

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

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**DIVISION OF ENVIRONMENTAL CHEMISTRY  
227<sup>th</sup> American Chemical Society meeting  
Anaheim, CA  
Monday, March 29, 2004**

**Organizers: T. Zachry**

**Presiding: R. Hirsch**

| <b>Time</b> | <b>Paper</b>   |
|-------------|--|
| 1:30 p.m.   | Introductory Remarks.  |
| 1:35 p.m.   | <b>Origin of selectivity in tunnel type inorganic ion exchangers.</b> <u>A. Clearfield</u> , A. Tripathi, D. Medvedev, J. Delgado and M. Nyman   |
| 1:55 p.m.   | <b>Development of dodecaniobate Keggin chain materials as alternative sorbents for Sr and actinide removal from high-level nuclear waste solutions.</b> <u>M. Nyman</u> and F. Bonhomme  |
| 2:15 p.m.   | <b>Molecular modeling investigation of cation siting in crystalline silicotitanate and polyoxoniobate materials.</b> <u>E.J. Maginn</u> and J.P. Larentzos   |
| 2:35 p.m.   | <b>Evaluation of new inorganic sorbents for strontium and actinide removal from high-level nuclear waste solutions.</b> <u>D.T. Hobbs</u> , M.D. Nyman, A. Clearfield, A. Tripathi and D. Medvedev   |
| 2:55 p.m.   | <b>Fundamental chemistry of the Universal Extractant (UNEX) for the simultaneous separation of cesium, strontium, lanthanides and actinides from acidic radioactive waste.</b> R.S. Herbst, <u>D.R. Peterman</u> , T.A. Luther, R.D. Tillotson, T.G. Garn, V.A. Babain, I.V. Smirnov and E.S. Stoyanov |
| 3:15 p.m.   | Intermission.  |

- 3:35 p.m. **Separation of fission products based on ionic liquids: Anion effect.** H. Luo, S. Dai and P.V. Bonnesen
- 3:55 p.m. **Extraction of uranium, neptunium and plutonium from caustic media.** L.H. Delmau, P.V. Bonnesen, N.L. Engle, K.N. Raymond and J. Xu
- 4:15 p.m. **Cesium and strontium uptake to clay minerals and their weathering products in a caustic waste.** S. Choi, M.K. Amistadi, S. Seraphin and J. Chorover
- 4:35 p.m. **Environmental weathering of aluminosilicate clay minerals: Solid-state NMR studies of transformations leading to radionuclide sequestration.** K.T. Mueller, G. Crosson, J. Chorover and S. Choi
- 4:55 p.m. Concluding Remarks.

## ABSTRACTS

**Origin of selectivity in tunnel type inorganic ion exchangers.** Abraham Clearfield<sup>1</sup>, Akhilesh Tripathi<sup>1</sup>, Dmitri Medvedev<sup>1</sup>, Jose Delgado<sup>1</sup> and May Nyman<sup>2</sup>; <sup>1</sup>Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, TX 77843-3255, Fax: 979-845-2370, [clearfield@mail.chem.tamu.edu](mailto:clearfield@mail.chem.tamu.edu); <sup>2</sup>Sandia National Labs.

The removal of highly radioactive species <sup>137</sup>Cs and <sup>90</sup>Sr from Weapon's Grade Tank Waste is a daunting task. The tanks normally are 5-7M in Na<sup>+</sup>, 1-3M in NaOH but only ~10<sup>-5</sup>M in the targeted species. Nevertheless several sorbents and ion exchangers have been found that are sufficiently selective to be considered for remediation purposes. We are involved in a collaborative study, joint with personnel at the Westinghouse Research Center, Sandia National Laboratory and University of Notre Dame to uncover the origins of this selectivity in these compounds. The presentation will be concerned with the framework of titanium silicates with the sitinikite and pharmacosiderite structures. Both compounds have been synthesized as pure titanium silicates or as Nb and Ge substituted forms. Their structures in the sodium and proton forms as well as the Cs<sup>+</sup> and Sr<sup>2+</sup> ion forms will be described together with insight into the exchange mechanism as determined by *in situ* X-ray studies of Cs<sup>+</sup> exchange utilizing synchrotron radiation.

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**Development of dodecaniobate Keggin chain materials as alternative sorbents for Sr and actinide removal from high-level nuclear waste solutions.** May Nyman and Francois Bonhomme; Geochemistry Department, Sandia National Laboratories, P.O. Box 5800, Albuquerque, NM 87185, Fax: 505-844-7354, [mdnyman@sandia.gov](mailto:mdnyman@sandia.gov).

The current baseline sorbent (monosodium titanate) for Sr and actinide removal from Savannah River Site's high level wastes has excellent adsorption capabilities for Sr but poor performance for the actinides. We are currently investigating the development of alternative materials that sorb radionuclides based on chemical affinity and/or size selectivity. The polyoxometalates, negatively-charged metal oxo clusters, have known metal binding properties and are of interest for radionuclide sequestration. We have developed a class of Keggin-ion based materials, where the Keggin ions are linked in 1-dimensional chains separated by hydrated, charge-balancing cations. These Nb-based materials are stable in the highly basic nuclear waste solutions and show good selectivity for Sr and Pu. Synthesis, characterization and structure of these materials in their nativeforms and Sr-exchanged forms will be presented.

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**Evaluation of new inorganic sorbents for strontium and actinide removal from high-level nuclear waste solutions.** D. T. Hobbs<sup>1</sup>, May D. Nyman<sup>2</sup>, Abraham Clearfield<sup>3</sup>, Akhilesh Tripathi<sup>3</sup> and Dmitri Medvedev<sup>3</sup>; <sup>1</sup>Savannah River Technology Center, Westinghouse Savannah River Company, 773-A, B-117, Aiken, SC 29808, Fax: 803-725-4704, [david.hobbs@srs.gov](mailto:david.hobbs@srs.gov); <sup>2</sup>Sandia National Laboratories; <sup>3</sup>Department of Chemistry, Texas A & M University.

Monosodium titanate (MST), a hydrous metal oxide sorbent, is the baseline material for the removal of <sup>90</sup>Sr and *alpha*-emitting radionuclides (principally <sup>238</sup>Pu, <sup>239</sup>Pu, <sup>240</sup>Pu and <sup>237</sup>Np) from alkaline waste solutions generated during the processing of irradiated nuclear materials at the Savannah River Site. This material exhibits excellent performance characteristics for strontium removal. Plutonium removal is also good, but problematic at the estimated bonding concentration. We are currently developing new inorganic materials for improved sorption characteristics. These materials include sodium nonatitanates, pharmacosiderites and heteropolyniobates. We will present results evaluating the performance of these materials with simulated and actual high-level nuclear waste solutions.

We acknowledge financial support of this project (#81949) by the Environmental Molecular Science Program in the Office of Science, Department of Energy.

**Molecular modeling investigation of cation siting in crystalline silicotitanate and polyoxoniobate materials.** Edward J. Maginn and James P. Larentzos; Department of Chemical and Biomolecular Engineering, University of Notre Dame, 182 Fitzpatrick Hall, Notre Dame, IN 46556, Fax: 574-631-8366, [ed@nd.edu](mailto:ed@nd.edu).

Separation of radionuclides from high-level nuclear waste solutions is a vital step to minimize the amount of nuclear waste volume for final disposal. A number of inorganic ion exchangers have demonstrated the ability to selectively remove low concentrations of radionuclides in the presence of high sodium ion content and alkalinity. Various classes of crystalline silicotitanates (CST), pharmacosiderates and polyoxoniobates are being synthesized by collaborators at Texas A&M and Sandia National Laboratories. The ion exchange performance of these materials may be improved by introducing suitable structural modifications, such as partial substitution of niobium for titanium in the framework structures.

In this work, the origins of ion exchange selectivity and kinetics are investigated through atomistic level simulations. The primary focus has been to develop a transferable potential model that can be used to accurately predict structural characteristics of the ion exchangers of interest. Energy minimizations and molecular dynamics simulations are applied to the CST and polyoxoniobate materials. Structural characteristics, such as cation and water sites, coordinating environments and the energetics associated with the sites are determined, providing additional molecular-level insight into the stability of the structures.

**Fundamental chemistry of the Universal Extractant (UNEX) for the simultaneous separation of cesium, strontium, lanthanides and actinides from acidic radioactive waste.** R. Scott Herbst<sup>1</sup>, Dean R. Peterman<sup>1</sup>, Thomas A. Luther<sup>1</sup>, Richard D. Tillotson<sup>1</sup>, Troy G. Garn<sup>1</sup>, Vasily A. Babain<sup>2</sup>, Igor V. Smirnov<sup>2</sup> and Evgenii S. Stoyanov<sup>3</sup>; <sup>1</sup>Idaho National Engineering and Environmental Laboratory, P.O. Box 1625, Idaho Falls, ID 83415-2208, Fax: 208-526-3499, [herbrs@inel.gov](mailto:herbrs@inel.gov), [petedr2@inel.gov](mailto:petedr2@inel.gov); <sup>2</sup>Khlopin Radium Institute; <sup>3</sup>Institute of Catalysis.

Scientists at the INEEL and KRI collaboratively developed and validated the concept of a Universal Extractant (UNEX) for simultaneously removing the major radionuclides (Cs, Sr, actinides and lanthanides) from acidic radioactive waste in a single solvent extraction process. The UNEX solvent incorporates three active extractants: chlorinated cobalt dicarbollide, polyethylene glycol and a carbamoylmethylphosphine oxide derivative, dissolved in a suitable organic diluent to simultaneously extract target radionuclides. The process chemistry is unique, but complicated, since the extractants operate synergistically to extract the radionuclides. Results indicate that water dissolved in the organic phase dramatically impacts the process chemistry. In order to investigate this phenomenon, we have varied the amount of water dissolved in the organic phase by using several different organic diluents. The results of <sup>137</sup>Cs and <sup>89</sup>Sr batch distribution studies for the different organic diluents will be presented. These data and

data from other spectroscopic techniques will be used to elucidate the details of the extraction mechanism.

**Separation of fission products based on ionic liquids: Anion effect.** Huimin Luo<sup>1</sup>, Sheng Dai<sup>2</sup> and Peter V. Bonnesen<sup>2</sup>; <sup>1</sup>Nuclear Sciences & Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, [luoh@ornl.gov](mailto:luoh@ornl.gov); <sup>2</sup>Chemical Sciences Division, Oak Ridge National Laboratory.

The applications of ionic liquids (ILs) as new separation media have been actively investigated recently. The most commonly studied class of ILs for such applications is based on dialkyl imidazolium cations. In comparison with conventional molecular solvents, ILs exhibit enhanced distribution coefficients for a number of complexing neutral ligands in extraction of metal ions from aqueous solutions. The effect of the alkyl chain length of imidazolium cations on the distribution coefficients of solvent extraction using crown ethers was the subject of a number of the previous investigations. The distribution coefficients have been found to decrease with the alkyl chain length of the IL cations. This observation implies that the extraction process also involves the exchange of the IL cations with metal ions. The longer the alkyl chain lengths of the IL cations are, the more hydrophobic the IL cations are and the more difficult to be transported into aqueous phases *via* ion exchange. Accordingly, the ion-exchange process is another unique property of IL-based extractions involving charged species. Here, we report the investigation about the effect of the variation of IL anions on the solvent extraction of metal ions using crown ethers as extractants. The elucidation of different solvation effects involved in ionic liquids could lead to optimized separation media for these novel solvents.

**Extraction of uranium, neptunium and plutonium from caustic media.** Lætitia H. Delmau<sup>1</sup>, Peter V. Bonnesen<sup>1</sup>, Nancy L. Engle<sup>1</sup>, Kenneth N. Raymond<sup>2</sup> and Jade Xu<sup>2</sup>; <sup>1</sup>Chemical Separations Group, Chemical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, MS-6119, Oak Ridge, TN 37831-6119, [delmaulh@ornl.gov](mailto:delmaulh@ornl.gov); <sup>2</sup>College of Chemistry, UC Berkeley.

Fundamental research on uranium, neptunium and plutonium separation from alkaline media using solvent extraction is being conducted. Specific extractants for these actinides from alkaline media have been synthesized to investigate the feasibility of selective removal of these elements. Two families of extractants have been studied: terephthalamide and tetra(hydroxybenzyl)ethylene diamine derivatives. Fundamental studies were conducted to characterize their extraction behavior from a wide variety of aqueous conditions. The terephthalamide derivatives exhibit a significant extraction strength along with a discriminatory behavior among the actinides, plutonium being extracted the most strongly. Quantitative extraction of plutonium and moderate extraction of neptunium and uranium was achieved from a simple caustic solution. Interestingly, strontium is also quantitatively extracted by these derivatives. However, their stability to highly caustic solutions still needs to be improved.

Tetra(hydroxybenzyl)ethylene diamine derivatives exhibit a very good stability to caustic conditions and are currently being studied.

**Cesium and strontium uptake to clay minerals and their weathering products in a caustic waste.** Sunkyung Choi<sup>1</sup>, Mary Kay Amistadi<sup>1</sup>, Supapan Seraphin<sup>2</sup> and Jon Chorover<sup>1</sup>; <sup>1</sup>Department of Soil, Water and Environmental Science, University of Arizona, Shantz 429, Building #38, Tucson, AZ 85721, Fax: 520-621-1647, [skchoi@ag.arizona.edu](mailto:skchoi@ag.arizona.edu); <sup>2</sup>Department of Materials Science and Engineering, University of Arizona.

Weathering behavior and contaminant (Sr and Cs) uptake by specimen clays (illite, vermiculite, montmorillonite and kaolinite) and their secondary solid phase products were studied in batch systems under geochemical conditions characteristic of leaking tank waste at the Hanford Site in WA (0.05 M Al<sub>T</sub>, 2 M Na<sup>+</sup>, 1 M NO<sub>3</sub><sup>-</sup>, pH ~14, Cs<sup>+</sup> and Sr<sup>2+</sup> present as co-contaminants). Time series experiments were conducted from 0 to 369 days, with initial Cs<sup>+</sup> and Sr<sup>2+</sup> concentrations ranging from 10<sup>-5</sup> to 10<sup>-3</sup> M. Cesium sorption after 369 d reaction was the greatest in the order of vermiculite, illite, montmorillonite and kaolinite at 10<sup>-3</sup> M Cs/Sr. In the case of Sr, vermiculite showed highest Sr sorption and was followed by kaolinite, montmorillonite and illite at highest loading Cs/Sr after 369 d. Secondary phase products were feldspathoid sodium aluminum nitrate silicate, sodium aluminum nitrate silicate hydrate, Na-Al chabazite and zeolite X in weathered clays. Discrete Sr single phases were found in kaolinite and illite systems after 369 d at 10<sup>-3</sup> M Cs/Sr.

**Environmental weathering of aluminosilicate clay minerals: Solid-state NMR studies of transformations leading to radionuclide sequestration.** Karl T. Mueller<sup>1</sup>, Garry Crosson<sup>1</sup>, Jon Chorover<sup>2</sup> and Sunkyung Choi<sup>2</sup>; <sup>1</sup>Department of Chemistry, Penn State University, 152 Davey Laboratory, University Park, PA 16802, Fax: 814-863-8403, [ktm2@psu.edu](mailto:ktm2@psu.edu); <sup>2</sup>Department of Soil, Water and Environmental Science, University of Arizona.

Mobilities of radionuclides (such as <sup>137</sup>Cs and <sup>90</sup>Sr) are governed by their interactions with natural soil particles in the saturated and unsaturated zones at Department of Energy sites. High surface area aluminosilicate clay minerals are a component of the natural soils beneath the leaking waste tanks at these sites and serve as possible radionuclide sorbents. However, due to the characteristics of the contaminant medium (high pH, high Al and high ionic strength), clay minerals are susceptible to transformations during exposure to tank waste leachates. We are currently studying the transformation of clays under specific chemical conditions that mimic the composition of known contaminant solutions. In these studies, specimen clay samples are reacted for varying time periods (up to one year) with simulated tank waste leachate solutions. Mineral dissolution and transformation are followed with solution analysis, x-ray diffraction and a number of other analytical methods. We report here results from <sup>27</sup>Al MAS NMR at variable magnetic field strengths (up to 18.8 T), <sup>29</sup>Si MAS NMR and

$^1\text{H}/^{29}\text{Si}$  CPMAS NMR and evaluate these results along with those of other parallel analytic studies.