SOLUBILITY OF COPPER OXIDES IN WATER AND STEAM

Donald A. Palmer, Pascale Bénézeth and J. Michael Simonson
Chemical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008
Oak Ridge, TN 37831-6110, U.S.A.

The solubilities of cuprous and cupric oxides have been measured mainly using flow techniques from 25 to 350°C in aqueous solutions across the pH range corresponding to 10^{-3} mol·kg^{-1} CF_3SO_3H to 0.1 mol·kg^{-1} NaOH. The corresponding solubilities in steam were measured from *ca.* 200 to 400°C at pressures near the saturation vapor pressure of water, except at 400°C where greater variations were possible.

Cupric oxide (tenorite) solubility has been investigated in the past in liquid water to high temperatures with widely discrepant results and different analyses as to the dominant copper species in solution.[1,2] Difficulties arise in such studies through the need to control and estimate the pH of the solution at temperature, and to maintain an oxidizing environment. The former necessitates the use of pH buffering agents in the crucial middle pH range that can interact with the copper(II) in solution to produce elevated solubilities or adsorb on the oxide surface with unknown effects. The present study attempts to resolve these issues and provide a coherent solubility model with respect to temperature and pH. Tenorite solubility in supercritical steam has been well studied and is discussed here in relation to the largely sub-critical results obtained at ORNL.

Conversely, there appears to have been only one investigation of the solubility of cuprite (Cu_2O) in liquid water to high temperatures and even data at ambient conditions are sparse.[3] At 350°C, the solubility results from the present study are four orders of magnitude lower that that reported in this previous work. The problems inherent in measuring the solubility of tenorite are exasperated here due to the strong interactions of many potential pH buffers with Cu^+ that vary with temperature and the need to control the redox potential within a narrow range. Again the results of the present study will be presented in an attempt to provide a consistent, rigorous model for the solubility of Cu_2O in aqueous solutions. The limited results for its solubility in steam will also be discussed.

Acknowledgments

The financial support of the Electric Power Research Institute under the guidance of Dr. R. Barry Dooley is gratefully acknowledged. Oak Ridge National Laboratory is managed and operated by UT-Battelle, LLC, for the U.S. Department of Energy under contract DE-AC-00OR22725.

References

[1] L. Var'yash, *Geokhimiya*, 1003-1013 (1985).
[2] S.E. Ziemniak, M.E. Jones, and K.E.S. Combs, *J. Solution Chem.*, 29, 179-200 (1992).
[3] L.N. Var'yas h, *Geochem. International*, 26, 80-90 (1989).

"The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-00OR22725. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes."