Environmental Management Science Program

Project ID Number 55276

Fundamental Chemistry and Thermodynamics of Hydrothermal Oxidation Processes

Dr. John M. Simonson
Oak Ridge National Laboratory
Chemical and Analytical Sciences Division
Bldg. 4500-S, MS 6110
P.O. Box 2008
Oak Ridge, Tennessee  37831-6110
Phone: 423-574-4962
E-mail: xxs@ornl.gov

Dr. Robert E. Mesmer
Oak Ridge National Laboratory
Chemical and Analytical Sciences Division
Bldg. 4500-S, MS 6110
P.O. Box 2008
Oak Ridge, Tennessee  37831-6110
Phone: 423-574-4958
E-mail: rem@ornl.gov

James G. Blencoe
Oak Ridge National Laboratory
Chemical and Analytical Sciences Division
Bldg. 4500-S, MS 6110
P.O. Box 2008
Oak Ridge, Tennessee  37831-6110
Phone: 423-574-7041
E-mail: blencoejg@ornl.gov

Professor Peter T. Cummings
University of Tennessee
407 Dougherty Hall
Knoxville, Tennessee  37996-2200
Phone: 423-974-0227
E-mail: ptc@utk.edu

Ariel A. Chialvo
University of Tennessee
407 Dougherty Hall
Knoxville, Tennessee  37996-2200
Phone: 423-974-5242
E-mail: achialvo@utk.edu

June 1, 1998
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. Potential limitations to the use of HTO technology include formation of deposits (scale) from precipitation of inorganic solutes in the waste, corrosion arising from formation of strong acids on oxidation of some organic compounds (e.g., chlorinated hydrocarbons), and unknown effects of fluid density and phase behavior at high temperatures. Focus areas for this project include measurements of the solubility and speciation of actinides and surrogates 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. Advances in fundamental understanding of phase behavior, density, and solute speciation at high temperatures and pressures contribute directly to the ultimate applicability of this process for the treatment of DOE hazardous and mixed wastes.

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 after slightly less than two years of this three-year project.

Fluid-Phase PVT Properties and Fluid+Fluid Phase Equilibria. Using a unique, custom-designed, high-pressure vibrating-tube densimeter, we are performing experiments to determine the densities and phase relations of O$_2$-N$_2$-CO$_2$-H$_2$O fluids at 523-773 K and 5-100 MPa. Data from these experiments are now being used to develop accurate new equations of state (EOSs) for H$_2$O-CO$_2$ fluids at 573, 623, and 673 K. The new EOSs are based on fitting “excess pressure” as a function of molar volume. This approach, which differs radically from the usual method of representing excess volume data for mixtures as a function of composition at constant temperature and pressure, allows us to build on the highly accurate equations of state for pure fluids which are currently available, taking advantage of the apparently simple dependence of the excess pressure on composition at constant molar volume of the mixture.

Solubility measurements. A method for determining solubility of solids in aqueous solutions as functions of temperature and pressure involving continuous monitoring of uranyl species in solution at high temperature by UV-visible spectrophotometry was developed in the first year of this program. Experiments on the solubility of uranium(VI) oxide conducted in a {carbonate + bicarbonate} aqueous buffer mixture indicated that the UO$_2$(cr) solid phase was not stable at temperatures above 373 K. In order to test whether the observed solubility behavior was due to the formation of uranyl carbonates,
additional solubility measurements were made on a uranyl carbonate solid. Characterization of the solid phase before and after high-temperature solubility measurements on Na₄UO₂(CO₃)₃(cr) clearly revealed two different solid phases, indicating that this solid is not stable at 393 K in equilibrium with the aqueous medium investigated. Solubility measurements at lower temperatures, where the solid is stable, showed a strong decrease in the solubility with increasing temperature.

Molecular Dynamics Simulation Studies of Aqueous Systems at High Temperatures. Our molecular-based investigation of high-temperature speciation (ion association and hydration) in dilute aqueous solutions has centered on molecular dynamics simulations of model NaCl(aq) solutions to study the behavior of relevant solvation properties within the first hydration shell of ionic species at supercritical conditions. More specifically, we determined the local-solvent density, local pressure, strength of the local electric field, and an estimate of the local dielectric constant along a near-critical isotherm and a supercritical isochore. The simulation work allowed us to characterize the solvational behavior in the vicinity of the ions in solution. There is a clear need for a rigorous formalism to relate macroscopic properties, which may diverge for dilute solutions near the solvent critical point, to the profound microstructural changes of the solvent around the ions and to the compressibility of the solvent. A new, unambiguous statistical mechanical formalism has been developed which details a clear-cut separation between the structural changes associated with the solvation of ions and the coexistent slow-decaying structural correlation.

Planned Activities

Multiple uranyl species are present in solid phases equilibrated with aqueous carbonate buffer solutions at elevated temperatures, and additional emphasis will be placed on characterization of post-experiment solid phases from future runs. Solubility measurements on UO₂(cr) will be extended to higher temperatures, using classical sampling and analysis techniques.

Additional measurements of the densities and phase relations of binary and ternary aqueous mixtures will include O₂ to give data needed to represent the behavior of HTO processes which include excess oxidizer. Further refinement and application of the newly developed representation for the volumetric properties of mixtures will continue as the experimental results are obtained.

Further simulation studies will use this formalism as a basis for the separation of solvation-driven and compressibility-driven contributions to macroscopic thermodynamic properties. Studies are being extended to include acidic (e.g., HCl) and basic (e.g., NaOH) solutes due to their central importance in corrosion of structural materials at high temperatures and pressures.

Other Access To Information