
1:30 PM-5:00 PM Javits Convention Center -- 1A15/1A16

Environmental Management Science Program on Nuclear Waste Management
Modeling and Waste Treatment Chemistries

Presiding: P. Wang

Organizer: Tiffany Zachry

- 1:30 PM Introductory Remarks
- 1:40 PM 101 Modeling the chemistry in high-level waste tanks: Effects of radiation and heat on waste simulants
Donald M. Camaioni, Michel Dupuis, Tom Autrey, Wendy J. Shaw, Dan Meisel, Ian Carmichael,
Daniel M. Chipman, Gordon L. Hug, John Bentley
- 2:00 PM 102 Modified associate species thermochemical model of high-level nuclear waste glass compositions
Theodore M. Besmann, Nagraj Kulkarni, Karl E. Spear, J. D. Vienna
- 2:20 PM 103 Increasing safety of aging high-level radioactive waste storage tanks
Eric D. Steffler, Frank A. McClintock, Richard L. Williamson, Wilson R. Lloyd, John H. Jackson
- 2:40 PM 104 Development of an aqueous thermodynamic model for the Tc(IV) - Na⁺ - OH⁻ - H₂O - gluconate
system under basic conditions: Implications for HLW pretreatment at the Hanford Site
Nancy J. Hess, Y. X. Xia, Andrew R. Felmy
- 3:00 PM Intermission
- 3:25 PM 105 Behavior of technetium in alkaline solution: Identification of nonpertechnetate species in Hanford
waste tanks
Wayne W. Lukens Jr., David K. Shuh, Norm C. Schroeder, Kenneth R. Ashley
- 3:45 PM 106 Precipitation of aluminum containing species in tank wastes
Shas V. Mattigod, D.T. Hobbs, Kent E. Parker, David E. McCready, Li-Qiong Wang
- 4:05 PM 107 Speciation, dissolution, and redox reactions of chromium relevant to pretreatment and separation
of high-level wastes
Dhanpat Rai, Linfeng Rao, Sue B. Clark, Nancy J. Hess
- 4:25 PM 108 Actinides in Hanford tank waste simulants: chemistry of selected species in oxidizing alkaline
solutions
Kenneth L. Nash, Ivan Laszak, Marian Borkowski, Melissa Hancock, Linfeng Rao, Wendy A.
Reed
- 4:45 PM Concluding Remarks

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Modeling and Waste Treatment Chemistries

ABSTRACTS

NUCL 101 [657121]: Modeling the chemistry in high-level waste tanks: Effects of radiation and heat on waste simulants

Donald M. Camaioni¹, Michel Dupuis¹, Tom Autrey¹, Wendy J. Shaw¹, Dan Meisel², Ian Carmichael², Daniel M. Chipman², Gordon L. Hug², and John Bentley². (1) Chemical Sciences Division, Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, donald.camaioni@pnl.gov, (2) Radiation Laboratory, University of Notre Dame

Abstract

This report summarizes our research to develop quantitative and predictive understanding of the chemistry that is induced by radiation and heat in high-level waste (HLW) and computational capabilities to model that chemistry. The effort is meant to assist in establishing technical baseline knowledge required to make decisions on issues as they arise. We focus on complexants, which are ubiquitous in the waste and relevant to many issues concerning waste storage and site cleanup activities. Results to be presented include: a) elucidation of the mechanism for oxidation of complexants by NO₂ inferred from rate determinations, product studies, and electronic structure calculations, b) new insights on the role of aluminum ions in catalyzing the thermal oxidation of complexants by NO₂, c) advances in solvation models for calculating solution properties of oxoanions and radicals at the high ionic strength prevailing in HLW, d) measurement of thermochemical properties of key intermediates (e.g., E(NO_x⁻/NO_x²⁻) and D_fG and D_fH of radicals in water) using the techniques of pulsed radiolysis and pulsed photoacoustic calorimetry, and e) effects of particles on radiolytic production of H₂.

NUCL 102 [649757]: Modified associate species thermochemical model of high-level nuclear waste glass compositions

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Abstract

High-level nuclear waste glass compositions are complex mixtures of several metal oxide glass constituents that are designed to contain a large number of waste species. Although glass is a metastable material, it can be successfully thermochemically modeled as a supercooled liquid. Such a pseudo-equilibrium model has been developed using the associate species approach, which is a simple means for relatively accurately representing the thermochemistry of the liquid phase. The technique utilizes the assumption that the liquid is an ideal solution of liquid end member and compound species. A modification of the methodology is required when two immiscible liquids are present, thus requiring a positive interaction energy to be included in the representation.

NUCL 103 [657433]: Increasing safety of aging high-level radioactive waste storage tanks

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Abstract

Degradation of aging high-level radioactive waste (HLW) storage tanks due to cracking is a serious problem. Present fracture mechanics analyses assume small ductility and have limited applicability to these tanks. This research program addresses this limitation by combining slip line fracture mechanics (SLFM, a ductile fracture analysis approach) with fully plastic, 3-D finite element analyses to predict growth of part-through surface cracks to, and past, the point of penetration. An extensive experimental program supports the development. The sudden transition of stable ductile crack growth to unstable cleavage fracture, including event probability, is also examined. Developed capabilities will provide the basis for a reliable predictive model of fracture in HLW storage tanks across the DOE complex, but will also be applicable to spent nuclear fuel canisters, natural gas pipelines, and other safety-critical engineered structures. Experimental, numerical and analytical results are presented along with a roadmap of programmatic direction.

NUCL 104 [657348]: Development of an aqueous thermodynamic model for the Tc(IV) - Na⁺ - OH⁻ - H₂O - gluconate system under basic conditions: Implications for HLW pretreatment at the Hanford Site

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Abstract

The solubility of TcO₂·nH₂O(am) was measured over the pH range of 3 to 2M NaOH and in the absence and in the presence of 0.01 to 0.5 M gluconate. The presence of 0.01 M gluconate results in increased solution concentrations of reduced Tc species of nearly two orders of magnitude relative to measured Tc concentrations in the absence of gluconate throughout the pH range investigated. An aqueous thermodynamic model for the Tc(IV) - Na⁺ - OH⁻ - H₂O - gluconate system is developed based on these solubility experiments, spectrophotometric measurements, and XRD data. These experimental results are compared to the Th(IV) - Na⁺ - OH⁻ - NO₃⁻ - H₂O - gluconate system and the possible implications for pretreatment strategies of HLW at the Hanford Site is discussed.

NUCL 105 [653865]: Behavior of technetium in alkaline solution: Identification of nonpertechnetate species in Hanford waste tanks

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Abstract

Technetium is a long-lived (⁹⁹Tc: 213,000 year half-life) fission product found in nuclear waste and is one of the important isotopes of environmental concern. The known chemistry of technetium suggests that it should be found as pertechnetate, TcO₄⁻, in the extremely basic environment of the nuclear waste tanks at the Hanford site. However, other chemical forms of technetium are present in significant amounts in certain tanks, and these non-pertechnetate species complicate the treatment of the waste. The only spectroscopic characterization of these non-pertechnetate species is XANES spectra of actual tank waste. To better understand the behavior of technetium under these conditions, we have investigated the reduction of pertechnetate in highly alkaline solution in the presence of compounds found in high-level waste. These results and the XAFS spectra of these species are compared to the chemical behavior and XANES spectra of the actual non-pertechnetate species. The identity of the nonpertechnetate species is surprising.

NUCL 106 [654521]: Precipitation of aluminum containing species in tank wastes

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Abstract

Aluminosilicate deposit buildup experienced during the tank waste volume -reduction process at the Savannah River Site (SRS) required an evaporator to be shut down. Studies were conducted to, identify the insoluble aluminosilicate phase(s), characterize the chemistry, and determine the kinetics of the phase formation and transformation of such aluminosilicate phases. The data from tests conducted at 80°C revealed relatively rapid formation of sodalite and cancrinite. Although minor amounts of zeolite A were initially detected in some cases, rapid transformation of this phase into more stable phases were observed. Higher hydroxide concentrations appeared to initiate kinetically fast crystallization of sodalite and cancrinite. More recent testing at SRS has shown similar trends in the formation of aluminosilicate phases.

NUCL 107 [655943]: Speciation, dissolution, and redox reactions of chromium relevant to pretreatment and separation of high-level wastes

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Abstract

The objective of this project is to obtain fundamental data necessary to develop pretreatment processes for removing Cr from high-level waste sludges that are highly alkaline and contain multiple concentrated electrolytes. We are determining 1) the solubility of important Cr solid phases and aqueous speciation in a wide range of hydroxide and phosphate concentrations, 2) the effect of pH, temperature, and aging on the nature of Cr solid phases and aqueous speciation, and 3) the effect of the nature of Cr solid phases and aqueous speciation on their redox reactivity. A combination of thermodynamic and spectroscopic analyses is being used to characterize solid and aqueous species. The results on the development of a comprehensive thermodynamic model for the solubility of Cr(OH)₃(am) in the Cr(III)-Na⁺-H⁺-OH⁻-PO₄³⁻-H₂O system applicable to the HLW conditions along with the role aqueous speciation plays in oxidative dissolution of Cr(OH)₃(am) will be presented.

NUCL 108 [656445]: Actinides in Hanford tank waste simulants: chemistry of selected species in oxidizing alkaline solutions

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Abstract

To enhance removal of selected troublesome nonradioactive matrix elements (P, Cr, Al, S) from the sludges in radioactive waste tanks at the Hanford site, various chemical washing procedures have been evaluated. It is intended that leaching should leave the actinides in the residual sludge phase for direct vitrification. Oxidative treatment with strongly alkaline solutions has emerged as the best approach to accomplishing this feat. However, because the most important actinide ions in the sludge can exist in multiple oxidation states, it is conceivable that changes in actinide oxidation state speciation could interfere with hopes and plans for actinide insolubility. In this presentation, we discuss both the impact of oxidative alkaline leachants on actinide oxidation state speciation, and the chemistry of oxidized actinide species in the solution phase. Actinide oxidation does occur during leaching, but solubility behavior is complex. Mixed ligand complexes may dominate solution phase speciation of actinides under some circumstances. This work was supported by the U.S. Department of Energy, Offices of Science and Waste Management, Environmental Management Science Program under Contract.DE-AC03-76SF0098 at Lawrence Berkeley National Laboratory and Contract W-31-109-ENG-38 at Argonne National Laboratory.