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Project Title: **Chemical Speciation of Inorganic Compounds under Hydrothermal Conditions**

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# Chemical Speciation of Inorganic Compounds under Hydrothermal Conditions

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## A. XAFS

By employing XAFS spectroscopy we are seeking a better understanding of the high-temperature aqueous chemistry and speciation of those components that are troublesome to the treatment of the Hanford tank wastes: namely Cr, Re (surrogate for Tc), Fe, Ru (surrogate for Pu), and  $\text{NO}_3^-/\text{NO}_2^-$ . After initial experiments revealed that the high corrosivity of some of these aqueous systems renders the original high-pressure/high-temperature XAFS flow cell unsuitable of these systems, we have quickly implemented a new XAFS flow cell design made from Pt/Ir alloy. Over the last 12 months we have been able to obtain a number of groundbreaking results with this new XAFS cell, which we will briefly highlight.

### 1. Redox chemistry:

Figure 1 shows XANES spectra obtained at 400°C from 0.02 molal aqueous  $\text{Cr}(\text{NO}_3)_3$  solutions with and without 0.06 molal  $\text{NO}_2^-$ . The dominant peak in the spectra is a signature for Cr(VI) as demonstrate by the additional spectrum of solid  $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$ . Hence, at 400°C the aqueous chrome is fully oxidized from Cr(III) to Cr(VI) by  $\text{NO}_3^-/\text{NO}_2^-$  but is only to ~50% oxidized by  $\text{NO}_3^-$  alone. These spectra are to the best of our knowledge *the first reported in situ spectroscopic observation of homogeneous aqueous redox chemistry at temperatures beyond the critical temperature of water (>374°C)*. We also observed a time-dependence for the growth of the Cr(VI) XANES peak and have therefore obtained some kinetic information for this redox system as well.

In other studies we investigated the stability of aqueous  $\text{ReO}_4^-$  to high temperatures (up to 400°C). The  $\text{ReO}_4^-$  was found to maintain the oxidation state VII regardless of a wide range of solution pH.  $\text{ReO}_4^-$  remained stable to 400°C even in the presence of the reducing agent  $\text{NH}_4^+$ .

We have also obtained information on the high-temperatures redox behavior of aqueous  $\text{Cu}^{2+}$ , another tank waste species that is prone to redox chemistry during high temperature processing. We found aqueous solutions of  $\text{CuBr}_2$  to be extremely corrosive. At high temperatures, Cu(II) has a strong tendency to be reduced to Cu(I) by reaction with other metal species. With the new XAFS cell we were able to obtain *in situ* results to 300°C for aqueous solutions of  $\text{CuBr}_2$  that show that the copper is present as Cu(I), most likely reduced by dissolving Pt. High temperature spectra of  $\text{Cu}(\text{NO}_3)_2$  and  $\text{CuBr}_2$  with added  $\text{NH}_4\text{Br}$  were also obtained.

### 2. Oligomerization chemistry

Aqueous solutions of  $\text{CrO}_4^{2-}$  are known to undergo oligomerization reactions upon acidification. Isopolymerates are also formed by the other row VI elements, Mo and W. These kind of polymerization processes are in general very common in aqueous solutions as they apply for the precipitation mechanism of hydroxides and oxides at basic pH conditions.

As the first benchmark experiments we investigated the isopolytungstate system to high temperatures. The EXAFS spectra are very rich in information and show large changes with both temperature and (starting) pH with a dramatic reduction in complexity between 200°C and 300°C. In order to better understand and possibly quantify the observed spectral changes in the EXAFS we have turned to complimentary IR spectroscopic investigations. These IR measurements require a very short optical path length thus a new IR cell was specifically designed and built for this purpose. The combined results strongly indicate that besides the tungstate monomer a second, yet unidentified, species of simple geometry must be present at 300°C and starting pH value < 8. In contrast, recently

acquired XAFS spectra of aqueous chromate solutions to low pH values and high temperatures show little change, indicating that the chromate remains tetrahedrally coordinated with little or no changes in the Cr-O bond distances throughout all investigated experimental conditions. We have also acquired XAFS spectra for the molybdate systems to high temperatures enabling us to compare the high temperature aqueous oligomerization chemistry between the row VI transition elements.

### 3. Future directions

Further work will continue the CrIII/CrVI -- NO<sub>3</sub><sup>-</sup>/NO<sub>2</sub><sup>-</sup> redox investigations. These investigations will include a larger range of temperature conditions with attempts to obtain more refined kinetic information. Our new IR cell will come in handy to monitor the fate of the NO<sub>3</sub><sup>-</sup>/NO<sub>2</sub><sup>-</sup> anions and thereby obtain a complete understanding of this redox system.

So far we have not studied aqueous iron solutions because these systems are multi-phased and presently we are experimentally limited to systems that are homogeneous, i.e., single-phase. However, we plan to slightly modify the new IR cell design allowing us to use this design as a suitable XAFS cell for multi-phased systems including solid, liquid and gas. In particular, we hope to be able to also monitor changes that occur 500°C in solid phases and map out phase equilibria *and* oxidation state by x-ray imaging methods.

Recent improvements at the PNC-CAT beamline of the APS at the Argonne National Laboratory have increased the range of x-ray beam energies to include the high absorption edge Ru. Hence, we are now able to begin studies of aqueous solutions of ruthenium.

### 4. Status

As highlighted above we have obtained a large set of new *in situ* results. The data reduction and analysis is in various processing stages. However, our first results on the tungstate and perrhenate systems have already been presented at the 8<sup>th</sup> annual V. M. Goldschmidt conference, the EMSP conference and X-98 conference both last summer in Chicago, and in article form in Mineralogical Magazine and Chemical Geology (to be published this fall). Our more recent findings will be presented at the upcoming EMSP symposium at the ACS conference in New Orleans as well as at the ICPWS conference in Toronto.

As mentioned in our EMSP proposal we have also attempted to use quartz capillaries as XAFS cell for our measurements. During these attempts we made the unexpected observations that Ni<sup>2+</sup> is absorbed by the capillary at 425°C, most likely to form a nickel silicate. These findings prompted to envisage the use of silica as a new selective sequestering method for aqueous ionic waste streams.

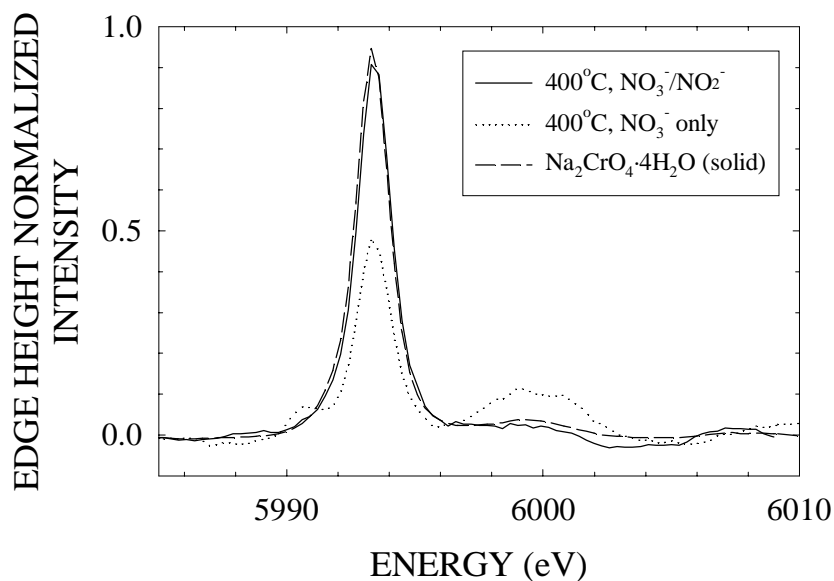


Fig. 1 Comparison of high-temperature Cr solution spectra with solid  $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$ . Time at  $400^\circ\text{C}$  was approximately one hour.

## B. Anomalous Diffuse Elastic X-ray Scattering

This effort has concentrated on building and commissioning the Rowland Circle (RS) x-ray spectrometer for recording the elastic portion of the diffuse scattered x-rays from the water solutions. These measurements will complement the XAFS measurements discussed in Sect. A by adding the pair distribution function of atoms about the ion of interest to larger distances.

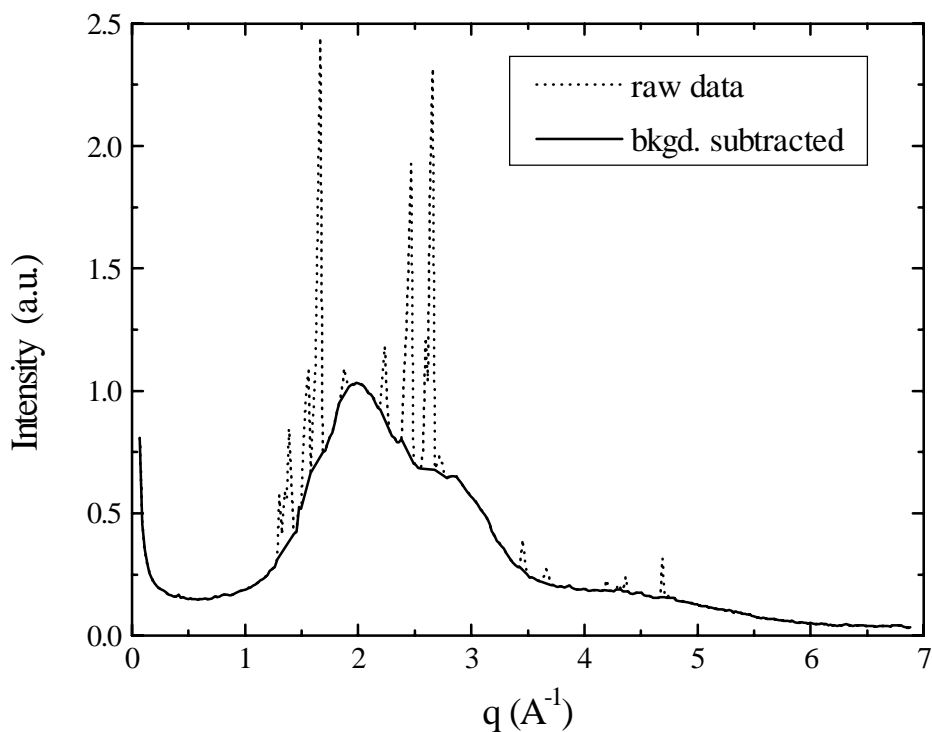
During the last year the apparatus has been constructed and tested successfully. Presently the apparatus is being commissioned to optimize its operation. The tests have shown that the reflected efficiency of the x-rays is about an order of magnitude below the optimum and steps are being made to improve this efficiency. These include slightly damaging the bent silicon single crystal used for focusing to increase its rocking curve width, and minimizing the variations in the thickness of this same crystal to improve its focusing power. Even in its present non-optimum state the RS is still useful for measuring the data required to obtain the radial distribution function about dissolved ions in water.

Anomalous scattering measurements have been performed on Sr ions formed by dissolving strontium bromide in water under ambient conditions. These measurements have been made for the same cell configuration to be used under supercritical conditions. This cell consists of a hollow cylinder of boron carbide (BC) that is sealed to titanium tubing on both ends by a pressure fit. The Ti tubing is then connected to the pressure pump that causes the supercritical solution to flow through the cell. A heater is placed around the cell to produce the required temperature. The anomalous scattering measurements have indicated the need to make further improvements in monitoring and

controlling the alignment of the apparatus to minimize spurious variations. Scattering measurements have also been made on pure water in the cell to investigate the background signal from the cell.

Figure 1 shows the scattering data obtained for pure water in the cell. Note that besides the diffuse scattering from the solution, sharp Bragg peaks coming from the polycrystalline BC cell are also present. Efforts are being made to minimize these sharp peaks, though, because they are so much sharper than the diffuse scattering spectra, it is possible to remove this background reasonably reliably from the fluid signal. The measured signal that is produced by scattering from both the water and the cell is shown by the solid plus dotted plots. The scattering from pure water is shown by the solid line where the sharp Bragg peaks have been subtracted

As implied above, the complete setup for measuring diffuse elastic x-ray scattering from supercritical solutions has been assembled. The cells and their seals have been successfully tested up to the maximum pressure. What remains for the sample containing portion of the apparatus is to test it under supercritical conditions by adding the elevated temperature.



**Fig. 2.** Diffuse elastic scattering from pure water placed in the sample cell to be used for supercritical water solution measurements. Dotted curve, Bragg peaks from cell. Solid curve, the contribution from the water obtained by subtracting the cell contribution.