

Solubility of Copper Oxides in Water and Steam

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The solubility of cupric and cuprous oxides was measured in water over the range 25 to 350 °C in the presence of various chemical agents (NaOH, NH₃, B(OH)₃, H₃PO₄, (OHCH₂)₃CNH₂, (OHCH₂)₃CN(OHCH₂CH₃)₂, HF₃CSO₃, HNO₃ and mixtures thereof), and in steam to 400 °C as a function of pressure. Large discrepancies exist between the various experimental studies, especially at high temperatures for cuprous oxide, where the current solubilities are orders of magnitude lower. The solubilities of both oxides in water are highly pH dependent, but are virtually pH independent in steam.

1. Introduction

In 1997 a report on the “State of Knowledge of Copper in Fossil Plant Cycles” [1] set the stage for the establishment of “Program Copper” by EPRI. Subsequent reports have advanced our understanding of copper chemistry from the standpoint of the underlying science and the practical applications to plant operations [2-10].

In the 1960’s two important studies [11,12] were reported dealing mainly with the solubility of CuO (tenorite) in superheated steam. The latter also provided data on CuO solubility in “pure” water from ambient to the critical temperature of water. Hearn *et al.* [12] claimed that the small amount of solid oxide exposed to a relatively fast flow of steam in the former experiments [11] may have led to non-equilibrium results. They also sited the presence of corrosion in the reactor used by Pocock and Stewart [11] as providing a possible sink for copper deposition. Pocock and Stewart also reported limited data for the solubility of Cu₂O (cuprite) in superheated steam.

Two studies of CuO solubility in liquid water at sub-critical conditions [13,14] also led to different solubilities as a function of temperature and pH (*i.e.*, to different speciation schemes for the soluble hydrolyzed copper(II) species). Var’yash [15] reported the only comprehensive study of Cu₂O solubility over a wide range of pH to 350 °C. Petrov [16] summarized the extensive experimental studies of copper solubility performed in Russia since the early 1960’s mainly involving cupric

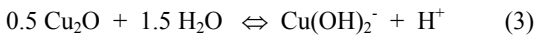
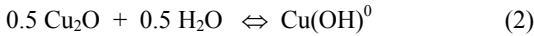
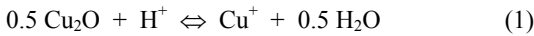
oxide and hydroxide. Virtually all of the investigations cited above used dynamic, flow-through techniques. Finally, the computer codes MULTEQ [17] and SUPCRT97 [18] provide estimates CuO solubility based on experimental data.

Previous reports indicated that the solubility-enhancing effect of complexing ligands present in boiler water as impurities (*e.g.*, chloride and acetate) would not be significant, even at elevated temperatures under oxidizing conditions [19,20]. New measurements of the analogous copper(I) complexes, which are relatively strong [21,22], also show that these do not contribute significantly to the level of dissolved copper in solution under reducing conditions.

Finally, Lvov *et al.* [2] constructed Pourbaix diagrams showing that cupric oxide is the stable form of copper in equilibrium with air-saturated aqueous solutions at least from ambient to 300 °C. The stability of copper(II) extends to deoxygenated aqueous solutions that do not contain added reducing agents, although spontaneous reduction to Cu(I) was observed occasionally in the present laboratory study, which focuses on the thermodynamics of the dissolution and precipitation of CuO and Cu₂O, and therefore does not address such issues copper reduction on wetted surfaces (*e.g.*, on magnetite) [1] or adsorption of ionic copper species onto magnetite surfaces [23,24], although these processes provide tangible sinks for copper in fossil plant water/steam cycles. The stability field of copper(I) with respect to ORP is

narrow and in the current experiments it was maintained by using deoxygenated solutions and added copper metal to maintain a controlled, slightly reducing ORP..

As an example of how experimental solubility data are treated in the present study and how the solubility varies as a function of pH, consider the equilibria involved in the dissolution of cuprous oxide in aqueous solutions:



$$\begin{aligned} [\text{Cu}^+]_{\text{total}} &= m\{\text{Cu}^+\} + m\{\text{Cu}(\text{OH})^0\} + m\{\text{Cu}(\text{OH})_2^-\} \\ &= K_{s0}(m\{\text{H}^+\}) + K_{s1} + K_{s2}/(m\{\text{H}^+\}) \end{aligned} \quad (4)$$

where $m\{\}$ is the molality of a given species. For the sake of simplicity, activity coefficients are ignored in Eq. (4), but are considered in the actual data treatment. By regression analysis of the measured total copper concentration, $[\text{Cu}^+]_{\text{total}}$, as a function of $m\{\text{H}^+\}$ at each temperature, the solubility constants, K_{sn} , are derived.

2. Experimental Methods

Four types of experiments were performed. These involved the use of a stirred Teflon-lined batch reactor (for use to 300 °C), a static platinum-lined autoclave from which liquid and vapor samples were withdrawn, operating to 350 °C [3], a high-temperature flow-through apparatus made from a Zircalloy 4 alloy for use to 400 °C and low-temperature version using a series of three PEEK® flow-through columns (<100 °C) [10].

The bulk of the results were obtained with the high-temperature flow cell, which allowed the pressure to be controlled for measurements in liquid water and steam. The flow rates were varied to ensure that equilibrium was established. Solutions of either acid or base were also pumped into the sample line inside the furnace to prevent re-deposition of copper oxide upon cooling. Field measurements of copper (particulates and dissolved) levels in steam were shown by Howell and Weisser [25] to be compromised by precipitation of copper in the sampling lines, indicating that copper transport might be underestimated when based on sampling around the steam cycle. It should be noted that precipitation of copper oxide was also observed in our study when

no acid or base was injected, particularly when sampling copper(I) solutions. The sample lines are made from a platinum/rhodium alloy to prevent adsorption or reduction of copper on the walls of the tubing.

The feed solutions were pressurized (< 0.1 MPa) with helium, argon-hydrogen mixtures, oxygen, or CO₂-free air depending on the oxide being studied. The pH of the solutions was controlled by addition of excess acid or base, or a suitable pH buffer agent.

Commercial crystalline cupric oxide was used without further purification. The fine-grained cuprous oxide was recrystallized by heating in a copper metal boat under a blanket of steam inside a closed autoclave at 550 °C for two weeks. Therefore, the charge of Cu₂O contained a significant quantity of copper metal, which then served as a redox buffer to scavenge trace amounts of oxygen in the water and steam. These starting oxides, and oxide samples taken after the experiments, were characterized by XRD, SEM, TGA and BET (in some cases, IR) to ensure the composition and crystallinity of the solubility-determining phase.

3. Results and Discussion

The solubilities of Cu₂O and CuO, were studied in solutions of known pH from 25 to 350 °C (generally at 50 °C intervals) under redox control in corrosion-free vessels. Their solubility in steam was measured from 200 to 400 °C, and as a function of pressure mainly at 350 and 400 °C. These results are presented under sub-headings that detail the effects of process variables (pH, temperature, redox potential and chemical agents). Although the emphasis of this research was to obtain reproducible, rigorous thermodynamic data, the following discussions will attempt to concentrate on the observed phenomena, rather than on the underlying equilibrium results.

It is important to note that the solubility data presented here represent true equilibrium values for crystalline cupric and cuprous oxide phases. Super-saturated solutions can be generated by perturbations of temperature, pH and above all, a change in the oxygen partial pressure. Under-saturated copper solutions can be found when the contact time is too short (fast flow rates) to allow the kinetics of dissolution to reach equilibrium. Finally, if the copper oxides are not well

crystallized or even amorphous, or are present as fine particulates, then higher solubilities than reported here will inevitably result.

3.1. Solubility of CuO and Cu₂O in Water

Figures 1 and 2 show the fitted solubility curves for crystalline CuO and Cu₂O, respectively, in liquid water plotted against pH_t, which is based on $m\{H^+\}$ at the experimental temperature, t . It is immediately apparent that the temperature dependence of the solubility is quite complicated. It is also apparent that the crucial parameter in these measurements is pH, which must be controlled and known accurately. The curves for Cu₂O in Fig. 2 are very different from those reported by Var'yash [15], *i.e.*, as much as five orders of magnitude lower in the near neutral pH range.

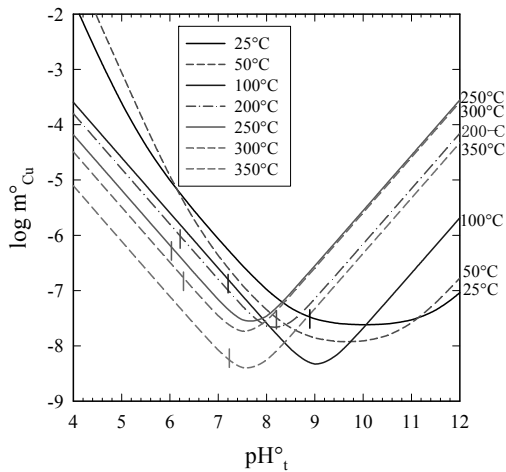


Fig. 1 This figure represents fits of our experimental data on the solubility (m°_{Cu} in units of $\text{mol}\cdot\text{kg}^{-1}$ (H_2O)) of cupric oxide in water as functions of pH_t (pH at temperature, t °C) where the vertical line for each curve corresponds to a pH_{25°C} of 9.

3.1 Effect of pH on the Solubility of CuO and Cu₂O

First, it is obvious from the curves in Figs. 1 and 2 that the solubilities of the oxides with respect to pH exhibit broad minima at low temperatures. In other words, at ambient temperature variations in pH

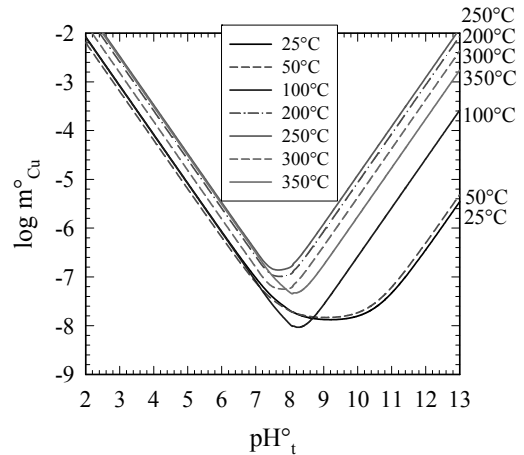


Fig. 2 This figure represents fits of our experimental data on the solubility (m°_{Cu} in units of $\text{mol}\cdot\text{kg}^{-1}$ (H_2O)) of cuprous oxide in water as functions of pH_t (pH at temperature, t °C).

from 9 to 11 for CuO and 8.5 to 10 for Cu₂O will have little effect of the concentration of copper in solution at about 2 and 1 ppb, respectively. However, by 350 °C (16.5 MPa) the broad solubility minima are replaced by a V-shaped profile, so that a one unit shift in pH_t on either side of the minima causes an order of magnitude increase in copper concentration. Fortunately, at this operating temperature, a pH_{25°C} of *ca.* 9 corresponds to solubilities for the two oxides close to the minima, but on opposite sides (see next section for more discussion of this trend).

In terms of the underlying chemistry, the pH dependencies establish that at low temperatures (<100 °C) the neutral species, $\text{Cu}^{\text{II}}(\text{OH})_2^0$ and $\text{Cu}^{\text{I}}(\text{OH})^0$ are dominant in water under mildly alkaline conditions, whereas at high temperature these species are unimportant and the copper species in solution are in the form of ions. Since $\text{Cu}^{\text{II}}(\text{OH})_2^0$ and $\text{Cu}^{\text{I}}(\text{OH})^0$ are the only volatile forms of dissolved copper in dilute solutions, their decreasing importance at high temperature may account for the observation that the partitioning of copper to steam increases only marginally with increasing temperature. Finally, the occurrence of copper as ions at high temperature introduces the strong possibility for their adsorption onto the metal internal surfaces of a boiler, *e.g.*, on magnetite [26]. The adsorption of Zn^{2+} , Ni^{2+} and Co^{2+} ions onto rutile, TiO_2 , has been shown to increase

dramatically with increasing temperature and pH from experiments performed to 300 °C at ORNL.

3.3. Effect of Temperature on the Solubility of CuO and Cu₂O The effect of temperature on the solubility of copper oxides was an integral part of the preceding discussion on the pH effect. Clearly these two variables are strongly coupled. From Fig. 1 it can be seen that at pH values below neutral, the solubility of CuO decreases substantially and systematically with increasing temperature. This behavior is typical of other divalent metal oxides. On the basic side the behavior is more complicated; the solubilities of both oxides increases to about 250 °C, then decreases; a similar trend is observed for Cu₂O in acidic to neutral solutions, but the overall variation is small.

Perhaps of more practical interest is the change in concentration of solutions saturated with Cu^I and Cu^{II} at a pH typical of fossil-fired drum units as the temperature is raised from ambient to the operating temperature. The remarkable change in copper concentration in parts per billion (ppb) is illustrated in Fig. 3 for both copper oxides as the temperature is raised from 25 to 350 °C at fixed pH_{25°C} values chosen randomly at 9.0 and 9.5. There is a clear maximum in each curve that is higher at pH_{25°C} 9.0 than 9.5 so that copper levels change from 1 to 2 ppb at 25 °C to up to almost 150 ppb for Cu₂O at pH_{25°C} = 9, before falling off to much lower values at normal operating conditions. It must be remembered that the kinetics of dissolution and precipitation are also faster with increasing temperature. Thus, these results would also imply that cycling of temperature in a boiler would potentially lead to wild variations in the copper content of the water with the opportunity for strong surges in the partitioning of copper to the steam through droplet carry-over. These maxima with temperature are more acute at lower boiler water pH as the logarithm of the copper concentration increases linearly with pH on the acidic legs of the solubility curves shown in Figs. 1 and 2.

Figure 3 also illustrates that at 25 °C the solubility of both oxides in the pH_{25°C} range of 9 to 9.5 is ≤ 2 ppb and is only slightly higher for Cu₂O at an operating temperature of 350 °C.

Stodola *et al.* [19] found copper levels between 2.2 and 13.1 ppb in boiler water at 18.2 MPa (357 °C) during full load, whereas at startup the concentration varied from 387 ppb to a maximum

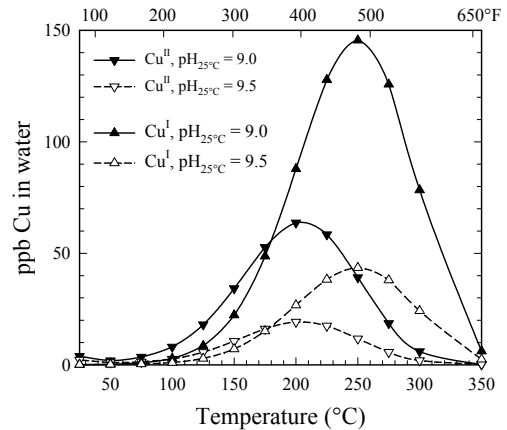


Fig. 3 The dependence of the solubilities of cupric (Cu^{II}) and cuprous (Cu^I) oxides in water on temperature at two fixed pH_{25°C} values, namely 9.0 and 9.5.

of 611 ppb, and finally to 240 ppb (pH_{25°C} changed from 9.82 to 9.53 to 9.13). The change in pH notwithstanding, this trend is very similar to that predicted in Fig. 3 based on the variation in copper oxide/s solubility with temperature.

3.4. Effect of Oxygen on the Solubility of CuO and Cu₂O Pourbaix diagrams have been constructed for the Cu/Cu₂O/CuO system from 25 to 300 °C with somewhat conflicting results [2,27], because they are based on different assessments of the available literature data. However, both models predict that at 25 °C, Cu₂O is only stable over a narrow band of potential midway between the oxygen and hydrogen lines, and in near neutral to mildly basic solutions. By 300 °C, the Cu₂O stability field virtually disappears leaving only copper metal and CuO as the stable solids. Clearly these predictions will have to be seriously modified based on the new results of this study.

Atomic Force Microscopic (AFM) flow-through experiments in the presence of ammonia (pH = 9, NH₃ buffered at 100 °C) showed that under reducing conditions with the oxidation-reduction potential (*versus* Ag/AgCl electrode, saturated KCl) CuO was the stable solid phase at +100 mV, whereas at -350 mV, Cu₂O persisted [9]. The former forms a rougher (higher surface area and presumably more rapid dissolution kinetics) coating on the admiralty brass test strip. Therefore, it is important to remember that the solubilities of CuO

and Cu_2O can only be compared under the different prevailing ORP conditions. In the experiments at ORNL, the solubility of the former was studied in the presence of dissolved oxygen or in dilute nitric acid to ensure an oxidizing environment, although this practice was limited because of concerns of corrosion of the Zircalloy pressure vessel. All experiments with Cu_2O were conducted with Cu metal present at the up-steam end of the pressure vessel to scavenge oxygen from the feedwater. At a $\text{pH}_{25^\circ\text{C}}$ of 9 (100 °C), the concentrations of copper in equilibrium with CuO and Cu_2O are 9.4 and 2.7 ppb, respectively. This reflects the condition of the University of Surrey experiments [9], although equilibrium may not have been attained in this earlier study with respect to well-defined crystalline phases.

At ORNL one series of experiments were carried out at 100 °C with only pure copper metal beads present in a dilute caustic feedwater saturated with CO_2 -free air (slow flow rates or $0.1 \text{ mL}\cdot\text{min}^{-1}$ at +100 mV). A constant solubility was attained over the duration of the experiment (one month) that was significantly super-saturated with respect to crystalline Cu_2O surface layer by a factor > 5 . Clearly, under these conditions a passive Cu_2O layer was not formed.

3.5. Effect of Chemical Additives on the Solubility of CuO and Cu_2O The chemicals added to the feedwater or bulk liquid phase in this research served to control the pH of the solution such that it could be calculated from either the known excess of a free acid (HNO_3 or HCF_3SO_3) or free base (NaOH), or from a known buffer mixture, such as NH_3 and NH_4^+ . The strong organic acid, HCF_3SO_3 , is known not to complex significantly dissolved metal ions. Indeed varying its concentration only showed the predicted effect of pH. Nitric acid was used sparingly in some CuO experiments to establish an oxidizing environment and the presence of nitrate ion did not have any measurable effect on the solubility of CuO.

Ammonia is known to form strong complexes with copper ions in water potentially leading to enhancement of copper concentrations in solution. However, based on recent data by Trevani *et al.* [28] for the formation of complexes of the type, $\text{Cu}^{\text{II}}(\text{NH}_3)_n^{2+}$, in water containing 2 ppm NH_3 at 25 °C ($\text{pH} = 9$) the solubility of cupric oxide would be raised by less than 1%. This effect decreases with increasing temperature. There is clear evidence from the current study that

$\text{Cu}^{\text{II}}(\text{OH})(\text{NH}_3)_n^+$ complexes are formed, but are still not strong enough to raise the copper concentration significantly. However, $\text{Cu}^{\text{I}}(\text{NH}_3)_n^+$ complexes are much stronger under the same conditions by almost four orders of magnitude, so the copper levels in solution would be raised by a factor of 15 for 2 ppm ammonia at 25 °C, $\text{pH} = 9$. This effect is less significant at high temperatures and higher pH. The pH buffers, Tris ($(\text{OHCH}_2)_3\text{CNH}_2$) and Bis-Tris ($(\text{OHCH}_2)_3\text{CN}(\text{OHCH}_2\text{CH}_3)_2$), were tried at 25 °C and had a huge effect on the solubility of both copper oxides, producing ppm levels of copper at near neutral pH when used at ppm concentrations. These buffers are substituted forms of the readily available chemical, triethanolamine, which has the potential of being an excellent cleaning agent for removing copper oxide films at low temperatures.

Contaminating anions such as chloride, sulfate and acetate form complexes with Cu^{2+} and Cu^+ , but only become strong at high temperatures, where Cu^{2+} is not present. Therefore, ppb levels of these ions will have little effect on the solubility of copper oxides. Complexes of Cu^{2+} with carbonate are known to be strong, but are unlikely to contribute to the dissolved copper inventory at any temperature around the water/steam cycle.

3.6. Solubility of CuO and Cu_2O in Steam The solubility of Cu_2O and CuO in steam was studied from 200 to 400 °C. Partitioning experiments (200 – 350 °C) were also conducted with CuO where the solid was equilibrated with water containing dilute NaOH and steam. In very general terms, below 350 °C at near saturation vapor pressures, the solubilities of Cu_2O and CuO proved to be very similar and fairly independent of temperature, *viz.* 0.5 – 3 ppb. It is assumed that the dominant species of copper in steam are the neutral hydroxide molecules, $\text{Cu}(\text{OH})^0$ and $\text{Cu}(\text{OH})_2^0$, which implies that their concentrations are independent of pH. Stodola *et al.* [19] reported copper levels of 1.0 to 2.0 ppb (five tests) in main steam under full load from a 500 MW unit (18 MPa drum boiler, equivalent to 357°C), single reheat with copper condensers and both low- and high-pressure feedwater heaters. Clearly these levels are consistent with homogeneous vaporous carryover of copper as predicted from the present experimental results. The initial high levels of copper in steam reported by Stodola *et al.* [19] over time during startup must be due to mechanical

carryover of droplets and particulates, if the results of the present study are applicable.

At supercritical conditions ($> 374\text{ }^{\circ}\text{C}$), where the pressure (and consequently the density of the solvent water) can be varied over a wide range, there is a distinct increase in solubility with increasing pressure (water density). There are a number of experimental studies of CuO solubility in steam [3,10,11,12,27,28], but only one was found for Cu_2O [11]. Interestingly, it appears from the present results at subcritical conditions that Hearn *et al.* [12] actually may have had Cu_2O in their system, rather than CuO . A linear empirical relation, which is known to be valid for more precise data available for electrolytes such as NaCl , was applied to these scattered results.

Clearly, variations in the temperature and pressure of steam passing to the superheater and high pressure turbine, and through changes in load, would provide opportunities for deposition and redissolution of either oxide.

Acknowledgments

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