XAFS Fluorescence Measurements of Dilute Hydrothermal Solutions

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Introduction

The hydration and coordination chemistry of ionic species in aqueous solutions at elevated temperatures is an important aspect of homogeneous catalysis, geochemical systems, and corrosion processes. X-ray absorption fine structure (XAFS) spectroscopy provides the details about the first-shell coordination structure around ions at temperatures near the critical point of water (375°C).[1] Often, the species of interest are highly dilute, with concentrations at the millimolar or sub-millimolar level. In these cases, XAFS fluorescence spectroscopy provides the necessary sensitivity for systems of this type. In this report, we describe a fluorescence cell suitable for XAFS measurements on dilute hydrothermal systems. Other approaches have also been recently described.[2,3]

Methods and Materials

The strontium K-edge (16.1 keV) XAFS spectra were collected on the insertion device beamline of sector 20 (PNC-CAT) at the Advanced Photon Source (Argonne National Laboratory). Fluorescence spectra were acquired using a 13-element Ge detector. With this detector located at 20 cm from the sample, approximately 2% of the fluorescence emission is collected from the available solid angle of 40°. The reported high-temperature spectrum represents the average of fifteen, 20-min scans whereas the ambient spectrum is an average of four scans. Figure 1 shows the
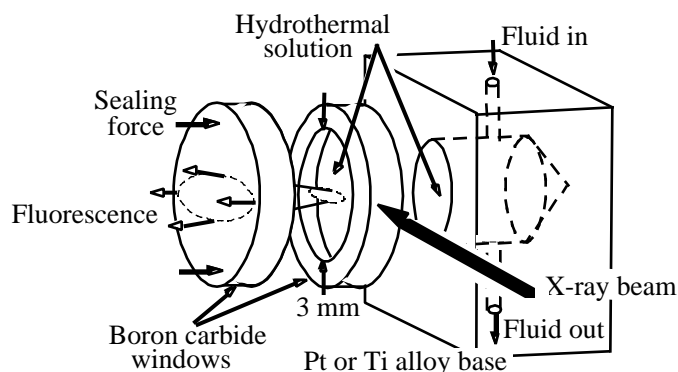

FIG. 1. Schematic of fluorescence cell for high-pressure systems.

90° geometry of the cell, with the x-ray beam entering through the side of a boron carbide ring, and the fluorescence emission exiting through the boron carbide disk. All mating surfaces were optically polished to establish and maintain the seal directly to the boron carbide windows that have a thickness of 1 mm and an outer diameter of 5 mm. A compressive force on this assembly was maintained using a series of disk springs in a geometry that is similar to what has been previously described.[4] This cell has been routinely operated at 350°C and 200 bar. Use of polycrys-

talline diamond components would greatly extend this range. As a further note, it is essential to provide a high degree of temperature uniformity for these hydrothermal solutions in order to obtain high-quality XAFS. Since the compressibility of the solvent is quite high at these temperatures, small thermal fluctuations can lead to appreciable density fluctuations that can significantly perturb the quality of the XAFS spectra. For this reason the cell is fully insulated to minimize thermal radiative losses, and the cell is also placed into a vacuum can to eliminate convective losses.

The primary advantages of this design are (1) the relatively long pathlength (3 mm) for best sensitivity, (2) the use of high-strength, x-ray transparent window materials that are nonreactive with the often aggressive hydrothermal solutions, (3) no Bragg peak interference when using boron carbide windows, (4) a flow-cell configuration wherein a series of samples can be rapidly loaded using a syringe pump, (5) no focusing of the ID beam is required and thus potential beam damage of the sample is minimized, and finally (6) precise pressure measurements can be made with an in-line electronic strain-gage transducer.
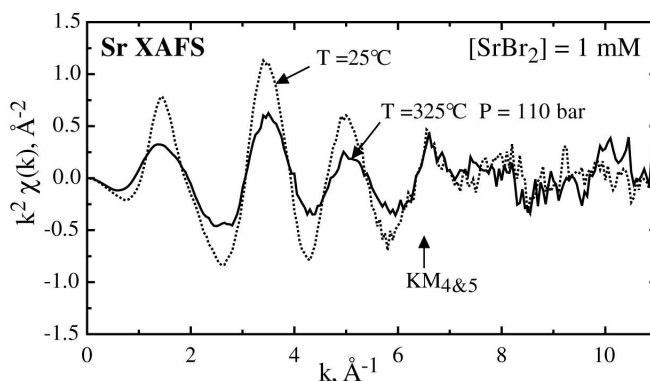

FIG. 2. Sr K-edge XAFS spectra for an ambient solution and a hydrothermal solution at 325° C and 110 bar. Both solutions contain 1 millimolar SrBr₂.

Results

Figure 2 shows the k^2-weighted chi data for two, 1 millimolar SrBr2 solutions. One solution was aquired under ambient conditions and the other at 325°C. The oscillations are due to backscattering from weakly bound waters in the first hydration shell. At the elevated temperature, the large reduction in the amplitude of the oscillations is primarily due to loss of nearly half of the waters in the first shell. The sharp feature at $k = 6.4$ ang^{-1} is a multi-electron excitation for the KM4&5 transition.[5] The contribution from this multielectron excitation is relatively high in comparison to the XAFS component, because the first shell structure is moderately disordered . Thus, the multi-electron excitation must be removed by appropriate methods in order to recover

accurate structural parameters from the XAFS analysis. With this correction, the usable chi data extends to at least k = 9 ang^{-1} to provide good estimates of the distance, Debye-Waller factor, and the anharmonicity. As can be seen by the signal-to-noise ratio in the spectra of Fig. 2, the current cell design allows for collection of good quality XAFS spectra at the millimolar concentrations for this more disordered system. By using a detector that collects a much larger percentage of the available solid angle even lower concentrations could be achieved.

Acknowledgments

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