

Fundamental Chemistry and Thermodynamics of Hydrothermal Oxidation Processes

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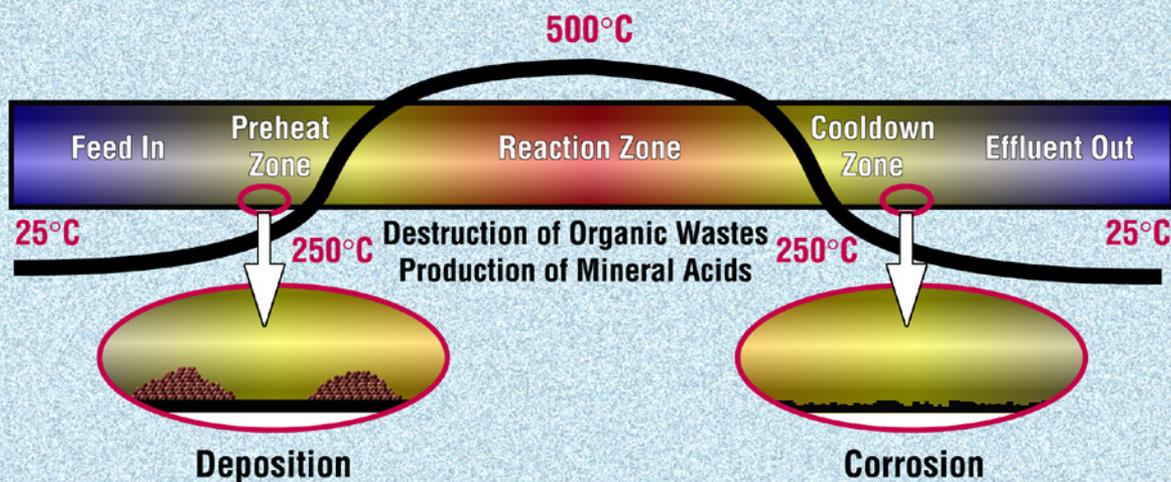
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HTO Processing and DOE Needs

Hydrothermal oxidation (HTO) offers the possibility of treating DOE aqueous hazardous and mixed wastes with minimal environmental consequences. A simplified schematic of the process shows waste being heated to high temperature ($\sim 500^\circ\text{C}$), where hazardous organic compounds are oxidized to CO_2 , H_2O , and other products (e.g., acids and salts). Destruction of organic wastes is efficient and complete, and all process products can be completely contained for later release or reuse, making the process safe from unwanted emissions.

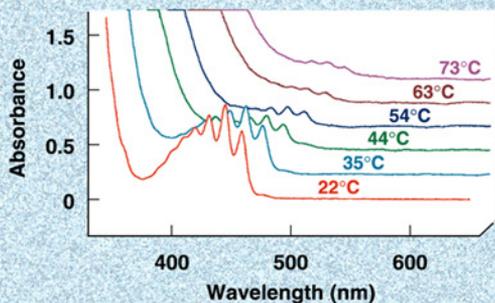


While organic wastes are completely destroyed, inorganic compounds can cause processing problems. Salts or solids in the feed can form deposits, particularly in the system preheating zone, causing restricted flow or plugging in the system. Oxidation of organics containing heteroatoms (e.g., CH_2Cl_2) produces acids which can corrode the system, particularly in the cooldown zone. Fluids may phase-separate in parts of the reaction zone, leading to unstable multiphase-flow conditions.

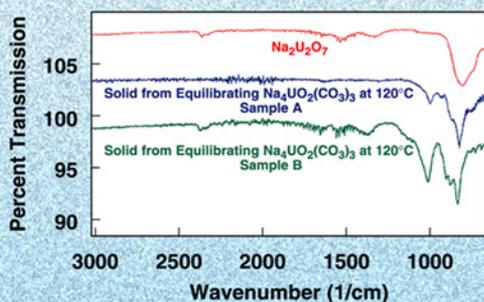
In this program we are addressing these process problems through experimental measurements and model development focusing on inorganic components of DOE aqueous wastes. Solubilities of uranium(VI) compounds are being measured to high temperatures to assess the possibility of scale formation which might contain significant amounts of U(VI). Determining fluid densities and phase relations in the trans-critical region ($300\text{-}500^\circ\text{C}$) leads to better understanding of the behavior of flowing mixtures at high temperatures and pressures. Molecular-dynamics simulations of reactions at high temperature are being performed to gain insight into the molecular-level processes which give rise to observed phenomena, and to help develop process chemistry models valid over the entire range of process conditions. Results from this project should permit better-informed decisions to be made on the application of HTO to DOE hazardous and mixed aqueous waste.

Solubility Measurements

Salts or solid oxides can be present in HTO-treated wastes, or can be created during the process. Our earlier studies on this process⁽¹⁾ focused on the solubility of inorganic bases (acid neutralizers), and indicated that these materials could be useful given appropriate process conditions. The focus in this work has been on the solubility of U(VI) solids, where 'hide out' of solids is a potentially serious problem.



UV-visible spectra of aqueous carbonate solutions equilibrated with $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$ solid at various temperatures.



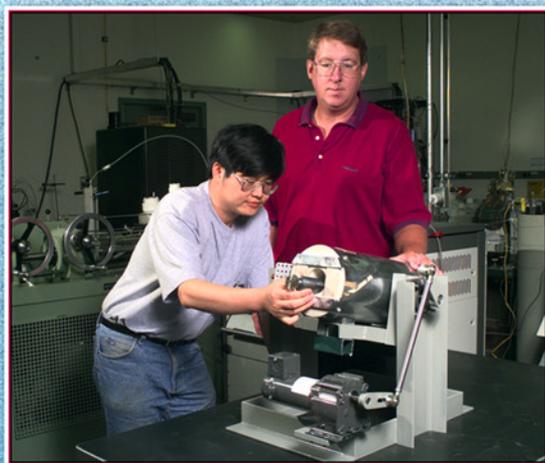
FTIR analysis of solids after 4 weeks equilibration with aqueous carbonate solutions showing decreased intensity of solid-phase carbonate peaks.

References:

(1) Moore, R. C.; Simonson, J. M., Mesmer, R. E. (1997) *J. Chem. Eng. Data* 42, 1078-1081.

(2) Dai, S.; Burleigh, M.; Simonson, J. M.; Mesmer, R. E.; Xue, Z.-L. (1998) *Radiochimica Acta*, in press.

Our early experiments on the solubility of $\text{UO}_3(\text{cr})$ in a {carbonate + bicarbonate} aqueous buffer mixture, involving continuous spectrophotometric monitoring of uranyl carbonates,⁽²⁾ indicated that $\text{UO}_3(\text{cr})$ was not stable at temperatures above 100°C . Additional solubility measurements on $\text{Na}_4\text{UO}_2(\text{CO}_3)_3(\text{cr})$ showed a strong decrease in solubility with increasing temperature, but analyses clearly revealed two different solid phases after extended equilibration at temperatures above 120°C . In addition, the low concentrations of $\text{UO}_2^{2+}(\text{aq})$ at higher temperatures make it impossible to use the spectrophotometric technique. We are currently investigating solubilities of $\text{UO}_3(\text{cr})$ at higher temperatures using batch sampling techniques with ICP analyses of solution concentrations and post-run analyses of solid-phase compositions.



Sheng Dai (left) and Mike Simonson

Fluid-phase PVT Properties and Phase Equilibria

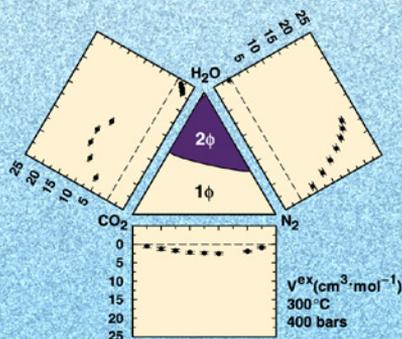
Using a unique, high-pressure vibrating-tube densimeter, we are performing experiments⁽¹⁾ to determine the densities and phase relations of O₂-N₂-CO₂-H₂O fluids at 250–500°C and 50–1000 bars. Data from these experiments are now being used to develop equations of state for fluid mixtures at high temperatures and pressures. These new equations accurately represent "excess pressure" as a function of molar volume V at temperature T and mole fraction x as defined by the relation:

$$P^{ex}(T,V,x) = P(\text{obs}) - n_1 P_1^\circ(T,V) - n_2 P_2^\circ(T,V).$$

This approach, which differs radically from the usual method of representing excess molar 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 observed simple dependence of the excess pressure on composition at constant T and V^(2,3). For the two-component system {H₂O(1) + CO₂(2)} the excess pressure is a simple function of the mole fractions:

$$P^{ex} = x_1 x_2 (x_1 W_2 + x_2 W_1).$$

Representation of the parameters W₁ and W₂ as functions of temperature and volume will lead to new equations of state for aqueous mixtures with the high accuracy needed to predict fluid properties under HTO process conditions.



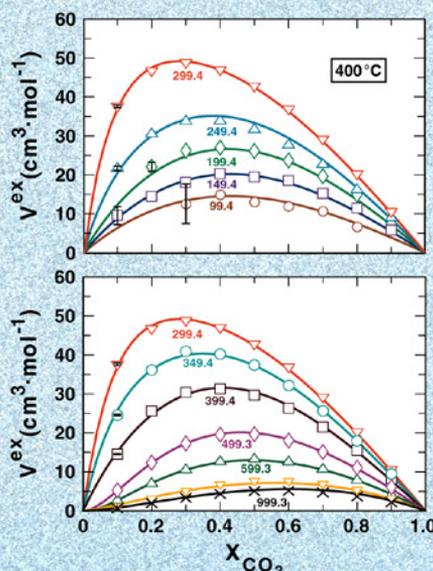
Phase relations in {H₂O + CO₂ + N₂} mixtures at 300°C, 400 bars.

References:

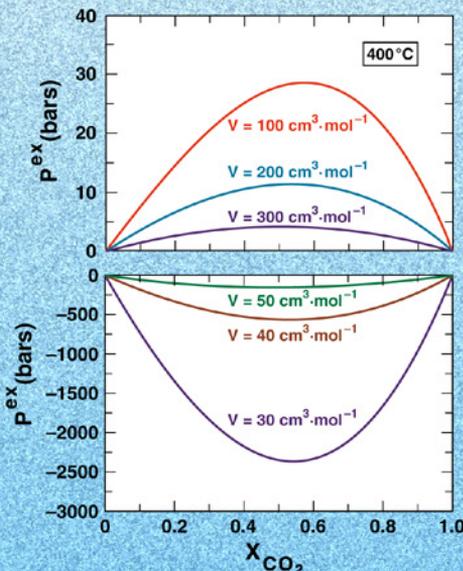
- (1) Seitz, J. C.; Blencoe, J. G. (1998) *Geochim. Cosmochim. Acta*, accepted for publication.
- (2) Blencoe, J. G.; Seitz, J. C. (1998) *Geochim. Cosmochim. Acta*, accepted for publication.
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Jim Blencoe and Jeff Seitz prepare pumps for density measurements.



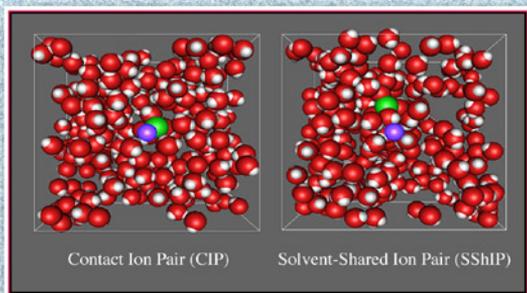
Excess molar volumes in {H₂O + CO₂} mixtures at 400°C.



Excess pressures calculated from volumetric data at 400°C.

Molecular Dynamics Simulation Studies 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.



Ion pair and solvation structures in near-critical NaCl(aq)

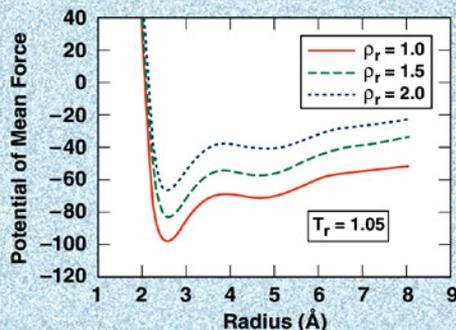
A new, unambiguous statistical mechanical formalism has been developed which details a clear-cut separation between the structural changes associated with the solvation of ions and the coexistent slow-decaying structural correlation.⁽³⁾ It is expected that this new formalism will provide the basis for development of more reliable semiempirical models of solution properties spanning the critical region.

References:

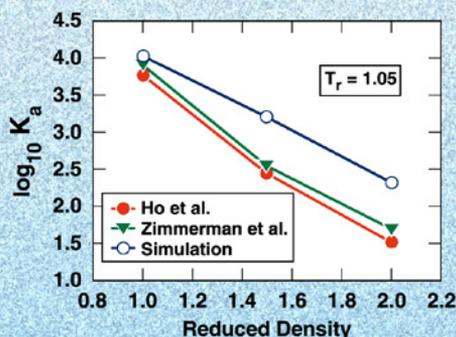
(1) Chialvo, A. A.; Cummings, P. T.; Simonson, J. M.; Mesmer, R. E. *Fluid Phase Equilibria*, in press (1998).

(2) Chialvo, A. A.; Cummings, P. T.; Simonson, J. M.; Mesmer, R. E. *J. Chem. Phys.*, submitted for publication (1998).

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From potentials of mean force calculated for pairs of ions in SPC water at high temperatures⁽¹⁾ (above), we determined the extent and type of ion-pair formation. The simulation work gives reasonably good agreement with experimental values (below), as well as a molecular-scale picture of solvent behavior in the vicinity of the ions in solution.⁽²⁾



Ariel Chialvo (left) and Peter Cummings