**Five digit Project ID number:** 60050
**Project Title: Chemical Speciation of Inorganic Compounds under Hydrothermal Conditions**
**Publication Date**: February 29, 2000
**Lead Principal Investigator:** Edward A. Stern, University of Washington, Department of Physics, Box 351560, Seattle, WA 98195-1560, Phone: (206) 543-2023, email: stern@phys.washington.edu.
**Co-Investigator(s)**: John L. Fulton, Pacific Northwest National Laboratory, P. O. Box 999 MS P8-19, Richland, WA 99352, Phone: (509) 376-7011, email: jl_fulton@pnl.gov.
Gerald Seidler, , University of Washington, Department of Physics, Box 351560, Seattle, WA 98195-1560, Phone: (206) 616-8746, email: seidler@phys.washington.edu.
**Number of graduate students/post-doctorates actively involved in the project**: Total of three, two at UW and one at PNNL.
**Specific DOE problems that are being addressed by this project:**
X-ray spectroscopy of high-temperature solutions is being used to define inorganic hydrothermal reaction chemistries relevant to the treatment of the Hanford tank wastes. The basic science derived from this project will be relevant to a number of different tank-waste remediation areas including calcining, and vitrification.
**Research Objective:**
This project utilizes the high-intensity x-rays available at the Advance Photon Source (APS) to study the inorganic chemistry associated with tank waste vitrification. Although the chemical conversion of waste under high-temperature conditions is an integral part of these processing technologies, there is virtually no information in the published literature about the chemical speciation of inorganic compounds under actual processing conditions. This is primarily due to the lack of techniques that are capable of making in situ measurements of aqueous systems above 300°C. The ongoing x-ray-based studies are identifying the chemical species, oxidation states and ion pairing of inorganic compounds under extreme solvent conditions. It is imperative to make in situ measurements since we have shown that the chemical speciation is strongly dependent on temperature. Several complimentary techniques are being used in this study including x-ray absorption fine structure (XAFS), diffuse anomalous x-ray scattering (DAS) and vibrational (IR & Raman) spectroscopy. Thus, the results of this work are providing information critical to the calcining and vitrification of tank wastes. The results will also have a direct bearing on specific issues such as volatility of Tc (or Re) compounds and the complex chemistry of chromium compounds.
**Research Progress and Implications:**
The following brief paragraphs summarize the most significant results after 2-1/4 years of the 3-year project. 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 kinetic information for this redox system as well. We feel that these new techniques, if employed on actual waste components will elucidate the underlying chemistry.
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 reducing agent $NH_4^+$.
We have also obtained information on the high-temperatures redox behavior of aqueous $Cu^{2+}$, another 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 .
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 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 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 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.

The project has supported the complete construction (finished Nov. 1999) of a device for DAS measurements of high temperature solutions at the APS. Measurements of radial distribution functions for high-temperature salt solutions (SrBr2 and NiBr2) are in progress. These types of studies complement the XAFS results by illuminating the full structure of contact ion pairing that has an effect on the kinetics and pathways of the inorganic chemistry that might be missed by XAFS. This device will also have importance in defining more completely the micro-structure in radionuclides in waste glasses to help access their long-term stability.

**Planned Activities:**

A comprehensive study of chromate speciation from XAFS and FT-IR studies at temperatures to 425°C and pH from 1 to 13, will be completed in about 2 months. Anomalous scattering measurement of radial distribution function for the Sr2+ and Ni2+ systems will be completed by the end of this fiscal year. XAFS studies of vapor-phase Sr2+ species will also be completed by the end of the year.

**List of Publications:**


1. "Studying in situ Hydrothermal Reactions with X-ray 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-pathlength, 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 Ni2+ Complex in High-Temperature Aqueous Solutions from X-ray Absorption Spectroscopy", Fulton, J. L.; Darab, J. G.; Hoffmann, 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. Hoffmann, M. M., Darab, J. G., APS User Activity Report, (1999), In press.
8. "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., Hoffmann, M. M., Darab, J. G., Chemistry of Materials, (2000), submitted.
9. "An X-ray Absorption Fine Structure Study of the Structure of Sodium Perrhenate in Aqueous Solutions at High Temperatures", Darab, J. G., Hoffmann, M. M., Fulton, J. L., Chemistry of Materials, (2000), submitted.