

Speciation of Cu^+ in Hydrothermal NaCl Brines from Molecular Dynamics

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It is well known that the complexation of Cu by Cl^- ligands is important in increasing the solubility of copper sulphide phases in hydrothermal solutions. In the conditions found in the earth's crust, copper exists in the 0, +1, and +2 oxidation states. In the absence of complexing ligands such as Cl^- or HS^- , Cu^+ is unstable in aqueous solution. With increasing Cl^- concentration however, Cu^+ becomes stable at the expense of Cu^{2+} (Figure 1). This is based on current estimates of stability constants that imply that $\text{Cu}^+\text{-Cl}^-$ complexing is stronger than $\text{Cu}^{2+}\text{-Cl}^-$ complexing. It is therefore assumed that only $\text{Cu}^+\text{-Cl}^-$ complexes are significant in hydrothermal solutions. Even under oxidised conditions associated with sedimentary red bed deposits Rose (1976) assumed that Cu was transported as cuprous chloride complexes in solutions formed near 75 °C.

However there is disagreement within the literature over which species are dominant in $\text{Cu}^+\text{-Cl}^-$ solutions. According to Helgeson et al (1969) CuCl_2^- and CuCl_3^{2-} are the dominant species up to 300°C, whilst Crerar and Barnes (1976) concluded that CuCl^0 is dominant in the range 200-350°C. In a recent study Xiao et al (1998) calculated equilibrium constants for $\text{Cu}^+\text{-Cl}^-$ complexes. They found reasonable agreement with previous calculations up to 150°C, but variable agreement at higher T. They were in particular disagreement with the theoretical results of Sverjensky et al. (1997), which suggest that CuCl_2^- and CuCl_3^{2-} are the dominant species up to 350°C. Xiao et al (1998) considered Cl^- concentrations up to 1m only. They provide no data at higher Cl^- concentrations such as those in natural brines. Examples of these natural brines are sedimentary brines with high chloride concentrations of around 150 000ppm (4M), (Warren and Smalley, 1994), and modern day geothermal brines such as the Salton sea geothermal system in California, (Helgeson, 1969).

Preliminary Results

Using Density Functional Theory (DFT) we have developed a Lennard-Jones (LJ) pair-wise interaction potential for $\text{Cu}^+\text{-OH}_2$, this is then combined with the $\text{Cl}^-\text{-OH}_2$ interaction from Smith and Dang (1994), with cross terms giving the $\text{Cu}^+\text{-Cl}^-$ interaction. We have used this in molecular dynamics (MD) simulations to determine the speciation in 0.5M CuCl + 1.5M and 5M NaCl solutions at 327 and 227°C respectively and at 1kbar pressure.

Direct analysis of the speciation shows ~84% of the Cu^+ atoms exist as single ions in 0.5/1.5M solution, with the remainder existing mainly as CuCl^0 pairs. In the 0.5/5.0M

solution only 25% of ions exist as Cu^+ , whilst 50% are CuCl^0 , ~15% are CuCl_2^- and CuCl_3^{2-} , with rest making higher order complexes. We find a Cu-O distance of ~1.86Å and a Cu-Cl distance of ~2.26Å. The Cu-O distance is in good agreement with the DFT bond length, although the Cu-Cl distance is longer than the Cu-Cl distance of the DFT calculations (~2.2Å). This may be due to the small system in the DFT calculations (only the immediate hydration shell is used). We are currently carrying out MD simulations to include 0.5M CuCl in 1, 3, and 5M NaCl, and elevated temperatures.

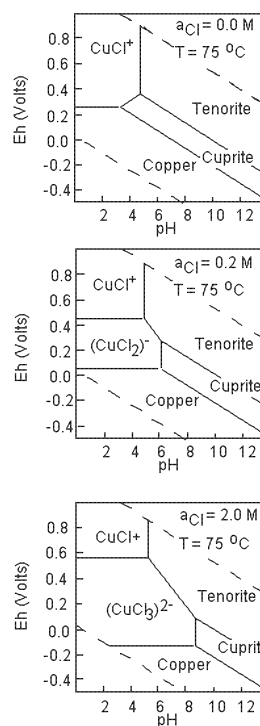


Figure 1:

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