

- The effect of pH in the range (8.5 – 11.5) under reducing and oxidizing conditions for admiralty brass and 90-10 Cu-Ni indicates a possible minimum in the release rate of copper at around pH 9.0 – 9.3.

**1.3.2 Corrosion of Copper Alloys in High Pressure Feedwater Heater Environments.** Work was conducted on admiralty brass, 90/10 copper/nickel, and Alloy 400 at 150 and 250°C across a range of pH (8-10) and ORP[7, 8]. The following are the key results:

- Reducing conditions minimize copper alloy corrosion. These are achieved at low dissolved oxygen levels and the presence of a reducing agent. This was found to be the case for all materials and environments investigated.
- The metal release rates (copper and nickel) increase as temperature increases independent of the feedwater chemistry, but are generally higher under oxidizing conditions.
- Transient conditions are the worst operating regimes to promote copper corrosion and transport. However, the highest metal release rates occur during upset to oxidizing conditions compared to recovery from oxidizing conditions. The metal release was 75% higher in the case of an upset to oxidizing conditions. Consequently, air in-leakage should be strictly controlled during normal operating conditions.
- The worst transient conditions were for the case of unprotected startup followed by unprotected shutdown.
- The importance of using a reducing agent was confirmed after deaeration to low levels of dissolved oxygen (<5 ppb). The presence of a reducing agent is important even at low temperatures and at higher levels of dissolved oxygen.
- The most severe corrosive conditions, or the least protective surface oxide films, are formed under conditions where cuprous oxide is not completely stable and tends to convert into cupric oxide (or vice versa).

**1.3.3 Solubility of Copper Oxides in Water.** Work was carried out from 25 to 400°C as a function of pH[9-11]. The following are the key results (Figs. 2 and 3):

- As temperature increases from 25 to 350°C the solubility of both Cu<sub>2</sub>O and CuO increases first to a maximum between 200 and 250°C, and then decreases to a minimum level at 350°C. Increasing pH decreases the maximum solubility for both oxides.
- Below 100°C there is a broad minimum in solubility for both oxides from pH 8 – 11, which is around 1-2 ppb. Thus varying pH across this range has very little effect at low temperatures.
- Above 100°C the solubilities of both oxides are highly pH dependent with a very sharp minimum occurring between pH 9 and 10 for temperatures 200 – 350°C.

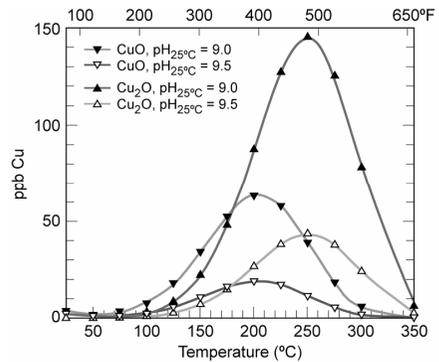


Fig. 2. The temperature dependence of the solubilities of CuO and Cu<sub>2</sub>O in water at pH 9.0 and 9.5. (Source: Reference 16)

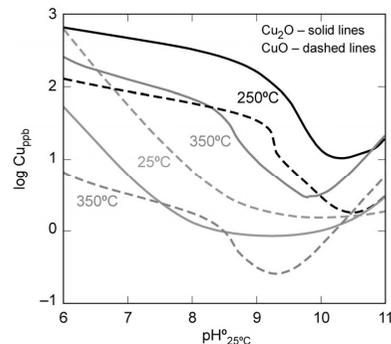


Fig. 3. Solubility of CuO and Cu<sub>2</sub>O in water as a function of pH and temperature. (Extracted from Palmer[15]).

**1.3.4 Solubility of Copper Oxides and Hydroxides in Steam.** Research was carried out from 200 to 400°C [9-11, 15]. Some of the key results (Figures 4 and 5):

- The dominant species in steam are the cuprous and cupric hydroxides ( $\text{Cu}(\text{OH})$  and  $\text{Cu}(\text{OH})_2$ ).
- The concentration of the hydroxides in steam is independent of steam pH and boiler water pH.
- Up to about 300°C the dependence on temperature is very slight and similar (1-2 ppb) for both copper species.
- The solubilities of both hydroxides in steam up to pressures of around 2400 psi (16.5 MPa) are very similar (<2 ppb). Above this pressure cupric hydroxide has a slightly higher solubility.

**1.3.5 Volatility and Partitioning of Copper Oxides and Hydroxides between Water and Steam.** Work was carried out from 25 to 400°C as a function of pH [9-11]. The following are the key results (Fig. 6):

- The dominant species in steam are the hydroxides,  $\text{Cu}(\text{OH})$  and  $\text{Cu}(\text{OH})_2$ .
- The partitioning constants for both copper hydroxides are relatively high across the whole temperature range (100 – 350°C).

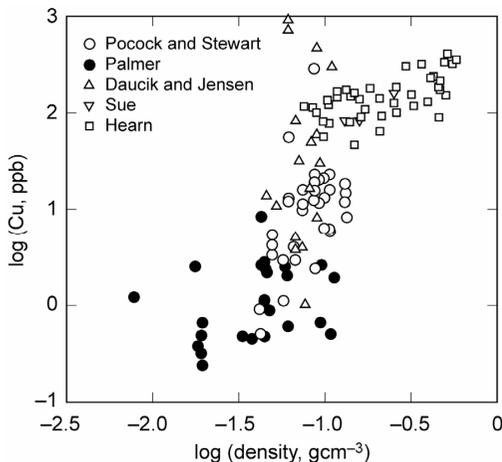


Fig. 4. Summary of the existing experimental data on the solubility of  $\text{CuO}$  in steam. (From reference 15 with data extracted from Refs. 3, 16, 19).

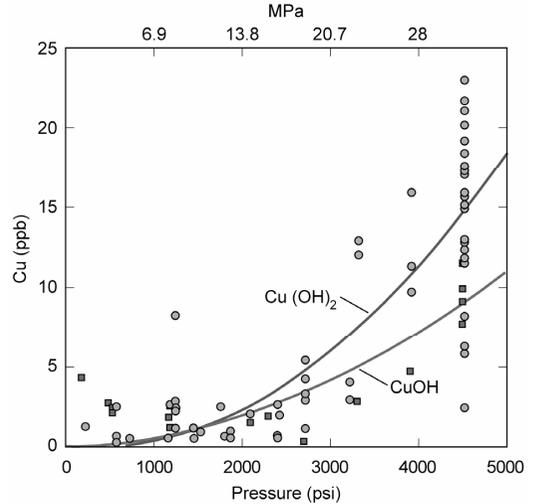


Fig. 5. Solubility of  $\text{CuOH}$  and  $\text{Cu}(\text{OH})_2$  in steam. (Extracted from reference 16).

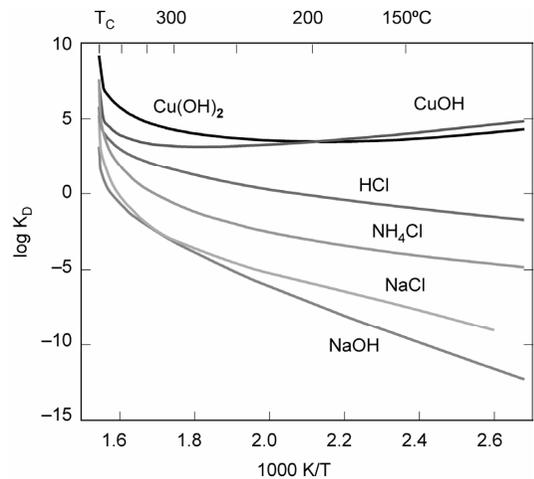


Fig. 6. Logarithm of the partitioning constants for  $\text{CuOH}$  and  $\text{Cu}(\text{OH})_2$  as a function of temperature with comparisons to those for  $\text{HCl}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NaCl}$  and  $\text{NaOH}$ . (Extracted from reference 16).

**1.3.6 Other Key Research Results.** Pourbaix diagrams (potential/pH) were developed for admiralty brass, copper/nickel alloys, and Alloy 400 in feedwater environments at temperatures from 25 to 300°C. [12]

To understand the deposition phenomena within the high pressure turbine, a converging nozzle was designed, constructed and used at two fossil plants. The key result was that the deposits grow from a vaporous transport mechanism and

not as the result of copper or copper oxide/hydroxide particulate deposition.

## 2. Application of Research Results to Understand Copper around a Fossil Plant

**2.1 Copper in Feedwater System.** Copper alloys are used in the condensate and feedwater systems of many fossil cycles. As indicated in Figure 1, the optimum location for chemical feed into the feedwater of mixed-metallurgy feedwater system is at either the condensate pump discharge or at the condensate polisher outlet (if included in the design).

Minimization of copper transport can only be achieved by detailed monitoring, and optimization of treatment for the specific unit of interest. The Program Copper research has verified the importance of controlling the oxidizing-reducing potential (ORP), which must be kept reducing during all periods of operation and shutdown. EPRI refers to this treatment as all-volatile treatment (reducing) or AVT(R).

AVT based on use of neutralizing amines (such as morpholine and/or cyclohexylamine) plus a reducing agent is the next most common feedwater treatment for units with copper alloys in feedwater heaters. Although optimal control of iron and copper transport may not be possible, this water treatment approach can be used satisfactorily, with appropriate operation and layup steps, particularly in units with condensate polishers. However, neutralizing amines and alternate reducing agents thermally decompose at normal fossil plant steam temperatures; the plant cycle must be monitored and these decomposition products identified. There has also been evidence of increased copper levels in the feedwater with morpholine additions. Use of chelants, polymeric dispersants, and organic oxygen scavengers for optimization of feedwater treatment needs to be properly evaluated with respect to their decomposition, monitoring, analytical interferences, and toxicity. None of these chemicals are desirable, needed, or recommended in utility steam cycles.

In recent years, a number of utilities have used only hydrazine or other reducing agents to establish the desired feedwater pH and provide the reducing environment. This approach is problematic as it makes control of the ORP more difficult and typically results in excessive levels

of the reducing agent and possibly a stronger than needed reducing environment in the HP feedwater system.

Another common international trend has been observed which involves injecting the reducing agent after the deaerator. The original thoughts were that the oxygen levels in the LP feedwater system were high due to air in-leakage and that reaction between this high oxygen level and the reducing agent would be very slow.

Contaminants (chloride, sulfate, carbon dioxide) may enter the condensate part of the cycle during normal operation. Research within Program Copper has clearly indicated that it is air-inleakage into the condensate that makes attainment of the desired reducing ORP conditions very difficult in the field. Oxygen must be low (<10 ppb) so that a reducing agent can be added to provide the reducing environment necessary to minimize corrosion of the copper alloys in the LP system. High air in-leakage that increases oxygen levels in the condensate has had a major effect on the corrosion of copper alloys in the LP feedwater system. The common practice of adding aerated makeup water into the cycle leads to variations in the feedwater environment; this is particularly pronounced during unit startups. Those organizations that have performed most deficiently in these areas generally will be those that have had the greatest difficulty in controlling copper levels in the feedwater. Table 1 provides the latest feedwater guideline limits for mixed-metallurgy systems[13,14]

Program Copper research has shown that cuprous oxide ( $\text{Cu}_2\text{O}$ ) is the protective, more passive, oxide of choice for feedwater waterside surfaces. This oxide is formed and remains stable when the feedwater environment is reducing, with an optimum ORP as indicated in Table 1.

Feedwater ORP should be monitored at the deaerator inlet to protect copper in the LP feedwater heaters; this also protects any copper alloy HP feedwater heaters present.

Air in-leakage control is integral to attaining the desired reducing environment. If the air in-leakage is kept below 1 scfm/100MW then the level of oxygen measured at the condensate pump discharge (CPD) can be kept below 10 ppb. It is now clear that the old oxygen limit at the CPD (20 ppb) within the original EPRI guidelines, in combination with a reducing agent addition based

Table 1 Normal cycle chemistry limits for feedwater in cycles containing copper (economizer inlet).

Cycle Chemistry Parameter	Reducing AVT (Mixed Metallurgy)
pH	9.0 – 9.3
Ammonia (ppm)	Consistent with pH
Cation Conductivity ( $\mu\text{S}/\text{cm}$ )	<0.2
Fe, ppb	<2
Cu, ppb	<2
Oxygen (ppb)	<5 <sup>(a)</sup> <10 <sup>(b)</sup>
ORP (mV)	-300 to -350 <sup>(c)</sup>

- Notes: a at economizer inlet  
 b at condensate pump discharge  
 c ORP at deaerator inlet, measured with respect to Pt electrode vs. Ag/AgCV, sat. KCl reference electrode.

on the feedwater oxygen level (three times dissolved oxygen concentration) would not always ensure a reducing environment in the LP feedwater heaters.

The new approach indicated by Program Copper is to maximize the effort to minimize air in-leakage as needed to reduce oxygen in the condensate, and to add only sufficient reducing agent to reach and maintain the optimum ORP at the deaerator inlet. The research indicates that minimum copper corrosion, dissolution and transport will occur, and that a target total copper level of less than 2 ppb will be achievable (at the deaerator inlet and/or economizer inlet. Program Copper research has further indicated that if oxidizing conditions (ORP>0 mV) exist in the LP feedwater environment at temperatures up to 95°C then the surface oxide formed on copper alloys is cupric oxide (CuO), which is non-protective. This oxide has a much rougher surface morphology, which increases the copper dissolution into the feedwater substantially. Further, the conversion of protective Cu<sub>2</sub>O to non-protective CuO starts within a few hours of transitioning from the reducing to oxidizing environment; this change is measurable in the laboratory as an increase in copper transport within as little as 8-10 hrs. Unit operating conditions which cause the ORP at the deaerator inlet to become oxidizing (ORP > 0 mV) will facilitate this transition. Operating conditions likely to lead to this situation include:

increased air in-leakage; high rates of aerated makeup water transfer and an associated increase in oxygen at the CPD to above 10 ppb; and elimination, change or non-optimization of the reducing agent applied to the cycle. Under these conditions it will not be possible to keep LP and HP feedwater copper levels less than the desired upper limit of 2 ppb.

At 25°C, the solubility of CuO and Cu<sub>2</sub>O is approximately the same at about 1-2 ppb and there is not much variation across the pH range from 8-11. CuO is slightly more soluble than Cu<sub>2</sub>O under the conditions in the LP feedwater (up to 100°C). Figure 3 shows the effect of changing pH on the solubility of both copper oxides.

These findings have very important implications for unit shutdown, layup and startup. If, as desired, reducing conditions are maintained during shutdowns, then the protective Cu<sub>2</sub>O will be maintained on heater waterside surfaces. Conversely, if the feedwater during shutdown is allowed to become oxidizing, then the Cu<sub>2</sub>O will transition to non-protective CuO. Again, Program Copper research shows this transition is measurable as an increase in copper transport within 8-10 hours. The research findings are very consistent with field experience of units that do not use layup procedures to protect the heaters. During shutdown and layup, the two most likely factors that can cause the ORP to become

oxidizing are no addition or maintenance of reducing agent during the shutdown, and addition of air-saturated makeup water to the cycle.

For optimal (reducing environment), non-optimal (oxidizing environment), and shutdown operations, Program Copper research has shown basically the same trends for the HP heater waterside surfaces as described for LP heaters. When there is a deaerator in the cycle, the oxygen level in the HP feedwater can be very low during normal operation ( $< 1$  ppb). However, low oxygen readings alone do not necessarily mean that the ORP is at the optimum level (of  $-350$  to  $-300$  mV); this must be verified by direct measurement, and a reducing environment will require the addition of a reducing agent. In cycles with deaerators, the deaerator inlet is the preferred monitoring point for ORP. Generally, the ORP at the economizer inlet will be satisfactory if values monitored in the LP feedwater are in the optimum range. It is also possible that the HP feedwater will be reducing while the LP feedwater is oxidizing because of high condensate dissolved oxygen levels and/or addition of the reducing agent to the HP feedwater.

Under HP feedwater conditions (up to about  $280^{\circ}\text{C}$ ),  $\text{Cu}_2\text{O}$  is more soluble than  $\text{CuO}$ : for example Figure 2 indicates about 150 ppb at pH 9 for  $\text{Cu}_2\text{O}$  versus 60 ppb for  $\text{CuO}$  at  $250^{\circ}\text{C}$ .

Copper transport is an issue of concern in HP heaters, even when the materials do not include copper. The waterside surfaces of stainless steel HP heater tubes serve as deposition sites for copper transported from copper alloy LP heaters and condensers. The differences in solubility of  $\text{CuO}$  and  $\text{Cu}_2\text{O}$  at 25 and  $250^{\circ}\text{C}$  have been mentioned earlier in this subsection. Thus, it is imperative that the heaters are cleaned if a utility changes LP copper heaters to ferrous heaters so that an oxidizing feedwater (without a reducing agent) or OT can be considered.

The shell sides of the LP and HP feedwater heaters can also be a substantial source of copper in the feedwater via the cascading drains. There appears to be two influences, chemical and physical. The important feature for the former is to ensure that during shutdown/layout a protective nitrogen blanket is provided on the shell side. The thermal and physical effects can be severe during startup; reductions can be achieved by operating with the valves open so that thermal shock is reduced.

## 2.2 Copper in the Boiler

### 2.2.1 Copper in Boiler Water Wall Deposits.

When trying to understand the behavior of copper and its oxides in the boiler, it is necessary to consider both the status of the copper inventory deposited on the walls and the status of the copper inventory ( $\text{CuO}$  and  $\text{Cu}_2\text{O}$ ) as soluble and particulate compounds circulating in the boiler water. Feedwater copper corrosion products, consisting mainly of particulate  $\text{Cu}_2\text{O}$  and  $\text{CuO}$ , are transported from the feedwater system through the economizer and into the boiler drum and water walls. No serious problems have resulted from copper depositing out in economizers. However, when water wall tube specimens are removed for deposit analysis, extensive amounts of copper can be found interspersed in the magnetite layers. The presence of copper metal is predicted by the high temperature pH/potential diagrams.

During normal unit operation, deposited copper is present as elemental copper on the boiler water walls. It remains in this form so long as reducing conditions exist during operation and particularly during shutdown. During short-term layup/shutdown, the boiler pressure should prevent air ingress and minimize the dissolution of elemental copper from the walls. For intermediate to longterm shutdowns, the pressure will eventually decay and allow air ingress unless some protection is provided. The high temperature pH-equilibrium diagrams predict that a mixture of  $\text{CuO}$  and  $\text{Cu}_2\text{O}$  oxide will form in oxygen saturated boiler water during shutdown. Thus, when proper layup is practiced (a nitrogen blanket is applied, and/or a reducing agent is added to the boiler water), the dissolution of copper from the walls as  $\text{CuO}/\text{Cu}_2\text{O}$  will be minimized and controlled by the solubility limits of  $\text{CuO}$  and  $\text{Cu}_2\text{O}$  at around  $25^{\circ}\text{C}$  which as shown in Fig. 2 are relatively low. Without effective boiler layup, the boiler water will eventually become oxidizing and the  $\text{CuO}/\text{Cu}_2\text{O}$  solubility will increase. Research in Program Copper has also indicated that the solubility of  $\text{CuO}$  and  $\text{Cu}_2\text{O}$  will increase in boiler water with increased pH levels during the shutdown. The result in this case is that during subsequent startup, very high levels of copper (as oxides) will be measured in the boiler water, as has been observed at many utility plants.

Research in Program Copper has indicated that the solubility of CuO and Cu<sub>2</sub>O during the shutdown (below 100°C) is rather low (1-2 ppb) across a broad pH range (8-11). However, as the temperature is transitioning through 200-250°C (cooling or heating) there is a maximum in the solubility of both oxides (Fig. 2) with Cu<sub>2</sub>O being much more soluble at both pH 9 and 9.5. Figure 3 shows the effect of pH.

Once the boiler pressure and temperature start to increase, Program Copper research has shown that CuO and Cu<sub>2</sub>O have high levels of partitioning from the boiler water into saturated steam leaving the drum with the copper being predominantly as Cu(OH)<sub>2</sub> and CuOH. More importantly is the fact that the high levels of partitioning occur across the temperature range 100 - 350°C so that CuO and Cu<sub>2</sub>O (as hydroxides) transition into steam even throughout the startup period, with the maximum occurring in the temperature range 200-250°C where the maximum solubility of both oxides occurs in the boiler water. Thus, it is now clear that high levels of CuO and Cu<sub>2</sub>O in the boiler water on startup following unprotected shutdowns leads to CuO (as Cu(OH)<sub>2</sub>) and Cu<sub>2</sub>O (as CuOH) in saturated steam leaving the drum. To eliminate/reduce turbine copper deposition problems, the boiler must be protected (by maintaining reducing conditions) during all periods of operation and shutdown to minimize formation of CuO and Cu<sub>2</sub>O from the copper deposited on the walls, and subsequently minimizing the possibility of CuO (Cu(OH)<sub>2</sub>) and Cu<sub>2</sub>O (CuOH) partitioning to steam.

During the startup period, there is also a high probability of mechanical carryover due to poor drum level control and/or poor separation. Thus the saturated steam can also contain particulate and dissolved CuO and Cu<sub>2</sub>O as a result of this. Both of these means of transitioning copper oxides into steam mandate the necessity of monitoring copper in saturated steam during all phases of startup when an organization is attempting to develop unit specific approaches to copper transport control based on the EPRI Guidelines.

**2.2.2 Copper Oxides in Boiler Water.** As well as the elemental copper inventory on the boiler water walls, there are also particulate copper oxides, which continually enter the boiler with the feedwater. The solubility of CuO and Cu<sub>2</sub>O

change with temperature and pH in the same way as just discussed (Section 2.2.1), but in this case the controlling feature is the corrosion in the feedwater (Section 2.1). During normal operation these oxides can partition to saturated steam as discussed earlier. Also during normal operation the particulates can enter saturated steam due to mechanical carryover.

**2.3 Copper in Superheaters.** Results of primary superheater tube analyses suggest that the particulate copper oxides deposit on the tube surfaces. Program Copper has shown that other dominant species carrying over into steam are the hydroxides Cu(OH) and Cu(OH)<sub>2</sub> and that the concentrations are independent of pH of steam or boiler water. Figures 4 and 5 show that the solubility of the Cu(OH) decreases with temperature and increases with pressure above about 300°C; whereas for Cu(OH)<sub>2</sub> it increases with pressure and temperature. Below 300°C the solubility is very low (1-2 ppb).

Pocock and Stewart's<sup>(3)</sup> data showed a pressure effect on solubility with a critical steam pressure of around 2400 psi (16.5 MPa).

The latest Program Copper results are shown in Figures 4 and 5, which include Pocock and Stewart's data. Figure 5 shows the increasing trend of solubility for both copper hydroxides with pressure and a level of around 3-4 ppb in steam at around 2500 psi (17.2 MPa). Above this pressure Cu(OH)<sub>2</sub> is more soluble in steam than CuOH. Below this pressure, both copper oxides have low solubility. This "pressure effect" controls the transition/flow of "copper", from the boiler steam drum (saturated steam) to the primary superheater and, subsequently, to the turbine.

During unit startup, when the drum pressure is less than this "critical pressure", any Cu(OH)<sub>2</sub> and/or CuOH that partitions into the saturated steam will precipitate onto primary superheater surfaces as a crystalline growth of CuO and Cu<sub>2</sub>O. If any moisture is present in the saturated steam, the copper oxides will remain soluble until superheated steam predominates (no moisture remains) and then these oxides will also precipitate out on the tube surfaces. Field results clearly show a peak in copper deposition in the primary superheater compared to other superheater/steam tubes.

As unit startup proceeds and the drum pressure reaches and then exceeds the "critical

pressure”, the copper hydroxides that have partitioned from the boiler water will remain soluble in steam, but only up to the 2.5 – 4 ppb limit. The superheated steam now can transport the soluble copper hydroxides towards the turbine. Also, it should be noted that superheated steam has the ability to re-dissolve the copper oxides from the primary superheater tube surfaces, up to the solubility limit for the operating pressure. This phenomenon also allows for dissolution of any copper oxide in particulate form entering the superheater with attemperating spray water.

Should the pressure in the superheater fall below the “critical pressure” due either to sliding pressure operation or simply to pressure drop between the steam drum and the turbine, then the copper hydroxides will start to precipitate out at intermediate points in the superheater as oxides. Laboratory assessment of superheater tube specimens has verified this tendency. Conversely, in those units operating at drum pressures well in excess of the “critical pressure”, then the copper hydroxides can transport directly to the HP turbine without any intermediate precipitation points. This explains the observation of increased turbine deposition in units where the boiler is operated at overpressure for extended periods, typically to increase net generation by the unit. These observations further underscore the importance of optimizing the chemistry by keeping the feedwater environment reducing in order to maintain the 2 ppb copper limit.

**2.4 Copper in the High Pressure Turbine.** There is now a very good understanding, based on Program Copper research, on how copper is transported from unprotected feedwater heaters (oxidizing environment) to the boiler, and how copper oxides in the boiler water partition into saturated steam predominantly as hydroxides. The final transport step to the turbine involves the solubility of the  $\text{CuO/Cu(OH)}_2\text{-Cu}_2\text{O/CuOH}$  mixture, precipitation onto primary superheater tube surfaces below the “critical pressure” and re-dissolution into the steam at higher pressures. A substantial pressure drop occurs across the first control stage of the HP turbine; within the first few stages the pressure drops below the “critical pressure” for the solubility of the copper hydroxides. The  $\text{CuO/Cu(OH)}_2\text{/Cu}_2\text{O/CuOH}$ , individually and together, will then precipitate onto the blade surfaces as crystalline growth. EPRI converging nozzle tests in plant have

indicated preferential dynamic deposition, first of  $\text{Cu(OH)}_2$ , followed by  $\text{CuO}$ , and then  $\text{Cu}_2\text{O}$ . There is essentially no deposition due to impaction of crystals or particulates, and the rate of deposition is a function of surface roughness. Analyses of turbine blade surfaces confirm the prognosis of the converging nozzle tests.

## 2.5 Conclusions and Solutions for Copper Transport in Fossil Plant Units.

Complete understanding of transport of copper and its oxides around the fossil plant cycle has resulted from a series of research projects conducted under EPRI’s “Program Copper”. The results of this work have been used to develop an EPRI Guideline for copper, which includes solutions to all the currently known problems with copper in fossil plants<sup>(1)</sup>. Short term solutions are intended to eliminate the inventory of copper in deposits and include cleaning of the turbine, primary superheater, boiler waterwalls, and feedwater heaters, as needed in the specific unit. Longer term solutions, involving equipment changes include replacing copper alloy components with copper-free materials, cycle piping and design changes, retrofit of condensate polishers, improvement of steam separator devices, corrective actions to reduce air in-leakage, changes to permit oxygen removal from cycle makeup water, establishment of nitrogen blanketing capabilities, optimization of heater operating procedures, and evaluation of overpressure operation on copper transport activity. Solutions related to chemistry monitoring include upgrading of sampling systems, installation of an ORP monitor, and monitoring copper transport to evaluate the effect of other changes and solutions.

## Acknowledgments

The current understanding of copper transport in fossil plant cycles would not be possible without the contributions of several EPRI colleagues, and the organizations that have conducted the research in Program Copper. In recognition of their efforts, the authors gratefully acknowledge the contributions of: current and former EPRI colleagues Barry Syrett, Tom McCloskey, and John Tsou; EPRI Consultants Al Aschoff and Malcolm Ball; and key contractor personnel including Donald Palmer from Oak Ridge National Laboratories, James Castle from University of Surrey (UK), Walter Bogaerts from Katholieke Universiteit Leuven (Belgium), and Digby MacDonald and Sergei Lvov from Pennsylvania State University.

Special thanks to Don Palmer for assistance in developing plant specific figures.

### References

- [1] *Guidelines for Copper in Fossil Plants*. EPRI, Palo Alto, CA. 1000457. November 2000.
- [2] K.J. Shields and R.B. Dooley. "Copper Transport in Fossil Utility Cycles. International Water Conference. 2002. IWC-02-22.
- [3] F.J. Pocock and J.F. Stewart. "The Solubility of Copper and its Oxides in Supercritical Steam". *Transaction of the ASME, Journal of Engineering for Power*. Vol. 85, Series A, No. 1, January 1963.
- [4] "Copper Alloy Corrosion in High Purity Feedwater". EPRI, Palo Alto, CA. 100456, November 2000.
- [5] "Copper Alloy Corrosion in High Purity Feedwater". EPRI, Palo Alto, CA. 1007391, May 2003.
- [6] J.E. Castle and R.B. Dooley. "Minimizing Copper Pickup from Copper Alloys in the Feedtrain by Control of pH and ORP: New Operating Limits". 14<sup>th</sup> ICPWS. Kyoto, Japan. August 2004.
- [7] "Influence of Water Chemistry on Copper Alloy Corrosion in High Purity Feedwater". EPRI, Palo Alto, CA. 1004586, October 2001.
- [8] "Influence of Water Chemistry on Copper Alloy Corrosion in High Purity Feedwater". EPRI, Palo Alto, CA. 1007612, August 2003.
- [9] "Behavior of Aqueous Electrolytes in Steam Cycles: The Solubility and Volatility of Copper(I) and Copper(II) Oxides". Palo Alto, CA. 1003993, December 2001.
- [10] "Behavior of Aqueous Electrolytes in Steam Cycles: The Final Report on Solubility and Volatility of Copper (I) and Copper (II) Oxides". EPRI. Palo Alto, CA, 2004.
- [11] D.A. Palmer, P. Benezeth and J.M. Simonson. "Solubility of Copper Oxides in Water and Steam". 14<sup>th</sup> ICPWS. Kyoto, Japan. August 2004.
- [12] "Corrosion of Cu-Ni-Zn Alloys in Water-Ammonia Power Plant Environments". EPRI. Palo Alto, CA. TR-113697. November 1999.
- [13] "Cycle Chemistry Guidelines for Fossil Plants: All-volatile Treatment". EPRI. Palo Alto, CA. 1004187. November 2002.
- [14] R.B. Dooley and K.J. Shields. "Cycle Chemistry for Conventional Fossil Plants and Combined Cycle/HRSGs". *Power Plant Chemistry*. 2004, 6(3), pp 153-164.
- [15] D.A. Palmer, P. Benezeth and J.M. Simonson. "The Solubility of Copper Oxides around the Water/Steam Cycle". EPRI Seventh International Conference on Cycle Chemistry, June 2003. Also published in *Power Plant Chemistry*, 2004, 6(2), pp 81-88.
- [16] "Behavior of Aqueous Electrolytes in Steam Cycles". EPRI, Palo Alto, CA. 1011075. 2004.
- [17] K. Daucik and J.P. Jensen. "Solubility of Salts in Superheated Steam: International Collaboration Project 1996-2001". Final report, November 2001.
- [18] K. Sue, Y. Hakuta, R.L. Smith, Jr., T. Adschiri and K. Arai. "Solubility of Lead (II) Oxide and Copper (II) Oxide in Subcritical and Supercritical Water". *J. Chem. & Eng. Data*. Vol. 44 (1999), pp 1422-1426.
- [19] B. Hearn, M.R. Hunt and A. Hayward. "Solubility of Cupric Oxide in Pure Subcritical and Supercritical Water". *J. Chem. & Eng. Data*. Vol. 14, (1969), pp 442-447.