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## VOLATILITY OF COPPER

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### Abstract

The relevant aqueous thermodynamics of copper and its oxides are evaluated and summarized with emphasis on solubility, hydrolysis, and complexation. The solubilities of metallic copper, solid cuprous and cupric oxides in steam measured by Pocock and Stewart in 1963 are discussed and the latter data are fitted in the form of established empirical equations and compared to other existing results. No other sources of data were found for the solubility of copper and cupric oxide in steam and even these data are very limited. Discussion of corresponding available solubility data on both oxide phases in liquid water is given. The possible effects of complexing agents are considered. A brief discussion is provided of the role of surface adsorption in determining the fate of dissolved copper in the boiler.

### Background

The importance of the effect of copper oxide transport into the steam cycle can best be summarized by a quote from Jonas and Reiger<sup>1a</sup>: "Transport of oxygen to corrosion sites as an oxide which can be reduced after deposition on a surface has been long recognized. Copper oxides can be easily generated in the pre-boiler cycle (faster than the oxygen reaction with a scavenger) and transported into the steam generator and turbine where they may deposit and be reduced. Metallic copper is frequently found in turbine deposits." Cathodic corrosion in PWR steam generators instigated by copper oxides has been documented and similar reactions are believed to occur in turbines. The most prevalent oxides in turbine deposits are reported<sup>1b</sup> to be magnetite, hematite, copper and aluminum oxides, and in some cases iron and copper oxides make up the entire deposit. Analysis of the deposits through the various turbine stages presented in terms of weight percent versus specific volume (inverse pressure or density) establishes Cu<sub>2</sub>O (cuprite) and CuO (tenorite) to be predominant (together with sulfate and sodium) under the low specific volume conditions encountered in the HP turbine<sup>1c</sup>. Note that in a number of isolated cases the mass of deposited copper on the HP turbine is sufficient to cause severe loss of efficiency, necessitating frequent chemical cleaning<sup>2</sup>.

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The chemical forms of copper identified<sup>1d</sup> in steam and deposits in the water/steam cycle are  $\text{CuO}$ ,  $\text{Cu}_2\text{O}$ ,  $\text{Cu}_6\text{Fe}_3\text{O}_7$ ,  $\text{CuAlO}_2$ ,  $\text{Cu}_4\text{SO}_4(\text{OH})_6$ ,  $\text{Na}_2\text{Cu}(\text{SO}_4)_2$ ,  $\text{CuFe}(\text{OH})_2\text{SO}_4$ ,  $\text{CuCO}_3\text{Cu}(\text{OH})_2$ , and  $\text{Cu}_2(\text{OH})_3\text{Cl}$ . The stoichiometries of these deposits do not necessarily provide information as to the form of the copper species responsible for transport through the steam phase, but they do indicate the possible role of complexing anions in not only enhancing the solubility of copper in the boiler / make-up water, but also providing neutrally-charged solutes which are considered the dominant form responsible for homogeneous (chemical) carry over. Mechanical carry over of copper oxide particulates and copper compounds (or metallic copper) adsorbed on magnetite grains is well documented, but is not addressed in this paper due to the lack of quantitative, predictable information. However, in a discussion of the effect of water chemistry on the efficiency of condensate demineralizers in a subcritical drum-type unit, Mizumo et al.<sup>3</sup> reported that copper species were removed exclusively by ion-exchange polishers indicating that most of the copper was present as dissolved solutes.

There have been a number of studies of copper(II) oxide solubility to elevated temperatures, including the effects of added phosphate, chloride and ammonia, although there is considerable variance between the reported equilibrium constants and even the nature of the predominant species<sup>4-11</sup>. Some of the principal experimental difficulties inherent in such measurements were documented by Martynova<sup>12</sup> in 1974 and still pertain today; problems that are compounded by the low solubilities of copper and its oxides (despite vast improvements in the sensitivity of conventional analytical methods), as well as the prevalence of copper to undergo rapid oxidation at relatively low oxygen partial pressures. One landmark study of copper and copper oxide solubilities in steam was found<sup>13</sup>.

The mechanisms of adsorption of ions onto metal and metal oxide surfaces are understood qualitatively and from a thermodynamic view point the degree of adsorption on a given surface depends on: pH, relative to the zero-point-of-charge (zpc) of the surface; temperature; oxidation state; presence of other competitive adsorbents, complexing agents; surface area and morphology of the solid phase. The capacity for adsorption increases with temperature, while the pH of the zpc decreases with temperature<sup>14</sup>.

### Thermodynamics of the Solid Phases

The melting points are listed as:  $\text{Cu}$ ,  $1084^\circ\text{C}$ ; and  $\text{Cu}_2\text{O}$ ,  $1242^\circ\text{C}$ <sup>15</sup>. The following table lists the thermodynamic properties for copper and its oxides taken from a number of recent sources. The values of  $\Delta_f G^\circ$  given in Table I for  $\text{CuO}$  in the latter two entries were used by these authors to establish the corresponding values for the dissolved species and their preferred values vary significantly from the more commonly-accepted values<sup>16,17</sup>.

### Oxidation States of Copper

It is instructive to consider the stability fields of metallic copper and its oxides as a function of oxygen partial pressure and temperature. These can be calculated from the thermodynamic properties laid down by Robie et al.<sup>17</sup> and are illustrated in Figure 1. Clearly, from startup to

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Table 1  
Thermodynamic Properties at 25°C and 1 bar

Solid Phase	$C_p^{\circ a}$	$S^{\circ a}$	$\Delta_f H^{\circ b}$	$\Delta_f G^{\circ b}$	Reference
Cu	24.435	33.150	0	0	16
Cu <sub>2</sub> O	63.64	93.14	-168.6	-146.0	16
	62.59	93.14	-168.61	-146.03	17
CuO	42.30	42.63	-157.3	-129.7	16
	42.30	42.63	-157.32	-129.56	17
	42.26	42.68	-155.2	-127.53	9 <sup>c</sup>
	-	42.63	-155.77	-127.99	7 <sup>c</sup>

Units: <sup>a</sup> J·K<sup>-1</sup>·mol<sup>-1</sup>, <sup>b</sup> kJ·mol<sup>-1</sup>; <sup>c</sup> cited in these references.

normal operating conditions, even traces of oxygen in the make-up water will heavily favor the formation of a cupric oxide layer, even on dry copper surfaces. Noting that this argument does not take into account the competing kinetics of the oxidation/reduction reactions

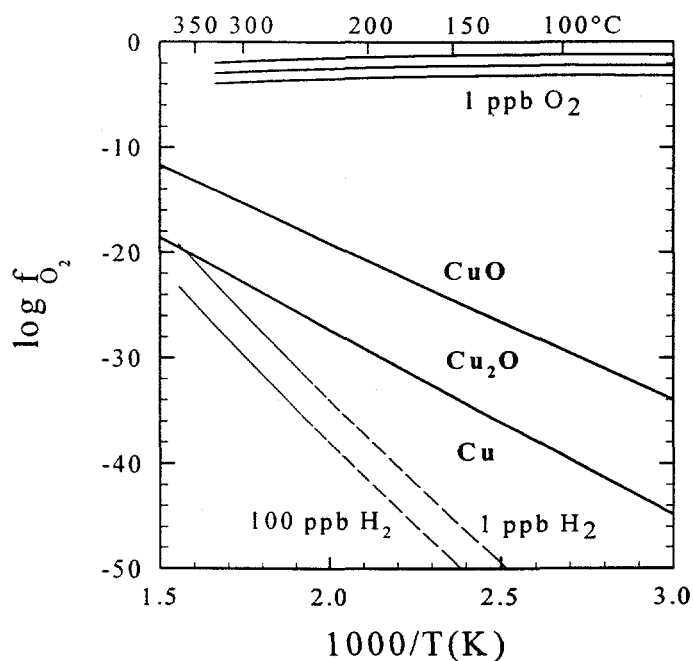


Figure 1. The phase transitions of metallic copper and its oxides are shown as a function of oxygen fugacity and temperature (Kelvin)<sup>17</sup>, where the remaining lines represent the log  $f_{O_2}$  values corresponding to: 1, 10 and 100 ppb O<sub>2</sub>; and 1 and 100 ppb H<sub>2</sub>. Henry's Law constants for O<sub>2</sub> and H<sub>2</sub> were calculated according to Clever and Han<sup>18</sup>.

According to Baes and Mesmer<sup>4</sup> the equilibrium constant for the disproportionation of copper(I) in water according to equation (1) is  $10^6$ , such that without the presence of either complexing agents or external oxygen fugacity buffers, the  $\text{Cu}^+/\text{Cu}^{2+}$  ratio is highly concentration dependent.



Thus, at total initial copper concentrations of 1 ppb and 1 ppm, when cuprous ion is added to unbuffered water, the ratio varies from 69 to 0.4 at ambient conditions. Note that throughout this report species are considered to be in the liquid phase unless indicated otherwise.

Var'yash<sup>8</sup> reported equilibrium constants for the oxidation of metallic copper according to reaction (2) at 300, 350 and 450°C (0.5 kbar), and at 350°C (1 kbar).



The equilibrium constant is defined by Var'yash<sup>8</sup> as:

$$K_0 = \frac{m_{\text{Cu}^+}}{p_{\text{O}_2}^{0.25} m_{\text{H}^+}} \quad (3)$$

with activity coefficients and the activity of water set at unity. The effect of pressure between 0.5 and 1 kbar is less than the combined uncertainty in the two  $K_{01}$  values (i.e., 0.14 log units) at 350°C. Although these experiments were conducted in HCl solutions, they were believed to be too dilute to cause any enhancement in copper solubility due to  $\text{CuCl}^0$  formation. The dependence of  $\log K_0$  at 0.5 kbar on the reciprocal temperature in Kelvin is approximately linear within the given uncertainty limits yielding equation (4).

$$\log K_0 = 3.19 + 2250/T \quad (4)$$

Note that this author also reported two constants for the equilibrium equivalent to equation (2) determined at higher pH and assigned to the formation of  $\text{Cu}(\text{OH})^0$  at temperatures of 350 and 450°C. However, correction of these constants to the form in equation (3) using the first hydrolysis constant measured independently gave  $\log K_0$  values that are +0.40 and -0.54, respectively, different from those determined from equation (4). This disagreement may indicate that the uncertainties in these measurements are greater than reported, but these results still provide a valuable independent working basis for calculation of the oxidation state of copper in a power plant.

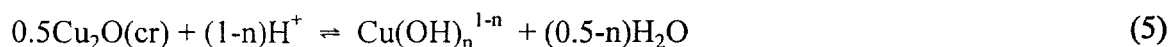
## Solubility

The solubility of solids imposes the upper limits on concentration and is the most effective (and some times the only) experimental method available to establish the speciation of hydrolyzable species in solution. In the absence of any data on the partitioning of aqueous copper solutes to

the steam phase, solubility in the liquid phase provides directly information on speciation and the pH dependence thereof, in turn indicating the maximum concentration in the vapor of neutral molecules for a three phase system. Moreover, in once-through units solubility is the key parameter in predicting the maximum degree of chemical (vaporous) carry over.

### ***Copper(I) in the Liquid Phase***

There appears to be only one comprehensive experimental study of the solubility of  $\text{Cu}_2\text{O}$  carried out by Var'yash<sup>8</sup> from 150 to 450°C in the presence of copper metal to buffer the oxidation potential of the solution. this study led to the calculation of the free energies of formation of  $\text{Cu}^+$ ,  $\text{Cu}(\text{OH})^0$ , and  $\text{Cu}(\text{OH})_2^-$  formed according to the reactions:



where  $n=0-2$ . The solubility profiles calculated from the equilibrium constants for equation (5) are given in Figure 2 as a function of pH (at temperature) and temperature. According to the references cited in this work, the equilibrium constants derived by Var'yash<sup>8</sup> are in fair agreement with three independent studies of each equilibrium, giving some degree of confidence that the dramatic increase in solubility with temperature is indeed valid. The constants given at 25°C were derived solely from these three independent studies. Certainly the shift in the solubility minimum to lower pH and the broadening of the stability field of the neutral hydrolysis product,  $\text{Cu}(\text{OH})^0$ , which predominates at the minimum, are properties manifested by other oxide phases such as  $\text{ZnO}$  (Ziemniak<sup>19</sup>, Palmer et al.<sup>20</sup>) and  $\text{Al}(\text{OH})\text{O}$  (Palmer et al.<sup>20,21</sup>). However, the

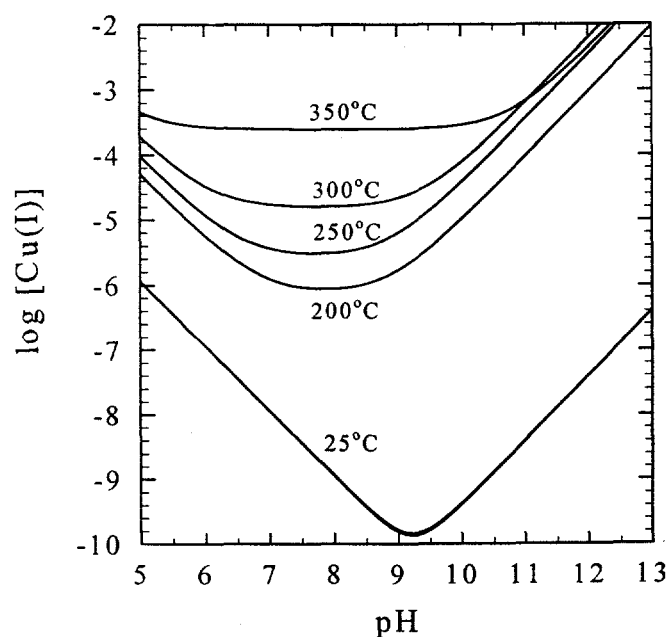
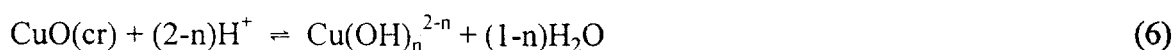


Figure 2. Solubility profile of  $\text{Cu}_2\text{O}(\text{cr})$  in molal units based on the Gibbs energies for the relevant species reported by Var'yash<sup>7</sup>.

extent to which the solubility minimum is raised is difficult to rationalize, as it must stem from a very endothermic reaction that is uncommon for equilibria of this type. The dramatically higher solubility and increasing importance of the  $\text{Cu(OH)}^0$  aqueous species with temperature provides a potential source for increased volatility by many orders of magnitude. Finally, the solubility profile illustrated in Figure 2 was constructed on the theoretical basis that only Cu(I) species stable, i.e., at some hypothetical oxygen fugacity at which only this oxidation state on copper exists.

### *Copper(II) in the Liquid Phase*

The principal equilibria involved in the dissolution of CuO are summarized by the general equation:



where  $n = 0-4$ . Baes and Mesmer<sup>4</sup> argue for the formation of one dimeric cation, namely  $\text{Cu}_2(\text{OH})_2^{2+}$ , being formed at high copper(II) concentrations, which nevertheless represents less than one percent of the total copper in solutions saturated with respect to CuO(cr) at 25°C as shown in Figure 3. The speciation given in this Figure was based on the free energies listed in Table V of Ziemniak et al.<sup>9</sup>, which in turn incorporated data from Baes and Mesmer<sup>4</sup>, and Paulson and Kester<sup>6</sup>, while noting that the "preferred" equations for  $\text{Cu}^{2+}$  and  $\text{Cu(OH)}^+$  lead to vastly different equilibrium constants for equation (6),  $n=0$  and 1, so that these were rejected at

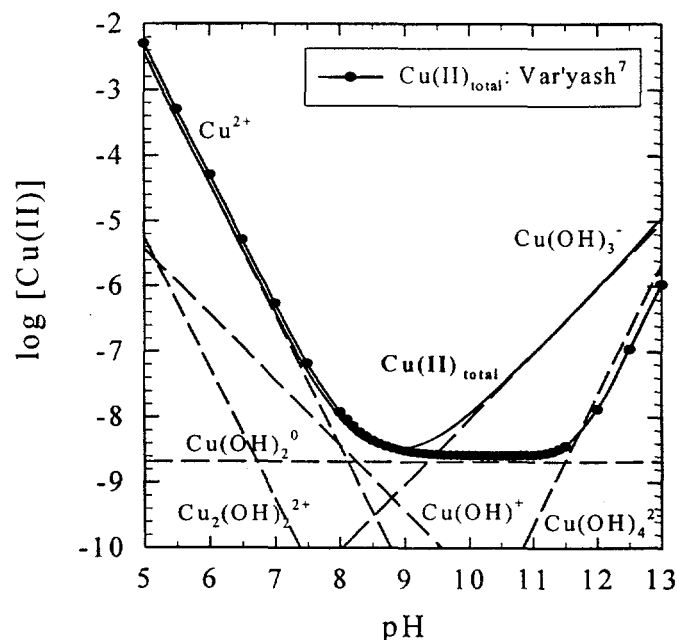


Figure 3. Solubility profile at 25°C for CuO(cr) in molal units based on the Gibbs energies reported (not measured) by Ziemniak<sup>9</sup> together with total copper as also reported by Var'yash<sup>7</sup>.



this time. Due to large differences in the reported solubility equilibria at higher temperatures, it is convenient to compare their predicted solubility profiles at ambient temperature in an attempt to access which studies are compatible with the bulk of the data published at this condition. In Table 1 are listed the step-wise hydrolysis constants as defined by equation:



The disparity between the two high temperature solubility studies becomes more extreme above ambient conditions as shown in Figure 4. The limited solubility curve attributed to Styrikovich et al.<sup>22</sup> was taken graphically from Figure 3 in this publication, which includes other data at 120 and 348°C along the saturation vapor curve. It is difficult to decide *a priori* which data set reflects reality, although the profile proposed by Var'yash<sup>7</sup> appears more consistent with the behavior of ZnO<sup>19,20</sup>. The general phenomenon that higher temperature favors increased importance of the neutral hydroxide species, as is the case for the well-studied aluminum hydrolysis system (i.e., boehmite solubility)<sup>20,21</sup> is also followed by the solubility profile of Var'yash. Ironically, whereas Ziemniak<sup>9</sup> contends that the dominant hydrolyzed form of Cu(II) in solution at pH ≥ 9.4 is Cu(OH)<sub>3</sub><sup>-</sup>, Var'yash<sup>7</sup> discounts this species entirely. Nevertheless, until further experimental evidence becomes available, the work of Var'yash is accepted here at this time and thereby establishes the greater field of stability of the potentially volatile Cu(OH)<sub>2</sub><sup>0</sup> species, albeit with a lower solubility minimum at neutral to moderately basic pH (appropriate to power plant conditions). Var'yash conducted solubility measurements at 200 and 250°C, yielding solubility constants that are two to three orders of magnitude lower for n=3 (the one equilibrium listed) than that cited in Table 2 of his paper and obtained from another source. Thus all of these values are tentative at best, but are preferred here over those of Zarembo et al.<sup>23</sup> who also list Gibbs energies of formation of the Cu(II) solution species from 25 to 350°C computed from an unknown data base.

Comparison of the solubility profiles in Figures 3 and 4 illustrates the general trend that the solubility minimum moves to lower pH with increasing temperature, remembering that the pH of neutral water also decreases. A further comparison with the solubility profiles of Cu<sub>2</sub>O in Figure 2 shows that the solubility minimum is about an order of magnitude lower than that for CuO at 25°C, but is significantly more soluble at temperatures approaching those in fossil-fired steam generators. This would indicate that Cu(OH)<sup>0</sup> could be more volatile than Cu(OH)<sub>2</sub><sup>0</sup> if their partitioning constants are similar, although under most operating conditions the oxidation potential would strongly favor the latter, thereby off-setting the greater solubility/volatility of Cu<sub>2</sub>O at high temperatures. However, if the unconfirmed results for Cu<sub>2</sub>O are correct, then lowering the oxidation potential in order to avoid substantial oxidation of copper surfaces to CuO could run the risk of approaching the stability field for the more soluble cuprous oxide phase. Clearly these results must be validated by independent measurements, difficult though they may be.

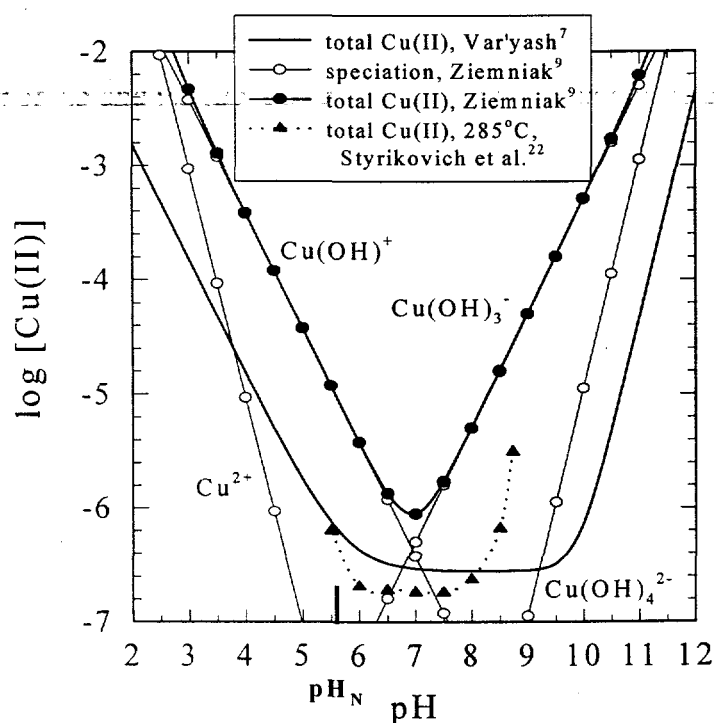


Figure 4: The solubility profile on a molal concentration scale for CuO(cr) at 250°C versus pH at temperature, comparing the compilation of Var'yash<sup>7</sup> and the graphical curve at 285°C of Styrikovich et al.<sup>22</sup>, both shown here only as total Cu(II) in solution, with that of Ziemniak<sup>9</sup>, including the species considered.  $pH_N$  indicates neutral pH for water at 250°C.

Table 2  
Step-wise Hydrolysis Constants According to Equation (7) at Saturation Vapor Pressure

$\log K_{ln}$	Ref. 4	Ref. 6	Ref. 9	Ref. 9 <sup>a</sup>	Ref. 7
n=1	-7.6 <sup>b</sup>	-7.93	-7.99	-9.58 <sup>c</sup>	-8.08
n=2	-9.7 <sup>b</sup>	-8.37	-8.25	-6.66	-8.22
n=3	-10.3 <sup>b</sup>		-9.35	-9.35	- <sup>d</sup>
n=4	-12.0		-13.64	-13.64	-
n=0/4 <sup>e</sup>	-39.6		-39.23	-39.23	-39.67

<sup>a</sup> These revised values incorporating results from Ref. 6 appear too inconsistent with other published results. <sup>b</sup> Given as approximate values. <sup>c</sup> There appears to be an inconsistency between this value derived from recommended  $\Delta G_f^\circ$  and that calculated from  $\Delta G^\circ$  of -10.31 values in Table VII, ref. 9. <sup>d</sup> Did not recognize the existence of  $\text{Cu(OH)}_3^-$ . <sup>e</sup> Overall equilibrium:  $\text{Cu}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Cu(OH)}_4^{2-} + 4\text{H}^+$ .

### *Copper (I and II) in the Vapor Phase*

Pocock and Stewart<sup>13</sup> conducted a pioneering investigation of the solubility of Cu, Cu<sub>2</sub>O and CuO in steam at two pH values for the feed water of 7.5 and 9.5 (25°C). By far the most extensive data are available for CuO. Tests were made to ensure that no copper particulate matter was entrained in the steam. However, it is not surprising that the difficulty of conducting such experiments has led to considerable scatter in the results which by necessity were undertaken over a relatively narrow range of temperature and pressure (density). Independent fits of these two data sets using the conventional functions of temperature and density<sup>28</sup> yielded the relationships presented in equations (8) and (9),

$$\text{pH} = 7.5: \quad \log [\text{Cu,ppb}] = 7.10 - 3260/T + 2.17 \log \rho_w \quad (8)$$

$$\text{pH} = 9.5: \quad \log [\text{Cu,ppb}] = 8.00 - 3230/T + 2.92 \log \rho_w \quad (9)$$

where T is the temperature in Kelvin and  $\rho_w$  represents the density of pure water. Taking the solubilities at the highest temperature of 620°C, linear fits of  $\log [\text{Cu,ppb}]$  versus  $\log \rho_w$  yielded slopes of *ca.* 2.2 and 1.9 for the pH values of 7.5 and 9.5, respectively. Given the scatter in the data and the limited range of T and  $\rho_w$ , an average value for the 1/T term of 3250 could be assigned with an approximate density parameter of 2. This implies a hydration number of two corresponding to the dominant species in the vapor phase being **CuO·2H<sub>2</sub>O** ( $\approx \text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$ ), following the same logic utilized in determining the slope of the lines for various solutes in the ray diagram. Incidentally, neutron scattering measurements of concentrated CuCl<sub>2</sub> in D<sub>2</sub>O solutions at ambient conditions resulted in a hydration number of  $3.4 \pm 0.2$  for Cu<sup>2+</sup> and  $4.1 \pm 0.3$  for the corresponding perchlorate solution<sup>24</sup>, which is consistent with a possible four coordinate, square planar configuration. The neutral copper(II) specie apparently has a smaller hydration shell.

The solubility data for CuO are summarized in Figure 5 where the thin solid curve was digitized from a plot given by Martynova<sup>12</sup>, but the source of these results was not cited. There is obviously excellent agreement with the results of Var'yash<sup>7</sup> published more recently, but based solely on the solubility of Cu(OH)<sub>2</sub><sup>0</sup>. The latter were fitted to a temperature/density function of the type shown in equations (8) and (9), which, as expected, did not extrapolate realistically to higher temperatures (i.e., >350°C). However, most surprisingly, the mean of equations (8) and (9), which were based on the limited range of conditions measured by Pocock and Stewart<sup>13</sup>, gives a dependence on temperature that mirrors that presented by Martynova<sup>12</sup> within a factor of 2 in copper concentration. The results of Hearn et al.<sup>5</sup>, who measured the solubility of CuO from 57 to 551°C at moderate pressures ranging from 76 to 419 bar (1100 to 6070 psi), are approximately an order of magnitude higher than those of Pocock and Stewart<sup>13</sup>. Hearn et al.<sup>5</sup> cite two possible sources of error in the former study, namely, insufficient equilibration time and the use of stainless steel which showed evidence of corrosion after completion of the study and was therefore a possible sink for copper.

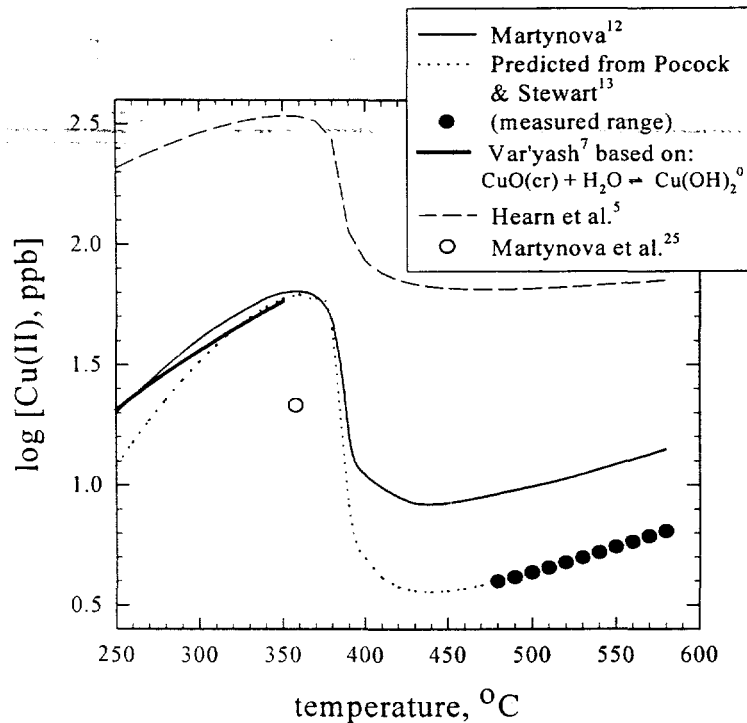


Figure 5: Solubility of CuO at 250 bar pressure from Martynova<sup>12</sup>; the mean of equations (8) and (9) based on solubility in steam by Pocock and Stewart<sup>13</sup>; Var'yash<sup>7</sup>; Hearn et al.<sup>5</sup>; and Martynova et al.<sup>25</sup> (corrected to 250 bar) taken from the pH independent region (pH{25°C} of 6 to 12).

The discrepancy between these two detailed and difficult studies remains unresolved with, on the one hand, the agreement between the measured and extrapolated data of Pocock and Stewart<sup>13</sup>, Martynova<sup>12</sup> (although it is unknown whether this treatment included results from Pocock and Stewart), and Var'yash<sup>7</sup>, giving weight to this entire data set. While on the other hand, the results of Hearn et al.<sup>5</sup> can not be ignored and are in fact similar in magnitude to the results of a field study reported by Petrova et al.<sup>26</sup> of 2-5 ppb copper in superheated steam from a once-through boiler under AVT at 550°C and 250 bar. Similar levels of copper (ca. 2 ppb) are listed in the guidelines for drum units operating under AVT treatment at the economizer inlet<sup>26</sup>. However, this raises the issue of the effect of ammonia (and possibly other complexing ligands) on the solubility of CuO.

The only experimental data for the solubility of Cu and Cu<sub>2</sub>O in steam found at this time again stem from Pocock and Stewart<sup>13</sup> at very high temperatures and over a small range of densities. A summary of these results is given in Table 3 for comparison with the corresponding values extrapolated to these conditions using an average of equations (8) and (9).

Table 3  
Solubility of Copper Metal and Cuprous Oxide in Steam<sup>13</sup>.

Temperature, °C	Pressure, bar	Density, g·cm <sup>-3</sup>	Cu <sub>2</sub> O, ppb	CuO, ppb
620.9	310.3	0.0871	9.1	16.7
619.8	310.3	0.0873	7.7	16.6
619.1	310.3	0.0874	9.9	16.6
621.1	310.3	0.0871	11.5	16.7
619.9	310.3	0.0873	11.5	16.6
621.4	310.3	0.0870	7.7	16.8
621.9	186.2	0.0491	0.3	3.9
621.6	269.0	0.0739	4.7	11.0
621.6	227.6	0.0612	2.8	6.9
			Cu, ppb	
621.8	310.3	0.0870	5.5	16.8
614.7	310.3	0.0882	7.2	16.2
618.3	186.2	0.0494	-0.9	3.8
620.7	310.3	0.0872	-0.8	16.7
613.9	310.3	0.0884	3.9	16.2
615.4	310.3	0.0881	9	16.3
628.3	310.3	0.0859	5.9	17.3

From a comparison of the solubilities listed in Table 3 it can be seen that at least at this high temperature and density of steam, CuO is the most soluble phase by a factor of about 2, with Cu metal and Cu<sub>2</sub>O being equally soluble within the experimental uncertainty. As anticipated the solubilities are all strong functions of density (pressure), but the effect of temperature for the latter oxides is at present unknown.

### Complexation of Copper in Solution

Complexation of copper in solution will enhance the solubility of the solid oxide phase and will therefore work synergistically with the presence of oxygen<sup>27</sup>. The stabilities of complexes formed between ions of opposite charge increase dramatically at high temperatures (>200°C)<sup>28</sup>. The following discussion deals with a number of potential ligands for which experimental data are mainly restricted to ambient conditions such that the predictions are only tentative at this time.

*Amines.* Formation constants for cupric amine complexes are available at 25°C for the general equilibrium,



for which  $\log K_n$  values are:  $n=1$ , 3.99;  $n=2$ , 7.33;  $n=3$ , 10.06; and  $n=4$ , 12.03<sup>11</sup>. Thus, considering only these four amine complexes (i.e., no mixed ligand complexes) at 25°C in the presence of 1 ppm ( $6 \cdot 10^{-5}$  molal)  $\text{NH}_3$ , the solubility of  $\text{CuO}$  would be enhanced over that in pure water by a factor of 1.65 with the predominant ion being  $\text{Cu}(\text{NH}_3)_2^{2+}$ . Moreover, as these complexes are ionic they should have an insignificant effect on the overall volatility. These data were obtained over a very restricted temperature range, but indicate that these amine complexes become weaker with increasing temperature. On the other hand, the EPRI cycle chemistry guidelines<sup>27</sup> state that copper alloy corrosion in condensate and feedwater systems is a function of oxygen, carbon dioxide, chloride, and ammonia levels. This argument was pursued in more detail by Allmon<sup>29</sup> confirming that the presence of ammonia reduces the volatility of copper in subcritical units by the formation of charged rather than neutral copper-amine complexes in solution, but the increase in solubility leads to enhanced carry-over in supercritical units.

*Carbonates.* Carbonate forms strong complexes with copper(II) and these are well documented at 25°C<sup>30</sup> with the formation constant of  $\text{CuCO}_3^0$  at 25°C being  $10^{6.8}$ . Considering a pH of 9 and 1 ppm total carbonate, this would result in a ratio of  $\text{CuCO}_3^0/\text{Cu}^{2+}$  of about 5. These complexes would definitely be far stronger at high temperatures, although the hydrolysis of  $\text{CO}_3^{2-}$  would tend to weaken them to some extent. Thus, carbonate may either enhance the solubility of  $\text{CuO}$  significantly or form basic carbonate solid phases, but no quantitative data are available at the conditions of interest. Complexes with bicarbonate ion can be ignored<sup>30</sup>.

*Chlorides.* The corresponding cupric chloride complexes are apparently three orders of magnitude weaker than the analogous amine complexes at 25°C<sup>11</sup>. Therefore, although the stability of these complexes will increase with increasing temperature (specifically  $\text{CuCl}^+$  and  $\text{CuCl}_2^0$  - the latter being potentially more volatile), their effect on the solubility of  $\text{CuO}(\text{cr})$  will be on the order of a few percent even at ppm concentrations of chloride. Limpo et al.<sup>11</sup> also list formation constants for mixed aminechloro complexes such as  $\text{CuCl}_3(\text{NH}_3)^-$  and  $\text{CuCl}(\text{NH}_3)_3^+$ , but based on these formation constants at ambient temperatures, they are unlikely to influence the copper chemistry in a plant operating under AVT conditions. Similar reasoning may be applied to the stronger acetate and sulfate complexes at boiler temperatures where by either of the diverse solubility profiles for  $\text{CuO}(\text{cr})$  given in Figure 4, the concentration of hydrolyzed copper in solution should far outweigh these complex concentrations. The only caveat to this conclusion being that the temperature dependencies of these formation constants are only estimates, and no reliable experimental values at high temperatures exist at present.

A possible exception are the cuprous chloride complexes, which are considerably stronger than the  $\text{Cu}(\text{II})$  analogues, although data only appear available for  $\text{CuCl}_2^-$  and  $\text{CuCl}_3^{2-}$  with  $\log K_n$  values of about 5 at 25°C<sup>31,32</sup>. However, in view of the projected high solubility of  $\text{Cu}(\text{OH})^0$  illustrated in Figure 2 and the relatively low pH at which  $\text{Cu}^+$  is predominant at high temperatures, it is unlikely that chloride will stabilize the +I oxidation state of copper to any appreciable extent. However, the strength of the  $\text{CuCl}^0$  complex relative to  $\text{CuCl}^+$  indicates that the cuprous complexes are covalently bound and as such will exhibit high volatility.

**Phosphates.** For the particular case of power plants operating under phosphate chemistry, Ziemniak<sup>9</sup> extracted three phosphate-containing complexes,  $\text{Cu}(\text{OH})_2(\text{HPO}_4)^{2-}$ ,  $\text{Cu}(\text{OH})_3(\text{H}_2\text{PO}_4)^{2-}$  and  $\text{Cu}(\text{OH})_2(\text{PO}_4)^{3-}$ , from solubility data collected from 19 to 262°C. At 250°C, 5 ppm total phosphate<sup>32</sup> would lead to 0.6 to 6 ppb ( $0.6$  to  $6 \cdot 10^{-8}$  m) complexed copper in solution, which is significantly less than the saturation level with respect to the hydrolyzed copper(II) species shown in Figure 4. An order of magnitude increase in phosphate results in the same increase in complexed copper. Considering the suspected uncertainties in the solubility data base of Ziemniak<sup>9</sup> at this time, extrapolation to higher temperatures consistent with phosphate treatment (i.e., operating at 325°C (*ca.* 1800 psi, or 124 bar), with 5 ppm phosphate at a 25°C pH of 9.5<sup>33</sup>), which is well outside the experimental range investigated, is unwarranted.

**Sulfides.** The stabilities of a number of bisulfide and dihydrogen sulfide complexes of  $\text{Cu}^+$  were measured by Crerar and Barnes<sup>34</sup> relative to sulfide-containing solid phases of Cu(I) and mixed Cu(I)/Fe(III) ( $\text{Cu}_2\text{S}$ ,  $\text{Cu}_5\text{FeS}_4$ ,  $\text{CuFeS}_2$ ) from 200 to 350°C. No neutrally-charged complexes were postulated to exist at their conditions, (only  $\text{Cu}(\text{HS})_2^-$ ,  $\text{Cu}(\text{HS})_2(\text{H}_2\text{S})^-$ ,  $\text{CuS}(\text{H}_2\text{S})_2^-$  were reported), and the conditions are probably too reducing to be appropriate for power generation applications.

### Adsorption of Cu(II) Ions

Recently, Ludwig and Schlindler<sup>35</sup> reported an experimental investigation of the adsorption of  $\text{H}^+$  and Cu(II) ions on anatase surfaces ( $\text{TiO}_2$ ) and although this work was carried out at 25°C, the general findings are of immediate interest and are expected to be analogous to adsorption onto magnetite without the complication of redox reactions at the surface. For example, at a pH of 9, which was the maximum value shown<sup>35</sup>, the dominant adsorption reaction onto an active surface site (designated as >S in equation 11) gave rise to the equilibrium expression in equation (12).



$$[>\text{SCu}(\text{OH})_2^0] = 10^{11.26} [>\text{S}] [\text{Cu}^{2+}] \quad (12)$$

Given a large active surface, the ratio of this particular form of surface-adsorbed copper to  $\text{Cu}^{2+}$  in solution is extremely large compared to the ratio of  $[\text{Cu}(\text{OH})_2^0]/[\text{Cu}^{2+}]$  of  $10^{1.76}$ , where  $\text{Cu}(\text{OH})_2^0$  is the dominant copper(II) species in solution at 25°C and pH = 9. Therefore, the equilibrium represented by equation (11) is highly favored and provides a stripping mechanism for copper(II) from solution. The pH of the zero-point-of-charge of this anatase sample was 6.58, similar to an approximate value of 6.9 (at 25°C) for magnetite<sup>36</sup>. The addition of ammonia complicates significantly the adsorption behavior of dissolved copper as demonstrated by Fuerstenau and Osseo-Asare<sup>37</sup>. In their study of the uptake of Cu (and Ni/Co) on metal oxides (including hematite) at 25°C, coordination by ammonia led to decreased adsorption and a complex dependence on pH with as many as five charge reversals on the surface. Machesky et al.<sup>14</sup> have shown that at least in the case of rutile ( $\text{TiO}_2$ ), the  $\text{pH}_{\text{zpc}}$  decreases with increasing temperature proportionally to the corresponding change in  $0.5\log K_w$  (where  $K_w$  is the dissociation constant of water) and the adsorption capacity of the surface increases significantly.

Hence the capacity for adsorption of copper(II) on metal oxides should be favored at higher temperatures. In view of the abundant surface sites and low copper concentrations, this mechanism may help explain the "deposition" of copper on the water walls of steam generators.

## Conclusions

- Cupric oxide is likely to be the most stable solid phase of copper in the water/steam cycle and is apparently slightly more soluble in steam than either Cu or  $\text{Cu}_2\text{O}$ . Solubility increases with temperature and steam density and can be described in the case of the data from Pocock and Stewart<sup>13</sup> by a simple function, which also appears to represent reasonably the solubility in liquid water if  $\text{Cu}(\text{OH})_2^0$  is considered to be the dominant copper species in solution. However, there are orders-of-magnitude differences in the solubilities and speciation reported by various experimentalists.
- One comprehensive study of the solubility of cuprous oxide in water was found, but indicates that concentrations on the order of tens of ppm are possible by 350°C over a wide range of pH. It is also apparent that cuprous-containing complexes in solution contain covalent bonds that will render these species far more volatile than those bound by electrostatic bonds.
- Based mainly on data at 25°C, complexation by standard inorganic ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ) and organic ( $\text{CH}_3\text{COO}^-$ ) ligands does not cause a substantial enhancement of the solubility of  $\text{CuO}(\text{cr})$  at the concentration levels expected for these solutes. Carbonate may be an exception. Under reducing conditions,  $\text{CuCl}^0$  formation may contribute significantly to the solubility of  $\text{Cu}_2\text{O}$ . The formation constants are generally poorly known at elevated temperatures, but are often orders of magnitude stronger at elevated temperatures when neutralization of charge is involved. It remains to be established in the laboratory whether amine complexes play a significant role in enhancing the solubility of  $\text{CuO}$  at elevated temperatures.
- Adsorption of  $\text{Cu}^{2+}$  and its hydrolyzed products on metal oxides is very strong at ambient temperatures and should increase with temperature, but decrease with coordination by ammonia (and possibly other ligands). Adsorption is expected to be even stronger when redox processes are involved (e.g., on magnetite surfaces).
- Finally and most significantly, if the solubility data presented by Var'yash<sup>7</sup> are valid, then control of the oxygen level in the feed-water system of a commercial power plant with copper metallurgy is crucial in order to avoid excessive oxidation of copper on the one hand, and to minimize the formation of the more soluble (and potentially volatile) copper(I) species on the other.

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