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Studying *in situ* hydrothermal reactions with X-ray Absorption Spectroscopy

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A complete understanding of the oxidation state and coordination structure of inorganic species under actual hydrothermal conditions is critical to areas such as geochemistry and corrosion science. However, fundamental studies on the chemistry of inorganic aqueous solutions at elevated temperatures are scarce. Such information is also of importance in the treatment of waste slurries, including processes such as drying, calcining and vitrification.

X-ray absorption spectroscopy (XAS) can provide information on bond distances and their strength or covalency, the coordination symmetry around a central atom and its oxidation state.^{1,2} All of these properties are subject to change during chemical changes at hydrothermal conditions. Indeed, in our previous XAS studies we were able to gain valuable information on the solvation environment of electro-

lytes in water at temperatures up to 425°C and to obtain direct evidence of contact ion pairs at high temperatures.³

In this paper we will present the first XAS studies of various inorganic chemical reactions at hydrothermal conditions (subcritical and supercritical). From these studies we obtained *in-situ* information on the hydrolysis, coordination and redox-chemistry at these severe conditions. For example, we studied the chemistry of tungsten in a 0.2 m Na₂WO₄ aqueous solution as a function of initial pH and temperature up to 200°C and 240 bar pressure. The pH of the starting solution was adjusted by addition of nitric acid. A description of the experimental equipment including the high-pressure, high temperature cell has been given in detail elsewhere.⁴

Figure 1 shows the Chi(k) k² plot for four different conditions. At room temperature and pH 8.5, the tungstate is present in solution as monomers.⁵ The corresponding, nearly sinusoidal spectrum in Fig. 1 is from the tetrahedrally coordinated oxygens as the primary backscattering source. Lowering pH,

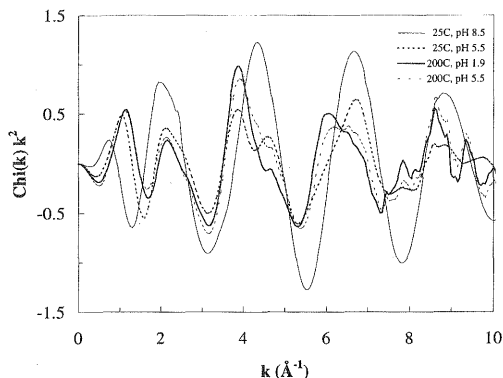


FIG. 1. Weighted Chi plot of a 0.2 m Na₂WO₄ solution at various conditions of temperature and pH (starting pH). The emerging second sinusoidal-like contribution is due to polymerization reactions at lower pH values and higher temperatures.

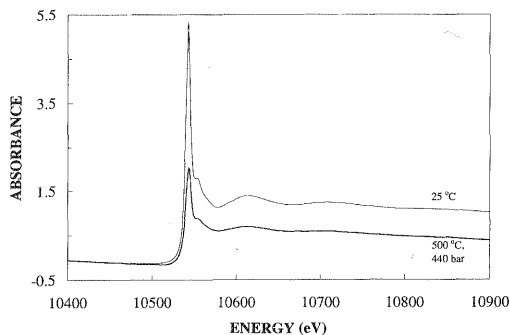


FIG. 2. Rhenium X-ray absorption spectra of NaReO₄ at ambient conditions and at 500°C and 440 bar.

and to a lesser degree raising temperature, causes the formation of tungstate polymer species with shared octahedral edges.⁵ As a result, a second back-scattering contribution from the new tungsten-tungsten proximity becomes increasingly important. Correspondingly, a second sinusoidal-like contribution emerges in Fig. 1. The polymeric species is found to be most prevalent at 200°C and pH 1.9, the most extreme set of conditions we studied for this series of experiments.

Figure 2 shows two rhenium X-ray absorption spectra of a 0.2 m sodium perrhenate solution. This solution was studied as a function of temperature up to 500°C and 440 bar pressure. Even at a pressure of 440 bar, the density is significantly lower than at room temperatures as is evident from the decrease in edge height in Fig. 2. Compared to the tungstate study, spectral changes are less pronounced. We noticed that the E_0 of the rhenium absorption edge increased slightly but steadily with increasing temperature up to 425°C (not shown) but dropped noticeably by about 1.5 eV at 500°C. We will report detailed results on the changes in the ReO_4^- coordination structure under these extreme conditions.

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