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Final Report of Project 60050, ***Chemical Speciation of Inorganic Compounds under Hydrothermal Conditions***

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There has been excellent progress in all task areas of the original proposal during the last 2 ½ years of the project. This progress and productivity is in part due to very talented post-doctoral and graduate students that have been involved in the project at both UW and PNNL. The following brief paragraphs summarize the most significant results after 2 ¼ years of the 3-year project. These significant results are fully documented in peer-reviewed scientific papers that are listed at the end of this section.

We have conducted measurements at 400°C of the oxidation of Cr (III) to Cr (VI) by NO_3^-/NO_2^-. 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 both kinetic information as well as structural information on the reactants and products at the reaction temperature. We feel that these new techniques, when employed on actual waste components will elucidate the underlying chemistry.

Aqueous solutions of CrO_4^{2-} are known to undergo oligomerization reactions upon acidification. Isopolymetalates are also formed by the other row. VI elements, Mo and W. These kinds 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 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 tetrehedrally coordinated with little or no changes in the Cr-O bond distances throughout all investigated experimental conditions. We have also acquired IR spectra for the chromate system to high temperatures enabling us to compare the high temperature aqueous oligomerization chemistry between the row VI transition elements. These results are of high relevance to tank waste chemistry and have immediate applicability to resolving long-standing chemistry issues.

In other studies we investigated the stability of aqueous ReO_4^- (surrogate for Tc compounds) to high temperatures (up to 400°C). The ReO_4^- was found to maintain the oxidation state VII regardless of a wide range of solution pH. ReO_4^- remained stable to 400°C even in the presence of the weak reducing agent NH_4^+. We plan to continue this effort in the next phase using more powerful reducing agents. We have completed some preliminary vapor phase studies of perrhenate and strontium solutions. For the strontium system, we have obtained good quality XAFS fluorescence spectra for a 0.001 m solution of Sr^{2+}. Vapor phase structure and chemistry will be a new area for the next EMSP phase. A major XAFS and DAS

analysis is underway for Sr^{2+} in water for a variety of conditions and concentrations. The goal is to determine the changes in hydration and ion pairing of this salt.

The project has supported the complete construction (finished Nov. 1999) of a device for diffuse anomalous scattering measurements of high temperature solutions at the APS. Measurements of radial distribution functions for high-temperature salt solutions ($SrBr_2$ and $NiBr_2$) are in progress. These types of studies will illuminate the full structure of contact ion pairing and the solvent-separated ion pairing that have an effect on the kinetics and pathways of the inorganic chemistry. This device will also have importance in defining the micro-structure in radionuclides in waste glasses to help access their long-term stability.

We have also obtained information on the high-temperatures redox behavior of aqueous Cu^{2+}, a less common tank waste species that is prone to redox chemistry during high temperature processing. At high temperatures, Cu(II) has a strong tendency to be reduced to Cu(I) by reaction with other metal species. High temperature XAFS spectra of Cu(I) salts have shown the existence of an unusual ion-paired species that loses all waters-of-hydration. MD simulations and density functional theory simulations support the existence of this previously-unknown species.

In addition to the results on inorganic chemistry listed above, part of the effort in the previous phase pertains to development of new analytical techniques for the study of hydrothermal systems. Foremost is the completion of the DAS instrument mentioned above that adds a significant new national capability for materials science issues, many of which are highly relevant to waste remediation and stabilization. In addition, an XAFS cell was developed to handle multi-phase systems. Since many of the tank-

waste mixtures contain solids in equilibrium with saturated liquid phases we developed a new technique to effectively handle these types of systems. The diamond micro-reactor cell has been used to acquire X-ray images and micro-XAFS of systems containing 2 different solid phases in equilibrium with a liquid and vapor phase to 350°C. For acquisition of vibrational spectra we have the two methods of Raman and FT-IR spectroscopy available. We have constructed and successfully used high-temperature FT-IR to 425°C on aqueous systems. Since many of the systems of interest were very dilute, IR offered the high sensitivity required for some of these samples.

Planned activities for the remainder of FY2000 are as follows. A comprehensive study of chromate speciation form XAFS and FT-IR studies at temperatures to 425°C and pH form 1 to 13 will be completed in about 3 months. Anomalous scattering measurement of radial distribution function for the Sr^{2+} and Ni^{2+} systems will be completed by the end of this fiscal year. XAFS studies of vapor-phase Sr^{2+} species will also be completed by the end of the year.

Publications and Presentations from this EMSP project

The following publications and presentation were produced under the currently funded EMSP project.

Publications (published, in press, submitted)

1. "Studying *in situ* Hydrothermal Reactions with X-rays Absorption Spectroscopy". Hoffmann, M. M.; Darab, J. G.; Fulton, J. L.; Stern, E. A., **Mineralogical Magazine,** 62A, 636-637 (1998).

2. "New Experimental Developments for *in situ* XAFS Studies of Chemical Reactions under Hydrothermal Conditions". Hoffmann, M. M.; Darab, J. G.; Heald, S. M.; Yonker, C. R.; Fulton, J. L., **Chemical Geology,** (2000) In press
3. "Short-pathlenght, High-pressure Flow Cell for Static and Time-Resolved Infrared Spectroscopy Suitable for Supercritical Fluid Solutions including Hydrothermal Systems". Hoffmann, M. M.; Addleman, R. S., Fulton, J. L., **Rev. Sci Instruments,,** 71, (2000), In press
4. "XAFS Studies of Aqueous Tungstate and Chrome Solutions at High Temperatures and Pressures", Hoffmann, M. M.; Darab, J. G.; Fulton, J.L., **Proceedings of the 13th International Conference on the Properties of Water and Steam,** Tremaine, P. R., Hill, P. G., Irish, D. E., Balakrishman, P. V., Eds., NRC Press, Ottawa, 2000, In press.
5. "A Transition from a Six – to a Four-Coordinate Ni^{2+} Complex in High-Temperature Aqueous Solutions from X-ray Absorption Spectroscopy", Fulton, J. L.; Darab, J. G.; Hoffman, M. M., **Proceedings of the 13th International Conference on the Properties of Water and Steam,** Tremaine, P. R., Hill, P. G., Irish, D. E., Balakrishman, P. V., Eds., NRC Press, Ottawa, 2000, In press.
6. "Corrosion of Nickel Metal Observed *in situ* in High Temperature Aqueous Sodium Tungstate Solution by IR Spectroscopy", Hoffmann, M. M.; Fulton, J. L.; **Corrosion Journal,** (2000), In press
7. "Imaging and Micro-XAFS of Hydrothermal Solutions in a Diamond Reactor Cell", Fulton, J. L., Hoffman, M. M., Darab, J. G., **APS User Activity Report.** (1999), In press.

8. "In situ XAFS Studies of Redox Chemistry in Hydrothermal Chromium Solutions", Hoffman, M. M., Darab, J. G., Fulton, J. L., **APS User Activity Report,** (1999), In press.
9. "Speciation of Metal Compounds in Heterogeneous Hydrothermal Mixtures using X-ray Imaging and X-ray Absorption Spectroscopy through a Diamond Micro-Reactor Cell", Fulton, J. L., Hoffman, M. M., Darab, J. G., **Chemistry of Materials,** (2000), submitted.
10. "An X-ray Absorption Fine Structure Study of the Structure of Sodium Perrhenate in Aqueous Solutions at High Temperatures", Darab, J. G., Hoffman, M. M., Fulton, J. L., **Chemistry of Materials,** (2000), submitted.

Manuscripts (in preparation)

1. "Copper(I) and Copper(II) Coordination Structure under Hydrothermal Condition at 325°C: An XAFS, and MD Study", Fulton, J. L., Hoffmann, M. M., Darab, J. G., Palmer, B. J., Stern, E. A., **J. Chem. Phys. A,** (2000), In preparation.
2. "Chromate, Bichromate and Dichromate Equilibria to 425°C Measures using X-ray Absorption Fine Structure and Fourier Transform Infrared Spectroscopy." M. M. Hoffman, J. G. Darab, J. L. Fulton, **J. Phys. Chem. A,** (2000), In preparation.

Oral Presentations and Posters

1. (oral) "XAFS and IR Studies of Aqueous Tungstate and Chrome Solutions to High Temperatures and Pressures", 13th International Conference on the Properties of Water and Steam, Toronto, Canada, Sept. 12-16, 1999.

2. (oral) "*In situ* XAFS Studies of Reacting Hydrothermal Solutions that are Relevant to the Treatment of the Hanford Tank Wastes", 218th ACS National Meeting, New Orleans, LA, Aug. 22-26, 1999.
3. (poster) "Changes in the Local Coordination Structure about Ni^{2+}, Cu^{2+}, Sr^{2+}, Rb^{+}, and Br^{-} -Ions Under Hydrothermal Conditions from *in situ* XAFS studies", 218th ACS National Meeting, New Orleans, LA, Aug 22-26, 1999.
4. (poster) "XAFS Studies of Inorganic Reactions in Hydrothermal Systems", EMSP Meeting, Chicago, Aug 22-26, 1999.
5. (oral) "*In situ* XAFS Studies of Chemical Reactions in High-Temperature Aqueous Solutions", PNC-CAT Members' Meeting, Seattle, WA, Mar. 11, 1999.
6. (oral) "Studying *in situ* Hydrothermal Reactions with X-ray Absorption Spectroscopy", V.M. Goldschmidt Conference 1998, Toulouse, France, Aug. 30-Sept. 4, 1998.