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Project Title: **Fundamental Chemistry and Thermodynamics of Hydrothermal Oxidation Processes**

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RESEARCH OBJECTIVE

The objective of this research program is to provide fundamental scientific information on the physical and chemical properties of solutes in aqueous solutions at high temperatures needed to assess and enhance the applicability of hydrothermal oxidation (HTO) to the remediation of DOE hazardous and mixed wastes. Focus areas for this project include measurements of the solubility and speciation of actinides in model HTO process streams at high temperatures, and the experimental and theoretical development of equations of state for aqueous mixtures under HTO process conditions ranging above the critical temperature of water. A predictive level of understanding of the chemical and physical properties of HTO process streams is being developed through molecular-level simulations of aqueous solutions at high temperatures.

RESEARCH PROGRESS AND IMPLICATIONS

Research in this project has been divided into individual tasks, with each contributing to a unified understanding of HTO processing problems related to the treatment of DOE wastes. This report summarizes progress attained during 2.5 years of this three-year project.

Fluid-Phase PVT Properties and Fluid+Fluid Phase Equilibria. The unique, high pressure vibrating-tube densimeter (VTD) was used to measure the densities of CO_2-N_2-H_2O fluids at 300°C, 8-100 MPa. Sufficient data were collected to tightly constrain the volumetric properties of each aqueous binary subsystem, and for the ternary system. A draft manuscript that presents and describes the volumetric data we obtained for N_2-H_2O mixtures has been prepared for submission to *Contributions to Mineralogy and Petrology*. The VTD was also used to obtain *L-V* data for binary and ternary CO_2-N_2-H_2O fluids from 300 to 350°C. Some of these data are tabulated in the manuscript we have prepared that describes our vibrating-tube technique for locating the *P-T-X* positions of *L-V* phase boundaries in mixed-volatile systems (see below). The remaining data, and additional *L-V* data we plan to acquire in the next few months, will be presented in papers we will write on *L-V* relations in (a) the CO_2-N_2-H_2O system at 300°C, and (b) the CO_2-H_2O and N_2-H_2O systems at 300-367°C.

No published equation of state for CO_2-H_2O mixtures accurately predicts the volumetric properties of these fluids at temperatures between 300 and 400°C. During this past year new types of equations for modeling the thermodynamic mixing properties of mixed volatile fluids were developed and tested. We have discovered that an empirical excess pressure equation accurately represents the excess molar volumes of CO_2-H_2O mixtures at 400°C, 10-400 MPa. We have also found that a modified Lee-Kesler (MLK) equation can be used to represent volumetric properties, using our excess molar volume data for 400°C to evaluate cross-virial coefficients. Excess molar volumes for 10-100 MPa calculated from the resulting expression are as accurate as those obtained from the excess pressure equation described above. The next task in this line of investigation is to assess the ability of the MLK equation to accurately represent the volumetric properties of CO_2-H_2O fluids at 400°C, 0-10 and 100-400 MPa.

Finally, a manuscript describing the vibrating-tube technique for delimiting liquid-vapor fields in mixed-volatile systems at elevated temperatures and pressures has been prepared. The method is highly precise and accurate, and in the article we present the data we have obtained that tightly constrain the *P-X* limits of the *L-V* regions in the CO_2-H_2O and N_2-H_2O systems at 300 and 350°C.

Solubility measurements. Methods were developed to measure conveniently for the first time solubilities of uranium oxide and related carbonates in aqueous solutions at elevated temperatures and to establish spectroscopic techniques to identify the solid uranium-containing phases in equilibrium with the fluid. Our main experiments focused on solubilities in (carbonate + bicarbonate) buffered solutions with and without additional NaCl. Three methods have been applied in these studies. A conventional quenching method, in which (solid + liquid) samples are sealed in fused quartz tubes and equilibrated at elevated temperature

with subsequent quenching to room temperature and analysis of solution, has been used at temperatures to ~150°C. A second method involving continuous monitoring of uranyl species in solution at high temperature by ultraviolet-visible spectrophotometry has also been developed in this program. The key to this method lies in the use of modified commercial micro-scale flow cells that can be thermostated directly in the beam of the spectrophotometer. This setup is expected to permit measurements on aqueous solutions up to 400^0C. High temperature autoclaves equipped with gold bags have also been used. In this method the (solid + liquid) sample is contained within a flexible gold bag in the autoclave, with external pressure applied by adding water to the annulus between the bag and the autoclave. The system is thermostated in a rocking furnace, and filtered liquid samples are withdrawn at intervals for analysis.

Early analysis by X-ray diffraction of the solid phase recovered from equilibrium experiments indicated that the phases produced at the high temperatures were amorphous. This prompted us to choose micro-scale diffuse reflectance Fourier-transform infrared spectroscopy (DR IR) as a primary technique to analyze structures of these solid phases. The possible solid phases are UO_2CO_3 and $Na_4UO_2(CO_3)_3$. It was found that the $Na_4UO_2(CO_3)_3$ solid phase is not stable at 120^0C in carbonate buffer solution. Our experiments indicate that the solubilities of UO_3 and $Na_4UO_2((CO_3))_3$ are governed by the hydrolysis reaction at high temperature (>100^0C). The strong complexation capability of carbonate anion plays little role in this process. Similar observations were made concerning the UO_2CO_3 system. This prompted us to investigate hydrolysis reactions involving uranyl species at elevated temperature. We used factor analysis (FA) and self-modeling (SM) as a new methodology to study uranyl uv-vis absorption spectral variations induced by temperature changes. Information concerning speciation and thermodynamic reaction enthalpy was also obtained. The main results have been published in *Radiochimica Acta*.

The solubility of UO_3(s) in 0.1 M carbonate buffer ($NaHCO_3/Na_2CO_3$) was measured as a function of temperature and ionic strength (as NaCl) from 112 to 149 °C. It was found that the solubility decreased with increasing temperature. DR IR spectra of the solids from high temperature exhibited signals characteristic of polymeric species. This indicates that the solid phase may convert from UO_3 to the polymeric species because of the hydrolysis reaction of uranyl ion at elevated temperature in basic solutions. Our spectroscopic analysis of solid phases indicates that the $Na_4UO_2((CO_3))_3$ solid phase is stable at temperature < 100^0C. The solubility in the 0.1 M buffer solutions decreases with temperature.

Molecular Dynamics Simulation Studies of Aqueous Systems at High Temperatures. Molecular simulation of HCl solutions was initiated, with particular emphasis on the modeling of the hydronium ion. We performed potential of mean force calculations for aqueous HCl solutions, based on the SPC/E model of water and Fornili's model for hydronium ion, toward the calculation of the association constant of HCl at near-critical conditions. We then modified the corresponding molecular dynamics codes to run the above system based on another type of hydronium ion potential model (Kusaka et al.), currently being used for the potential of mean force calculations.

We applied the Chialvo-Cummings solvation formalism to model electrolyte solutions, based on integral equation calculations of simple alkali halides. We tested a regression hypothesis currently used by experimentalists, and interpreted the microscopic mechanism behind its success. A portion of this work is included in a manuscript under submission, and a poster to be presented in the 4th. Liquid Matter Conference (Spain, July 1999).

PLANNED ACTIVITIES

Activities for the remainder of this project will focus on completion of research in progress as described above, and preparation of manuscripts for presentation and publication.

INFORMATION ACCESS: PUBLICATIONS

Blencoe, J. G., Anovitz, L. M. and Seitz, J. C., 1998, A Helmholz Free Energy Model for Supercritical H_2O-CO_2 Mixtures. *Geol. Soc. Amer. Abs. with Prog.*, V. 30, p. A-319.

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Seitz, J. C., Blencoe, J. G., Singh, J., and Anovitz, L. M. 1999, A Vibrating-Tube Technique for Determining the Pressure-Temperature-Composition Limits of Liquid-Vapor Fields in Mixed-Volatile Systems. *Amer. Mineral.*, in internal review.

Singh, J., Blencoe, J. G., and Seitz, J. C., 1998, Experimentally Determined Excess Molar Volumes for H_2O-N_2 Fluids at 300°C, 75-1000 Bars. *Geol. Soc. Amer. Abs. with Prog.*, V. 30, p. A-319.

Singh, J., Blencoe, J. G., and Seitz, J. C., and Anovitz, L. M., 1999, The H_2O-N_2 System: Experimental Determination of Volumetric Properties at 300°C and 75-1000 Bars. *Contrib. Mineral. Petrol.*, in internal review.

Several presentations at conferences and meetings have also been made on this project.