

**ENVIRONMENTAL AND WASTE MANAGEMENT:
ADVANCES THROUGH THE ENVIRONMENTAL
MANAGEMENT SCIENCE PROGRAM**

Separation, Sorption and Solution Chemistry

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Organizers: T. Zachry

Presiding: R. Hirsch

Time	Paper
8:30 a.m.	Introductory Remarks.
8:35 a.m.	Solvent extraction of sodium hydroxide using alkylphenols and fluorinated alcohols: Understanding the extraction mechanism by equilibrium modeling. <u>H.-A. Kang</u> , N.L. Engle, P.V. Bonnesen, L.H. Delmau, T.J. Haverlock and B.A. Moyer
8:55 a.m.	Structure and aqueous solubility of sodium isosaccharinic acid. <u>R.P. Bontchey</u> , R. Moore, M.D. Tucker and K. Holt
9:15 a.m.	Materials for Electroactive Ion-Exchange (EaIX) separations of pertechnetate ion. T.L. Hubler, <u>M. Stender</u> , W.H. Smyrl and M. Alhoshan
9:35 a.m.	Aqueous biphasic systems based on salting-out polyethylene glycol or ionic liquid solutions: Strategies for actinide or fission product separations. <u>R.D. Rogers</u> , K.E. Gutowski, S.T. Griffin and J.D. Holbrey
9:55 a.m.	Combined utilization of neutral crown ether and cation exchanger for volume reduction of alkaline tank waste by separation of sodium salts. <u>T.G. Levitskaia</u> , G.J. Lumetta and B.A. Moyer
10:15 a.m.	Intermission.

- 10:35 a.m. **Chemical speciation of Am, Cm and Eu with EDTA at high ionic strength.** K. Cernochova, J. Mathur and G.R. Choppin
- 10:55 a.m. **Influence of calcite solids and dissolved calcium on U(VI) sorption and desorption in Hanford subsurface sediments.** W. Dong, W.P. Ball, A.T. Stone, J. Bai, C. Liu and Z. Wang
- 11:15 a.m. **Influence of microscopic diffusive process on uranyl precipitation and dissolution in subsurface sediments at Hanford Site, USA.** C. Liu, J.M. Zachara, J.P. McKinley, Z. Wang and P. Majors
- 11:35 a.m. **Recovery and detection of uranium (VI) from building materials.** P.A. Greene, C.L. Copper, D. Berv, J.D. Ramsey and G.E. Collins
- 11:55 a.m. Concluding Remarks.

ABSTRACTS

Solvent extraction of sodium hydroxide using alkylphenols and fluorinated alcohols: Understanding the extraction mechanism by equilibrium modeling. Hyun-Ah Kang, Nancy L. Engle, Peter V. Bonnesen, Lætitia H. Delmau, Tamara J. Haverlock and Bruce A. Moyer; Chemical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, MS-6119, Oak Ridge, TN 37831-6119, Fax: 865-574-4939, kangh1@ornl.gov.

In the present work, it has been the aim to examine extraction efficiencies of nine proton-ionizable alcohols (HAs) in 1-octanol and to identify both the controlling equilibria and predominant species involved in the extraction process within a thermochemical model. Distribution ratios for sodium (D_{Na}) extraction were measured as a function of organic-phase HA and aqueous-phase NaOH molarity at 25 °C. Extraction efficiency follows the expected order of acidity of the HAs, 4-(*tert*-octyl) phenol (HA 1a) and 4-*n*-octyl-*a,a*-bis-(trifluoromethyl)benzyl alcohol (HA 2a) being the most efficient extractants among the compounds tested. By use of the equilibrium-modeling program SXLSQI, a model for the extraction of NaOH has been advanced based on an ion-pair extraction by the diluent to give organic-phase Na^+OH^- and corresponding free ions and cation exchange by the weak acids to form monomeric organic-phase Na^+A^- and corresponding free organic-phase ions.

Structure and aqueous solubility of sodium isosaccharinic acid. Ranko P. Bontchev, Robert Moore, Mark D. Tucker and Kathleen Holt; Sandia National Laboratories, P.O. Box 5800, MS 0779, Albuquerque, NM 87185-0779, Fax: 505-844-2348, rpbontc@sandia.gov.

It has been recently shown that isosaccharinic acid, C₆H₁₂O₆ (ISA), and its derivative salts have a great potential for practical application in the area of nuclear waste treatment and disposal sites' management. Several studies demonstrated the effect of ISA complexation on radionuclide solubility and sorptive properties, especially on actinides in (+4) oxidation state like Np(IV) and Th(IV). The presence of ISA and/or its derivatives strongly affects the migration of radionuclides by increasing their solubility in water by several orders of magnitude and Na-ISA has been proposed as a component of decontamination formulations for actinide-contaminated surfaces. Here we report the synthesis, crystal's structure and characterization (FTIR, TGA) of sodium isosaccharate, NaC₆H₁₁O₆•H₂O (Na-ISA). The structure has been solved by single crystal X-ray diffraction methods. The solubility of Na-ISA has been evaluated and compared to that of Ca-ISA based on the structural features of both compounds.

Materials for Electroactive Ion-Exchange (EaIX) separations of pertechnetate ion.

Timothy L. Hubler¹, Matthias Stender¹, William H. Smyrl² and Mansour Alhoshan²; ¹Pacific NW National Laboratory, P.O. Box 999, MS K8-93, Richland, WA 99352, Fax: 509-376-5106, tim.hubler@pnl.gov, matthias.stender@pnl.gov; ²Department of Chemical Engineering and Materials Science, University of Minnesota.

Many contaminants of interest to the U.S. Department of Energy (DOE) exist as anions (e.g. chromate, pertechnetate and nitrate). The objective of this study is to develop Electroactive Ion-Exchange (EaIX) materials. Such materials can be used to separate pertechnetate ion from radioactive wastes located at DOE sites while limiting the amount of secondary wastes generated. We have developed a synthetic strategy to prepare vinyl-bipyridyl and -terpyridyl ligands which allow incorporation of ion-selective architectures with a polymerizable handle. Fe complexes formed with these ligands provide the working core of the electroactive polymers. The polymers can be directly used as materials for EaIX or they can be incorporated into porous composite materials that are then used for EaIX.

Aqueous biphasic systems based on salting-out polyethylene glycol or ionic liquid solutions: Strategies for actinide or fission product separations. Robin D. Rogers,

Keith E. Gutowski, Scott T. Griffin and John D. Holbrey; Department of Chemistry and Center for Green Manufacturing, The University of Alabama, Box 870336, Tuscaloosa, AL 35487, Fax: 205-348-0823, RDRogers@bama.ua.edu.

Aqueous biphasic systems can be formed by salting-out (with kosmotropic, water-structuring salts) water soluble polymers (e.g., polyethylene glycol) or aqueous solutions of a wide range of hydrophilic ionic liquids based on imidazolium, pyridinium,

phosphonium and ammonium cations. The use of these novel liquid/liquid biphasic systems for separation of actinides or other fission products associated with nuclear wastes (e.g., pertechnetate salts) has been demonstrated and will be described in this presentation.

Combined utilization of neutral crown ether and cation exchanger for volume reduction of alkaline tank waste by separation of sodium salts. Tatiana G. Levitskaia¹, Gregg J. Lumetta¹ and B. A. Moyer²; ¹Radiochemical Processing Laboratory, Pacific Northwest National Laboratory, Richland, WA 99352, Fax: 509-373-9675, tatiana.levitskaia@pnl.gov; ²Chemical Sciences Division, Oak Ridge National Laboratory.

In this report, novel approaches to the selective liquid-liquid extraction separation of sodium hydroxide and sodium nitrate from high-level alkaline tank waste will be discussed. Sodium hydroxide can be successfully separated from alkaline tank-waste supernatants by weakly acidic lipophilic hydroxy compounds *via* a cation-exchange mechanism referred to as pseudo hydroxide extraction. In a multi-cycle process, as sodium hydroxide in the aqueous phase becomes depleted, it is helpful to have a neutral sodium receptor in the extraction system to exploit the high nitrate concentration in the waste solution to promote sodium removal by an ion-pair extraction process. Simultaneous utilization of an ionizable organic hydroxy compound and a neutral extractant (crown ether) in an organic phase results in the synergistic enhancement of ion exchange and improved separation selectivity due to the receptor's strong and selective sodium binding. Moreover, combination of the hydroxy compound and the crown ether provides for mutually increased solubility, even in a non-polar organic solvent. Accordingly, application of Isopar® L, a kerosene-like alkane solvent, becomes feasible. This investigation involves examination of such dual-mechanism extraction phases for sodium extraction from simulated and actual salt cake waste solutions. Sodium salts can be regenerated upon the contact of the loaded extraction phases with water. Finally, conditions of potential extraction/strip cycling will be discussed.

Chemical speciation of Am, Cm and Eu with EDTA at high ionic strength. Katerina Cernochova, Jagdish Mathur and Gregory R. Choppin; Department of Chemistry, Florida State University, Tallahassee, FL 32306-4390, Fax: 850-644-8281, choppin@chem.fsu.edu.

The solubility of the actinides in the high level waste tank solutions is enhanced by complexation of these metal ions with one or more of the organic components of the waste (e.g. EDTA, NTA, etc.). The complexation of Am³⁺, Cm³⁺ and Eu³⁺ with EDTA has been studied at an ionic strength of 5.0 M (NaClO₄) and pH 3.60 in the temperature range of 0 to 60°C by the solvent extraction technique using di-2-(ethylhexyl)phosphoric acid in heptane as the extractant. Stability constant values (log K) between 15 to 16 were obtained, which increased with increasing temperature. The complexation enthalpies have been obtained from the temperature dependence of the stability constants. The nature of the species of the Eu³⁺-EDTA complex formed in these

solutions was determined by time-resolved laser fluorescence spectroscopy and lifetime measurements. Between pcH 3.60 and 7.0 the species formed was $\text{EuEDTA}(\text{H}_2\text{O})_3^-$ whereas at a pcH of 9.0 it was $\text{Eu}(\text{OH})\text{EDTA}(\text{H}_2\text{O})_2^{2-}$.

This research was supported by an USDOE – EMSP contract.

Influence of calcite solids and dissolved calcium on U(VI) sorption and desorption in Hanford subsurface sediments. Wenming Dong¹, William P. Ball¹, Alan T. Stone¹, Jing Bai¹, Chongxuan Liu² and Zheming Wang²; ¹Department of Geography and Environmental Engineering, Johns Hopkins University, 3400 North Charles Street, Ames Hall 313, Baltimore, MD 21218, Fax: 410-516-8996, wenming@jhu.edu; ²Environmental Dynamics and Simulations, Pacific Northwest National Laboratory.

We have investigated U(VI) sorption and desorption with batch experiments conducted on core samples from the Hanford, WA, site as well as on sub-fractions of these materials and laboratory-grade calcite. In these studies, [U(VI)] was varied between 10^{-7} and 10^{-5} and pH between 7.2 to 10, at constant I (=0.05) and constant P_{CO_2} ($10^{-3.5}$ atm), using water that was saturated with respect to calcite. A carbonate-free (acetic-acid-treated) fraction of silt/clay material showed higher sorption than untreated material, suggesting that carbonates block access to higher affinity sites. Of particular interest was that U(VI) sorption on untreated material was maximum at pH=8.4, with substantially less sorption at lower and higher pH and in contrast to results from calcite-free studies, which show strong sorption at pH ~ 5 to 8. U(VI) speciation results suggest that aqueous-phase $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ was the source of the otherwise unexpectedly low sorption at pH <8.4.

Influence of microscopic diffusive process on uranyl precipitation and dissolution in subsurface sediments at Hanford Site, USA. Chongxuan Liu¹, John M. Zachara¹, James P. McKinley², Zheming Wang¹ and Paul Majors¹; ¹Environmental Molecular Science Laboratory, Pacific Northwest National Laboratory, 3335 Q Avenue, Mail Stop K8-96, Richland, WA 99352, Fax: 509-376-3650, chongxuan.liu@pnl.gov; ²Biogeochemistry, K3-61, Pacific Northwest National Laboratory.

Uranium in DOE Hanford sediments was found to be distributed as uranyl silicate precipitates almost exclusively within interiors of sediment grains. The precipitates were minute, generally 1-3 μm across in either radiating or parallel arrays in intraparticle microfractures of a few microns width and variable connectivity to particle surfaces. Grain-scale porosity, tortuosity and diffusivity of tracer (H_2O) and U(VI) were measured and imaged using various spectroscopic techniques. Simulations using a microscopic reactive diffusion model suggested that diffusion-limited mass transport generated a favorable thermodynamic condition within the grain microfractures for precipitation and concentration of uranium from waste plumes. The rate and extent of uranyl precipitate dissolution were studied in various electrolytes with variable pH under ambient CO_2 pressure. Uranium speciation and distribution before and after dissolution were

monitored by spectroscopic and imaging techniques. Experimental, spectroscopic and modeling results collectively indicated that dissolution of uranyl precipitates was controlled by diffusion-limited dissolution kinetics.

Recovery and detection of uranium (VI) from building materials. Philip A. Greene¹, Christine L. Copper¹, David Berv², Jeremy D. Ramsey² and Greg E. Collins²; ¹Department of Chemistry, United States Naval Academy, 572 Holloway Road, Annapolis, MD 21402, Fax: 410-293-2218, m042664@usna.edu; ²Chemistry Division, Code 6112, Naval Research Laboratory.

As a legacy of the United States' 50 year old nuclear weapons program, the Department of Energy is responsible for cleaning up and decommissioning contaminated sites that were used for the production of these weapons. The method presented here addresses the problem of detecting and quantifying uranium (VI) in concrete. Specifically, the uranium (VI) is removed from concrete surfaces using a low pH buffer rinse that dissolves the surface layer. The amount of uranium in the wash solution can be quite low, even with extraction efficiencies exceeding 50 %. Therefore, the uranium is complexed with an organic chelating agent (arsenazo III) and concentrated using C18 solid phase extraction. Because the absorbance maximum of arsenazo III shifts upon binding to uranium, the concentrated complex can be detected using ultraviolet-visible spectroscopy. Low part-per-billion levels of uranium (VI) in cement can be detected by this method. Results of work related to other building materials such as stainless steel and plexiglass will also be reported.