Environmental Management Science Program

Project ID Number 60050

Chemical Speciation of Inorganic Compounds under Hydrothermal Conditions

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June 1, 1998

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Research Objective

To obtain the chemistry of metallic solute ions under aqueous and hydrothermal conditions in order to obtain key insights pertinent to the removal of toxic wastes. Elements present in Hanford tank wastes will be investigated to get a better understanding of how the high temperatures involved in vitrification will affect the hydrolysis-polymerization reaction.

Research Progress and Implications

In the following summary of our x-ray absorption fine structure (XAFS) measurements under aqueous and hydrothermal conditions, most measurements below the critical temperature (375° C) were taken at about 200 bar pressure, while at supercritical temperatures the pressure was about 600 bar.

Chemistry of Na_2WO_4 Under Aqueous and Hydrothermal Conditions

Tungsten, molybdenum, vanadium and, to a lesser agree, chromium, niobium and tantalum form isopolymetallates, polymeric species of rather complicated structure and complex chemical equilibria, in aqueous solution upon acidification. Except Tantalum, all of these elements are present in the Hanford tank wastes and it is not well understood how the high temperatures involved in vitrification will affect the hydrolysis-polymerization reaction. In March 1998, we launched a series of XAFS experiments to resolve these questions. Measurements were obtained for 0.2 molal tungstate solutions as a function of temperature (to 200° C) and as a function of starting pH. The outcome of these measurements is providing key insights into this chemistry as follows:

1. A change from tetrahedral to octahedral coordination of the oxygen atoms around the tungsten center atom can be detected upon increasing extent of polymerization.
2. At least one new feature shows up in the Fourier Transform of the k-weighted Chi plot (closely related to a radial distribution function) which is unambiguously attributed to a tungsten-tungsten scattering path, only present in the polymeric species.
3. Perhaps most interestingly, the XAFS data indicate a higher extent of polymerization at higher temperatures for a given starting pH.

In order to confirm this finding and to obtain complementary pieces of information, which would assist a thorough analysis of the XAFS data, high temperature, high pressure IR spectra have been acquired for these tungstate solutions. These measurements have been carried out to even an higher temperature of 400° C and, as preliminary result, do confirm the trends observed with the XAFS experiments. These IR measurements will allow a quantitative analysis of the monomer-polymer equilibria since the IR band of the tetragonal monomer is nicely resolved and does not interfere with the resonances of the bands due to polymer species. Each of the resonant frequencies of all resolved tungstate bands shows a temperature dependence, providing further information on the

strengths of the tungsten oxygen bonds. This first detailed structural characterization by XAFS and IR of hydrothermal polymerization of isopolymetallates will allow us to model and predict the colloid chemistry which is of relevance to the early stages of tank waste vitrification.

Future XAFS work will extend the above studies not only to higher temperatures but will also include studies of molybdenum, chromium and vanadium. The studies are planned for our first visit to the Advanced Photon Source of Argonne National Laboratory in August.

Chemistry of NaReO₄ Under Aqueous and Hydrothermal Conditions

The results of ambient temperature/pressure and high temperature/pressure (i.e., hydrothermal) X-ray Absorption Spectroscopy (XAS) measurements on the NaReO₄-H₂O system have also provided significant new information. We are using Re as a surrogate for the radionuclide ⁹⁹Tc, which is typically encountered in nuclear waste streams [Darab]. The Re LIII white line energy (as determined by the maximum in the XAS spectra) for NaReO₄(s) was determined to be 10,544.5 eV while a 0.2m NaReO₄(aq) solution measured at ambient temperature/pressure exhibited a white line energy of 10,542.6 eV—a shift of -1.9 eV in going from a crystalline form to an aqueous solution. Since data points were collected every 0.3 eV, this shift is significant. We do not believe that the Re⁷⁺ species (i.e., ReO₄⁻) is being reduced through a decrease in the formal oxidation state of Re under these conditions, but rather that there are subtle variations occurring in the electronic charge density due to difference in chemistry. For example, the proximity of the Na⁺ cation to the ReO₄⁻ oxo-anion in NaReO₄(s) may certainly be different than that in solution, producing a difference in the charge distribution around the Re central atom.

As the temperature and pressure were increased, there was a systematic increase in the Re LIII white line energy to 10,544.4 eV—within experimental error equal to that for NaReO₄(s) (10,544.5 eV) as well as Re₂O₇(s) (10,544.1 eV). This may indicate a return to a NaReO₄(s)-like environment for hydrothermal solutions of NaReO₄ at 425° C. Alternatively, both crystalline Re₂O₇ and crystalline perhenic acid, HReO₄·⁵/2 H₂O or Re₂O₇·⁵/2 H₂O, contain binuclear Re species: a tetrahedral Re-O complex sharing a corner with an octahedral Re-O complex, i.e., O₃Re-O-ReO₃(H₂O)² [Cotton]. Thus, the shift in white line energy could also represent an approach to Re₂O₇·⁵/2 H₂O-like structures in hydrothermal solutions of NaReO₄ at 425° C. Detailed analyses, once performed, on the EXAFS obtained from these experiments will prove useful in elucidating the change in chemistry as the temperature and pressure are increased.

Finally, upon increasing the temperature from 425° C to 500° C, the Re LIII white line energy dropped significantly to a value of 10,543.2 eV—which is very close to that obtained from ReO₃(s) (10,543.5 eV). Thus, under these conditions, we believe that the Re⁷⁺, which is the most probable oxidation state at 425° C, is reduced to Re⁶⁺ at 500° C. Again, once detailed analyses are performed on the EXAFS obtained from these experiments, additional insight will be gained pertaining to the chemical changes taking place between 425° C and 500° C.

Chemistry of Cu(II) Under Aqueous and Hydrothermal Conditions

Scoping studies of the redox chemistry of Cu(II) were also completed in the spring XAFS runs at the Brookhaven synchrotron. Four different inorganic and organometallic copper compounds were tested at that time. To our surprise most of the redox chemistry was occurring well below 200° C. In addition we discovered that many of the special, high-temperature metal alloys present in the pumping and transfer system and in the XAFS cell itself were very likely reacting with the copper compounds. Thus, for all subsequent runs we will use only Pt-Ir and diamond for all wetted surfaces. The redox chemistry of Cu(II) (and of other ions such as Fe(III) and chromate) remains high on our list for future XAFS studies.

In addition to investigating by XAFS the frequency structure around solutes, we are fabricating instrumentation to measure their structure also with anomalous diffuse elastic x-ray scattering (ADEXS) for x-ray energies near the absorption edge of the solutes. The ADEXS complements the XAFS measurements because they can detect the more spatially smooth contributions to the pair distribution function that XAFS cannot detect. This allows information beyond the first coordination shell that usually is invisible to XAFS. However, this information is at the expense of sensitivity to

dilute solute concentrations that XAFS can detect. The combination of XAFS and ADEXS gives a more complete picture of the chemistry than can be obtained with either alone. The ADEXS measurements will be performed using the undulator A beamline at the PNC-CAT facilities in the Advanced Photon Source, a third-generation synchrotron radiation x-ray source. The elastic portion of the scattered x-rays will be detected by a Rowland circle spectrometer under construction.

References

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Planned Activities

X-ray Scattering

In addition to investigating by XAFS the aqueous structure around solutes, we are fabricating instrumentation to measure their structure also with anomalous diffuse elastic x-ray scattering (ADEXS) for x-ray energies near the absorption edge of the solutes. The ADEXS complements the XAFS measurements because it can detect the more spatially smooth contributions to the pair distribution function that XAFS cannot detect. This allows information beyond the first coordination shell that usually is invisible to XAFS. However, this information is at the expense of sensitivity to dilute solute concentrations that XAFS can detect. The combination of XAFS and ADEXS gives a more complete picture of the chemistry than can be obtained with either alone. The ADEXS measurements will be performed using the undulator A beamline at the PNC-CAT facilities in the Advanced Photon Source, a third-generation synchrotron radiation x-ray source. The elastic portion of the scattered x-rays will be detected by a Rowland circle spectrometer under construction. The ADEXS apparatus will be commissioned in the fall of 1998. The first measurements will be started in January 1999. These and subsequent measurements will be compared with the XAFS analysis on similar solutions from spring of 1999 until August 2000 in order to determine the full pair distribution function about the solutes as function of temperature and pressure in the subcritical and supercritical phases.