EVALUATION OF MODELS FOR SOLUBILITY AND VOLATILITY OF COPPER COMPOUNDS UNDER STEAM GENERATION CONDITIONS

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ABSTRACT: The loss in efficiency of power plants with mixed metallurgy, due to transport and deposition of copper and its oxides in HP turbines, has been recognized as one of the key problems to be solved in the utility industry worldwide. Within this context, the most important problem to be addressed is the solubility and volatility of copper compounds under steam generation condition. This paper presents an evaluation of different solubility and volatility models for copper compounds, and presents a comparison between the calculated and test data.

INTRODUCTION

Improvements in the reliability and efficiency of power plants are directly related to the purity of water and steam around the cycle. Copper transport is one of the problems that primarily affects the efficiency of power plants with copper-based metallurgy by causing deposition of copper and its oxides on HP turbines. This has been a problem for many years and currently is one of the top research priorities [1, 2]. Included in this topic, the solubility and volatility of copper compounds under steam generation conditions are of greatest importance.

Large-scale research programs on the solubility and volatility of copper compounds were performed in the USSR with the test rigs simulating power plant operation conditions, which covered a wide range of saturation parameters (120-358°C) and different types of water chemistry [3-6]. The only available cuprous oxide solubility study in water at saturation conditions (200-300 °C) was also performed in Russia [7]. The most comprehensive research on cuprous and cupric oxide solubility in superheated steam was performed in USA by Pocock and Stewart [8]. All of these studies established the following fundamental trends in copper solubility and volatility in the two-phase region, as well as the solubility in superheated steam [9]:

- Solubility of copper increases with pressure and temperature.
- Solubility of copper in high temperature water is minimal in most cases over the pH range of 6.5-10.0 and increases in both acidic and alkaline regions.
- Solubility of Cu_2O in water is much higher than that of CuO at elevated temperatures.
- Solubility of copper in the liquid phase is higher than that in saturated steam.
- Copper volatility increases with pressure.

On the basis of the available test data, several copper solubility models (empirical equations) have been derived:

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- Copper solubility (mol/kg) in superheated steam (Martynova *et al.* [3], test data [8]):

$$\log C_{CuO} = 1.87 \log \rho_{H_2O} - (11{,}280/4.57T) - 1.67 \quad (\text{pH} = 7.5) \tag{1}$$

$$\log C_{CuO} = 4.72 \log \rho_{H_2O} - (25{,}600/4.57T) + 5.01 \quad (\text{pH} = 9.5\text{, ammonia}) \tag{2}$$

$$\log C_{Cu_2O} = 5.41 \log \rho_{H_2O} - (18{,}900/4.57T) + 3.64 \quad (\text{pH} = 9.5\text{, ammonia}) \tag{3}$$

- Copper solubility (ppb) in superheated steam (Palmer *et al* [10], test data [8]):

$$\log C_{Cu} = 2.17 \log \rho_{H_2O} - (3{,}260/T) + 7.10 \quad (\text{pH} = 7.5) \tag{4}$$

$$\log C_{Cu} = 2.92 \log \rho_{H_2O} - (3{,}230/T) + 8.00 \quad (\text{pH} = 9.5\text{, ammonia}) \tag{5}$$

- Copper metal solubility (ppb) in the liquid phase (Tolmacheva and Batalina. [11], test data [5])

$$\log C_{Cu} = 0.98 \log \rho_{H_2O} - (14{,}500/19.1T) + 2.55 \quad (\text{pH} = 9.5 - 10.0\text{, KOH}) \tag{6}$$

In all of these equations ρ is in g/cm^3; T is in K.

In regard to the corresponding volatility models, Martynova *et al.* [3] determined values on the ray diagram for copper oxides. The question remains, whether these solubility and volatility equations provide a good fit to all the various test data, as well as a realistic estimation of copper transport and deposition around the cycle.

COMPARISON BETWEEN CALCULATED AND TEST RESULTS

Copper Solubility in High Temperature Liquid Water

Although only one solubility model (Eq. 6) describes copper metal solubility in liquid water, it may be assumed that solubility models developed for superheated steam may be extrapolated to some extent to saturation conditions and visa versa. Tables 1-3 present comparisons between calculated and test data for copper oxide solubility in water at different pH values.

Table 1. Calculated versus Test Results for Copper(II) Oxide Solubility in Water, pH = 7.5

Saturation temp., °C	Copper oxide (CuO) solubility, ppb					
	M [3]	*Pl* [10]	M [3]	Pt [12]	S [5]	V [6]
120	*0.6*	*0.06*			*ca.* 14	
200	*6.3*	*1.2*				*ca.* 8.4
250	*17.1*	*4.5*				*ca.* 16
285	*25.4*	*9.5*			*ca.* 16	
300	*35.6*	*12.4*				*ca.* 30

335	*49.4*	*19.9*		*ca.* 4.5		
344	*51.8*	*21.5*			*ca.* 18	
355	*52.8*	*22.5*		*ca.* 6.5		
358	*52.5*	*22.5*	*ca.* 22.5			

Table 2. Calculated versus Test Results for Copper(II) Oxide Solubility in Water, pH = 9.5

Saturation temp., °C	Copper oxide (CuO) solubility, ppb						
	M [3]	*Pl* [10]	*T*	M [3]	Pt [12]	S [5]	V [6]
120	*0.03*	*0.5*	*3.9*			*ca.* 4	
200	*4.7*	*9.8*	*7.7*				*ca.* 8.4
250	*44.2*	*34.8*	*10.1*				*ca.* 15.5
285	*145.7*	*68.2*	*11.6*			*Ca.* 11.7	
300	*220.7*	*85.9*	*12.1*				*ca.* 30
335	*438*	*124.3*	*12.7*		*ca.* 4.5		
344	*476.1*	*129.2*	*12.6*			*Ca.* 12.8	
355	*480.9*	*128.1*	*12.3*		*ca.* 6.5		
358	*468*	*125.4*	*12.1*	*ca.* 22.5			

Table 3. Calculated versus Test Results for Copper(I) Oxide Solubility in Water, pH = 9.5

Saturation temp., °C	Copper oxide (Cu_2O) solubility, ppb	
	M [3]	V [7]
200	*229.6*	*ca.* 60.7
250	*1025*	*ca.* 254
300	*2695.7*	*ca.* 850

The calculated results are in italics.

Analysis of the data given in these tables shows that at $pH_0 = 7.5$ there is a good agreement between copper oxide (CuO) solubility in water calculated with equation (4) (Palmer *et al.* [10]), and test results presented by Martynova *et al* [3]., Petrova and Martynova [12], and Styrikovich *et al.*[5] - i.e., the discrepancy does not exceed 18 ppb. However, the test results produced by Varyash [6] at the same pH are closer to equation (1) (Martynova *et al.* [3]) - the discrepancy does not exceed 5.6 ppb. The test results of copper oxide (CuO) solubility at pH = 9.5 given by Martynova *et al.* [3], Petrova and Martynova [12], Styrikovich *et al.* [5], and Varyash [6], are best described with the empirical equation (6) (Tolmacheva and Batalina [11]) with the discrepancy not exceeding 15.2 ppb.

There is poor agreement between copper (Cu_2O) solubility at pH = 9.5 calculated with equation (3) (Martynova *et al.* [3]) and test data presented by Varyash [7] (the discrepancy ranges from 170 to 1850 ppb). It is important to note that the equations developed by Martynova *et al.* [3] and Palmer *et al.* [10] were based entirely on the solubility of copper oxides under supercritical conditions [8]. Therefore, extrapolation to subcritical temperatures and high densities must be treated with caution. Also, these equations were derived with ammonia as pH buffering agent, whereas in most of the solubility tests at saturation conditions, KOH or NaOH was used.

Copper Solubility in Saturated Steam

A comparison of the calculations with the only available test data on solubility of copper (Cu^{2+}) in saturated steam (Petrova and Martynova. [12]) is shown in Table 4.

Table 4. Calculated versus Test Results for CuO Solubility in Saturated Steam, pH = 7.5-9.5.

Saturation temp., °C	Copper oxide (CuO) solubility, ppb				
	M [3] *(pH = 7.5)*	*M* [3] *(pH = 9.5)*	*Pl* [10] *(pH = 7.5)*	*Pl* [10] *(pH = 9.5)*	Pt [12]
335	*1.2*	*0.03*	*0.3*	*0.4*	*ca.* 0.5
355	*3.3*	*0.4*	*0.9*	*1.7*	*ca.* 1.2

These test results on copper(II) oxide (CuO) solubility in saturated steam are best described by the equations (4,5) (Palmer *et al.* [10]) at both pH = 7.5 and 9.5 (the discrepancy does not exceed 0.5 ppb).

Copper Solubility in Superheated Steam

The most comprehensive study of solubility of cuprous and cupric oxide in superheated steam was performed by Pocock and Stewart [8]. Based on these test results, several above-mentioned solubility models were derived (1-5). Tables 5-7 provide comparisons between the calculated solubility values and test results produced by Pocock and Stewart, and USSR scientists (Deeva [13], and Zenkevich and Kozina .[14]).

Table 5. Calculated versus Test Results for CuO Solubility in Superheated Steam, pH = 7.5.

Temperature, °C	Pressure, MPa	Copper oxide (CuO) solubility, ppb			
		M [3]	*Pl* [10]	P&S [8]	D* [13]
482.2	31.0	*16.2*	*7.3*	*ca.* 10**	
565.6	31.0	*20.2*	*10.7*	*ca.* 6.1	
610.0	29.4	*21.1*	*11.8*		*ca.* 11.5
621.1	18.6	*8.4*	*4.1*	*ca.* 3.1	
621.1	26.9	*18.1*	*10*	*ca.* 11.1	
621.1	31.0	*24.5*	*14.2*	*ca.* 15.4	
650.0	29.4	*24.2*	*14.5*		*ca.* 19

Table 6. Calculated versus Test Results for CuO Solubility in Superheated Steam, pH = 9.5.

Temperature, °C	Pressure, MPa	Copper oxide (CuO) solubility, ppb			
		M [3]	*Pl* [10]	P&S [8]	Z [14]
482.2	31.0	*16.5*	*13.8*	*ca.* 16.6**	
550.0	25.0	*6.2*	*7.1*		*ca.* 2

565.6	31.0	*24*	*16.1*	*ca.* 17**	
621.1	18.6	*2.3*	*3.7*	*ca.* 4.9**	
621.1	22.8	*10.3*	*7.1*	*ca.* 12.5**	
621.1	26.9	*16.2*	*12.2*	*ca.* 16	
621.1	31.0	*34.9*	*19.6*	*ca.* 17.3**	

Table 7. Calculated versus Test Results for Cu_2O Solubility in Superheated Steam, pH = 9.5.

Temperature, °C	Pressure, MPa	Copper oxide (Cu_2O) solubility, ppb	
		M [3]	P&S [8]
621.1	18.6	*0.5*	*ca* 0.2
621.1	22.8	*1.8*	*ca* 2.9
621.1	26.9	*5*	*ca* 4.9
621.1	31.0	*12*	*ca* 9.9**

* feedwater pH = 6.0; ** averaged test data

These data show that equations (4, 5) (Palmer *et al.* [10]) describe the test data [8] for CuO, on which the fits were originally based, reasonably well at both pH = 7.5 and 9.5 (the discrepancy does not exceed 5.4 ppb), whereas the discrepancy with equation (2) (Martynova *et al.* [3]) is somewhat larger (up to 17.6 ppb). The test data of Deeva [13] are also better represented by equation (4). On the other hand, equation (3) provides a very good representation for Cu_2O solubility in superheated steam [8] with a maximum discrepancy of 2.1 ppb.

Copper Volatility

The distribution of copper(II) between boiling water and equilibrated steam, taking into account the effect of pH_0, was first discussed by Martynova [15]. On the basis of the Pocock and Stewart test data [8], the coordination factor "n" was determined from the dependence of the distribution ratio K_d $\{m_{Cu\ vapor}/m_{Cu\ liquid}\}$ on the ratio of steam to water densities ($K_d = (\rho_s/\rho_w)^n$) at saturation conditions. The values of "n" derived in this manner were 1.87 at pH = 7.5 and 4.6 at pH = 9.5 with ammonia present [3]. The factor "n" for Cu_2O, also derived from the test data [8], was reported to be 5.4 at pH = 9.5 with ammonia buffer. Note, that at the pH_t imposed by ammonia, it is likely that the dominant copper species in the liquid phase are the neutral molecules, $Cu(OH)_2$ and Cu(OH), [6,7] and consequently the simple distribution ratio, which does not take into account other hydrolysis reactions of these two solutes, describes adequately the partitioning of copper under these conditions. However, comparison of the calculated data with the test data [3,4] shows that there is some disagreement between them. The "calculated" ray of CuO (n = 1.87) at pH = 7.5 is lower than the "test" ray (n = 1.18). It is likely that some ammonia was present at pH = 7.5 in the tests [8], for which the calculated value of 1.87 was obtained. It is believed [4] that the presence of ammonia influences the distribution ratio of copper: K_d decreases with increasing ammonia levels in water up to *ca.* 2.1 ppm. There is also large disagreement between the "calculated" ray (n = 4.6) and the "test" ray (n = 2.90) at pH = 9.5. One explanation for these discrepancies is that the calculated data were derived by extrapolation from superheated to the saturated steam region. However, these differences may also result from the effect of pH on the hydrolysis reactions with varying ammonia levels (hydrolysis of the neutral copper species in the liquid phase will tend to lower the values of K_d). An additional concern is the unquantified effect of copper complexation by ammonia in both phases at high temperatures.

CONCLUSIONS

Analysis and comparison of the existing copper solubility models with the available test data indicate that the equations given by Palmer *et al.* [10] (for CuO) and Martynova *et al.* [3] (for Cu_2O) may be suitable for the prediction of copper oxide solubility in superheated steam and, to a limited extent, at saturation conditions. However, the best representation for the liquid phase solubility of CuO is given by Tolmacheva and Batalina [11], although this equation covers a narrow pH_0 range. Therefore, the development of solubility and volatility models is needed that can be applied to saturation conditions over the wide range of pH values existing in power plant cycles (*ca.* 7.5 – 9.5). First, further experimental research on copper oxide solubilities and volatilities is required in order to verify the existing test data and to produce more quantitative understanding of copper behavior in power-generating cycles.

ACKNOWLEDGMENTS

This research project was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences of the U.S. Department of Energy, under Contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp. A. P. wishes to acknowledge his support from the Moscow Power Institute, Russia.

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