Imaging and micro-XAFS of hydrothermal solutions in a diamond reactor cell

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Introduction

Oxidation/reduction reactions and coordination structure of the transition elements under hydrothermal conditions are of importance to diverse fields of geochemistry and corrosion. Another area of interest relates to destruction and conversion of mixed and radioactive wastes. These types of reactions under homogenous hydrothermal conditions ($500° > T > 200°$ C) have been previously explored using pre-edge and extended x-ray absorption fine structure [1-3]. However, many systems of interest contain higher concentrations of solutes and are heterogeneous with one or more solid phases in equilibrium with a liquid and a vapor phase. Thermodynamic models are the primary tool to predict speciation at high temperatures [4]. Significantly, even for a simple system containing just Cu oxides and hydroxides, there still remain large uncertainties about the equilibrium species at temperatures just below and above the critical point of water ($375°$ C). For these reasons, we explore the possibility of using a high brilliance x-ray source to obtain *in situ* measurements of oxidation states (from the pre-edge) and coordination structures (from the extended fine structure). We report a new method to collect *in situ* x-ray absorption fine structure (XAFS) spectra on multiphase systems, thus permitting the measurements of kinetics and equilibria for hydrothermal solutions

Methods and Materials

The copper K-edge (8979 eV) XAFS spectra and x-ray transmission images were collected on the insertion device beamline of sector 20 (PNC-CAT) at the Advanced Photon Source (APS), Argonne National Laboratory. A 40 μm pinhole was placed before the I_0 detector. Images were acquired by rastering the cell across this beam and measuring the transmission response. Micro-XANES (x-ray absorption near-edge structure) and XAFS spectra were acquired with the same setup.

The cell design is similar to the ones previously described [1-3] with several important exceptions. The cell uses a static design rather than a flow cell. The solid and liquid compounds are loaded into the sample region under ambient conditions. Subsequently, the x-ray windows are installed, capping the "batch" solution in the cell. The cell is then heated to reaction conditions and the spectra were acquired. For these experiments, Cu compounds were the focus of the investigation. Hence, the cell itself was constructed from a small, pure copper tube having a 2 mm ID and a 3 mm OD. The height of the tube was 2 mm, which was the effective x-ray pathlength. The ends of this tube were highly polished to establish and maintain the seal directly to the single-crystal diamond windows having a thickness of 0.5 mm and a diameter of 3 mm. A compressive force on this assembly was maintained using a series of disk springs in a geometry that has been previously described [1]. This force was required to compensate for the internal force on the window generated from the self-pressurizing sample at elevated temperatures. The cell

tube could be constructed from almost any metal, including more inert materials such as Pt or Au. For these studies our intent was to prevent contamination from other metals that would interfere with the Cu(I,II) equilibria. For example, previous studies of solutions containing $Cu^{II}Br_2$ were found to be extremely corrosive and capable of oxidizing Pt^0.

The starting solution contained the equivalent of 0.2 m CuO (solid), a small amount of finely divided Cu powder, and water. At high temperatures, the Cu^{II} species are reduced through a reaction with the Cu^0. Additionally, pH-buffering mineral compounds could be added to the system. A second experiment was performed in which the starting solution was 0.2 m $Cu^{II}Br_2$ in water. This solution rapidly reacts with Cu^0 to form Cu^IBr that becomes soluble under hydrothermal conditions. In this case, the high-temperature solution ($325°$ C) contains a single liquid phase with dissolved Cu^IBr.

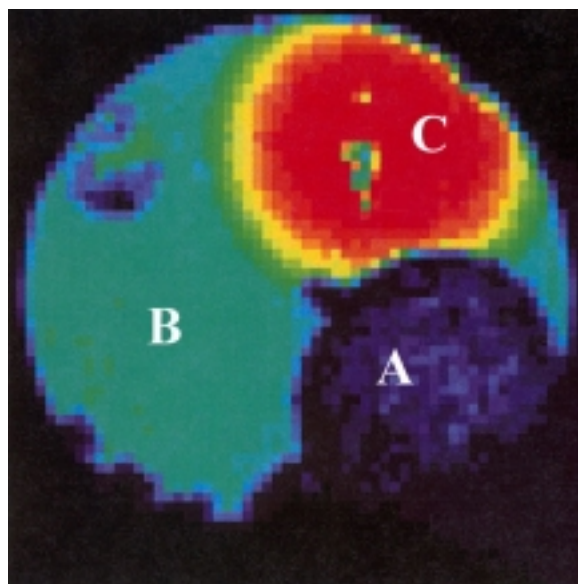Figure 1: X-ray transmission image through the diamond micro-reactor cell at $100°$ C, showing (A) solid region containing copper and copper oxide, (B) liquid phase with dissolved copper species, and (C) vapor phase (bubble). The internal diameter of the cell is 2 mm.

Results

Figures 1 and 2 show x-ray transmission images that were acquired at $100°$ C and $350°$ C, respectively. At $100°$ C, four phases coexist, including (A) solid Cu and solid $Cu^{II}O$, (B) an aqueous phase contains dissolved Cu species, and (C) a vapor phase. The different phase regions are clearly resolved in the transmission image. At $350°$ C, the vapor phase collapses into the liquid phase and we observe only the solid phase and a liquid phase. In addition, the weak adhesion forces that hold the solid

phases together in a spherical mass at 100° C are greatly diminished at 325° C. Thus, the solid phase tends to collapse towards the bottom of the cell in Figure 2. Micro-XANES on the solid and liquid phases demonstrate that at 350° C some of the CuO is slowly being converted to Cu_2O. Also at 350° C, there are copper oxide or copper hydroxide species that start to dissolve in the aqueous phase.
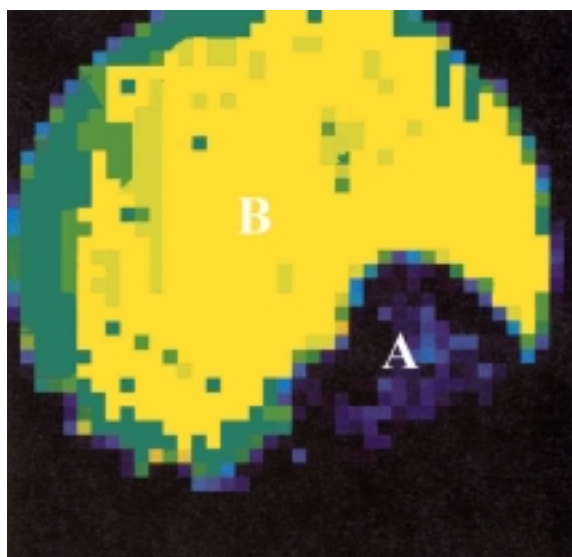

Figure 2: X-ray transmission image through the diamond micro-reactor cell at 350° C showing (A) solid region containing copper and copper oxides, and (B) the liquid phase with dissolved copper species.

The brilliance of the APS undulator source allowed us to acquired high-quality XANES and XAFS spectra from a single 20 minute scan of any particular microregion within the cell using an unfocused, 40 μm diameter beam. Three representative XANES spectra are shown in Figure 3. Spectrum A in Figure 3 was taken of the solid phase shown in the lower right-hand corner of Figure 2. It represents a matrix of Cu^0 powder with Cu_2O (solid). Spectrum B is from the liquid phase in Figure 2, and it shows that there is only a trace amount of a soluble or a surface Cu compound at this position. The spectrum L in Figure 3 was acquired from a different aqueous system that contained a homogeneous solution of Cu^IBr. The strong pre-edge band at 8982 eV is characteristic of Cu^I species. Analysis of Cu and Br XAFS spectra taken of the same solution in this cell is consistent with the single aqueous species, $Br^{-1}-Cu^{+1}-Br^{-1}$, having a linear structure.

It is important to realize that the results presented here do not necessarily represent the equilibrium concentrations. This could be established by testing the reversibility of the equilibrium at high temperature. It is also unrealistic to expect that the technique will be used to explore equilibrium conditions at temperatures much below 200° C since the kinetics for most systems are prohibitively long under these circumstances. This technique could also yield kinetic information if temperatures were selected such that the rates of reaction could be tracked using prominent pre-edge features of some of the transition metals.
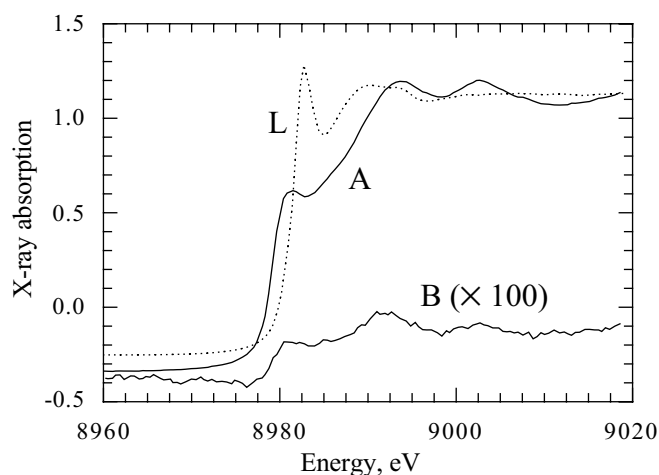

Figure 3: Micro-XANES spectra at 350° C of (A) the solid region shown in Figure 2 containing copper and copper oxides, (B) the liquid region shown in Figure 2, and (L) a liquid phase spectra of a new linear $Br^{-1}-Cu^{+1}-Br^{-1}$ species that was chemically reduced from a starting solution containing aqueous $Cu(II)Br_2$. The diameter of the beam is 40 μm.

Discussion

Multiphase systems that include a liquid and a solid phase are important systems in hydrothermal chemistry. The diamond microreactor cell approach described here allows one to obtain *in situ* information on these complex systems. A brilliant x-ray source enables a series of x-ray analysis methods for characterizing this type of chemistry. The ability to make *in situ* measurements of oxidation states and coordination structure about ions under hydrothermal conditions provides new insights into the thermodynamics and the kinetics of these systems. Studies using this approach may answer some long-standing questions about redox chemistry of hydrothermal systems near and above the critical point of water.

Acknowledgments

References

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