PROGRAM AND ABSTRACTS

SEPARATION SCIENCE & TECHNOLOGY FOR ENERGY APPLICATIONS

17TH SYMPOSIUM

October 23-27, 2011

Park Vista Resort
Gatlinburg, TN

17th Symposium

Separation Science and Technology for Energy Applications

Program Overview

SUNDAY, OCTOBER 23

6:00 - 9:00 PM	Early check-in/Registration

MONDAY, OCTOBER 24

7:00 - 8:00 AM	Check-in/Registration
8:00 AM	Welcome and Announcements
8:10 AM	Session I – Plenary
1:30 PM	Session II – Membrane Separations
6:00 PM	Session III – Reception/Poster Presentations

TUESDAY, OCTOBER 25

8:00 AM	Session IV – Adsorption and Ion Exchange
Afternoon	Free Time
6:30 PM	Session V – Novel Separations

WEDNESDAY, OCTOBER 26

8:00 AM	Session VI – Nuclear Fuel Cycle Separations
1:30 PM	Session VII – Solvent Extraction
6:30 PM	Banquet

THURSDAY, OCTOBER 27

8:00 AM	Session VIII – Department of Energy Applications

Monday, October 24

7:45 am	**Continental Breakfast**
8:00 am	**Welcome and Announcements**
SST Chair	David DePaoli, Oak Ridge National Laboratory
SST Co-Chair	Ken Nash, Washington State University

SESSION I — PLENARY

Chair	Ken Nash, Washington State University
Co-Chair	Jack Watson, Oak Ridge National Laboratory (retired)
8:10 am	**Nuclear Fuel Cycle Applications of Separation Science and Technology,** Andrew Griffith, Office of Nuclear Energy, U.S. Department of Energy
8:55 am	**Separation Science and Technology in U.S. DOE Environmental Management,** Mary Neu, Office of Environmental Management, U.S. Department of Energy
9:40 am	**Break**
10:00 am	**Mining Uranium from Seawater,** Sheng Dai, Oak Ridge National Laboratory
10:30 am	**Novel Approaches for Decorporation of Radionuclides,** Tatiana Levitskaia, Pacific Northwest National Laboratory
11:00 am	**The Role of a Transformed National Defense Stockpile in U.S. Strategic Materials Security,** Richard Lowden, Oak Ridge National Laboratory
11:30 am - 1:30 pm	**Lunch** (on your own)

SESSION II — MEMBRANE SEPARATIONS

Chair	Eric Peterson, Idaho National Laboratory
Co-Chair	Ramesh Bhave, Oak Ridge National Laboratory
1:30 pm	**Membrane Technology Overview,** Ramesh Bhave
1:40 pm	**Water Containing Gas Stream Separations at High Temperature,** John Klaehn, Idaho National Laboratory
2:05 pm	**Polyetherimide/ZIF-8 Asymmetric Mixed Matrix Hollow Fiber Membranes for Gas Separations,** Ying Dai, Georgia Institute of Technology
2:30 pm	**Steam Reforming of Methanol in a Pd-composite Membrane Reactor,** Shamsuddin Ilias, North Carolina A&T State University
2:55 pm	**Water Logistic Solution for Remote Locations: Membrane Separation of Water from Diesel Exhaust,** Melanie Moses-DeBusk, Oak Ridge National Laboratory
3:10 pm	**Break**

3:35 pm **New Composite Membranes for High Throughput Solid-Liquid Separations at the Savannah River Site,** Michael Poirier, Savannah River National Laboratory

4:00 pm **Simulant Development and Validation Using Bench-Scale Cross-Flow Filtration,** Philip Schonewill, Pacific Northwest National Laboratory

4:25 pm **Electrophoresis of Proteins in Polyacrylamide/Montmorillonite Hydrogel Nanocomposites,** Jeffery Thompson, Tennessee Technological University

4:50 pm **Methyl Acetate Separation by Pervaporation,** Thomas Winkler, Graz University of Technology

5:15 - 6:00 pm **Student Poster Presentations**
Brief, single-slide overviews of posters by student authors

SESSION III — POSTER PRESENTATIONS/MIXER

Chair: Jared Johnson, Oak Ridge National Laboratory
Co-Chair: Jon Garrison, Oak Ridge National Laboratory

6:00 - 8:00 pm **Drinks/Appetizers**
Poster abstracts begin on page 12
Brochures available for poster titles and numbers

Tuesday, October 25

7:45 am **Continental Breakfast**

SESSION IV — ADSORPTION AND ION EXCHANGE

Chair: Sotira Yiacoumi, Georgia Institute of Technology
Co-Chair: Eric Guibal, Ecole des Mines d'Alès

8:00 am **Application of Molecular Mechanics and CSTR Experiments to Study Metal Adsorption by Oxalate-modified Activated Carbons,** Henry Kasaini, Tshwane University of Technology

8:30 am **Rapid Removal of Mercury from Aqueous Solutions Using Thiol Functionalized Biosynthesized $Zn_{0.6}Fe_{2.4}O_4$ Nanoparticles,** Feng He, Oak Ridge National Laboratory

8:55 am **Evaluation of Potential Eluants for Non-Acid Elution of Cesium from Resorcinol-Formaldehyde Resin,** Kofi Adu-Wusu, Savannah River National Laboratory

9:20 am **Ion Exchange Kinetics Testing with SRF Resin,** Renee Russell, Pacific Northwest National Laboratory

9:45 am **Break**

10:10 am **Platinum(IV) Recovery from HCl Solutions Using Amberlite XAD-7 Impregnated with a Tetraalkyl Phosphonium Ionic Liquid,** Eric Guibal, Ecole des Mines d'Alès

10:35 am **Minor Actinide Separations Using Ion Exchangers,** Thomas Shehee, Savannah River National Laboratory

11:00 am **Improved Titanate Sorbents for Strontium and Actinide Separations.** Kathryn Taylor-Pashow, Savannah River National Laboratory

11:25 am **Modeling Adsorption Processes for Direct Capture of CO_2 from Ambient Air,** Ambarish Kulkarni, Georgia Institute of Technology

11:50 am - 6:30 pm **Open Afternoon** (on your own for lunch & dinner)

SESSION V — NOVEL SEPARATION METHODS

Chair: Mark Dietz, University of Wisconsin-Milwaukee
Co-Chair: Dale Ensor, Tennessee Technological University

6:30 pm **Chemical Moments,** Dale Ensor, Tennessee Technological University

7:00 pm **Evaluation of Hydroxyalkyl-Functionalized Imidazolium-Based Ionic Liquids as Solvents for the Extraction of Metal Ions,** Cory Hawkins, University of Wisconsin–Milwaukee

7:20 pm **Ionic Liquids for Radioisotope Separations Involving Thorium and Actinium,** Jason Bell, Oak Ridge National Laboratory

7:40 pm **High Solubility of CO_2 in an Ionic Liquid with the Tetracyanoborate Anion – An Insight from Molecular Simulation,** Ravichandar Babarao, Oak Ridge National Laboratory

8:00 pm **Recovery of Minor Actinide from Spent Fuel by Extraction Chromatographic Technique Using Immobilizing TPEN-gels,** Shin-ichi Koyama, Japan Atomic Energy Agency

8:20 pm **Break**

8:30 pm **Self-Assembled Capsule Receptors for Sulfate Recognition and Separation,** Radu Custelcean, Oak Ridge National Laboratory

8:50 pm **Electrosorption of Ions by Novel Mesoporous Carbon Materials,** Costas Tsouris, Oak Ridge National Laboratory

9:10 pm **Electrochemical Studies of Cation-cation Complexes Involving UO_2^+ and UO_2^{2+} in Chloride and Perchlorate Aqueous Systems,** John Freiderich, Washington State University

Wednesday, October 26

7:45 am **Continental Breakfast**

SESSION VI — NUCLEAR FUEL CYCLE SEPARATIONS

Chair: Terry Todd, Idaho National Laboratory
Co-Chair: Kevin Felker, Oak Ridge National Laboratory

8:00 am **Separation of Am(III) from Eu(III) Using Polymer Gels Cross-Linked with Nitrogen-Donor Ligands,** Kenji Takeshita, Tokyo Institute of Technology

8:25 am **Probing Ligand Exchange Kinetics in Solvent Extraction Systems using ^{31}P NMR,** Cecile Marie, Washington State University

8:50 am **Development of a Simplified Soft Donor Approach to Trivalent Actinide/Lanthanide Separations,** Leigh Martin, Idaho National Laboratory

9:15 am **Interaction between HDEHP and CMPO in Combined TRUEX-TALSPEAK Extraction System,** Peter Tkac, Argonne National Laboratory

9:40 am **Break**

10:05 am **From TALSqueak to TRUSqueak: Application of Aqueous Ternary Species,** Jenifer Braley, Pacific Northwest National Laboratory

10:30 am **Separation and Recovery of Uranium and Group Actinide Products from Irradiated Fast Reactor MOX Fuel via Electrolytic Reduction and Electrorefining,** Steven Herrmann, Idaho National Laboratory

10:55 am **Spectroscopic On-Line Monitoring for Process Control and Safeguarding of Radiochemical Streams,** Samuel Bryan, Pacific Northwest Laboratory

11:20 am **Secondary Rare Metals by Separation and Transmutation of Fission Products - From Adv.-ORIENT Cycle to Après ORIENT,** Masaki Ozawa, Tokyo Institute of Technology

11:45 am **Concluding Remarks**

11:50 am - 1:30 pm **Lunch** (own your own)

SESSION VII — SOLVENT EXTRACTION

Chair: Lætitia Delmau, Oak Ridge National Laboratory
Co-Chair: Mark Antonio, Argonne National Laboratory

1:30 pm **Solute Partitioning and Lanthanide Speciation in TALSPEAK Media,** Ken Nash, Washington State University

1:55 pm **Gamma Radiolysis of TBP/n-dodecane in the Presence of Nitric Acid Using the INL Radiolysis Test Loop,** Dean Peterman, Idaho National Laboratory

2:20 pm **Ionic Liquids: Unique Environments for f-Element Chemistry,** Robin Rogers, University of Alabama

2:45 pm **Investigations on the Synergistic Effects in Solvent Extraction Systems Combining TBP and DBP,** Mikael Nilsson, UC-Irvine

3:10 pm **Break**

3:25 pm **Ce(III) Extraction by Aliphatic Malonamide: A Micro- and Macro-Molecular Structural Study,** Ross Ellis, Argonne National Laboratory

3:50 pm **Synergistic Extraction of Americium and Europium Using bis-(o-trifluoromethylphenyl)-dithiophosphinic Acid and Neutral Donors,** Dale Ensor, Tennessee Technological University

4:15 pm **Functionalized Dipicolinic Acid Derivatives for Trivalent Actinide and Lanthanide Complexation,** Colt Heathman, Washington State University

4:40 pm **Cooperativity in Liquid-Liquid Anion Exchange by Lipophilic Quaternary Ammonium Salts in Combination with Neutral Anion Receptors,** Bruce Moyer, Oak Ridge National Laboratory

6:00 pm **DINNER BANQUET** - Park Vista Hotel
Non-Traditional Materials Research at ORNL: From Rare Earths and Actinides to Stainless Steel Crystals
Special Presentation by Lynn Boatner, ORNL Corporate Fellow and Battelle Distinguished Inventor, Oak Ridge National Laboratory

Thursday, October 27

7:45 am **Continental Breakfast**

SESSION VIII — DEPARTMENT OF ENERGY APPLICATIONS

Chair: Sam Fink, Savannah River National Laboratory
Co-Chair: Reid Peterson, Pacific Northwest National Laboratory

8:00 am **Vacuum Salt Distillation for the Removal of Chloride and Fluoride Salts,** Robert Pierce, Savannah River National Laboratory

8:25 am **Near-Tank Treatment of Hanford Tank Waste: Pilot-Scale Testing,** Philip Schonewill, Pacific Northwest National Laboratory

8:50 am **Real Time Raman Analysis of Near Tank Treatment System Process Streams,** Matthew Edwards, Pacific Northwest National Laboratory

9:15 am **Development of the Next-Generation Caustic-Side Solvent Extraction (NG-CSSX) Process,** Lætitia Delmau, Oak Ridge National Laboratory

9:40 am **Break**

10:00 am	**Synthesis and Evaluation of Guanidine Suppressors Used in the Next Generation Caustic Side Solvent Extraction (NG-CSSX) Process,** Nathan Duncan, Oak Ridge National Laboratory
10:25 am	**Performance Testing of the Next-Generation CSSX Solvent with Actual SRS Tank Waste,** Thomas Peters, Savannah River National Laboratory
10:50 am	**Investigation of Catalytic Pathways and Separations for Lignin Breakdown into Monomers and Fuels,** Joanna McFarlane, Oak Ridge National Laboratory
11:15 am	**Concluding Remarks**

PLENARY

Nuclear Fuel Cycle Applications of Separation Science and Technology

Andrew Griffith, Office of Nuclear Energy, U.S. Department of Energy, Washington, DC

The mission of the Office of Nuclear Energy's Fuel Cycle Technologies office is to provide options for possible future changes in national nuclear energy programs. While the recent draft report of the Blue Ribbon Commission on America's Nuclear Future stressed the need for organization changes, interim waste storage and the early establishment of a permanent repository for nuclear waste management, it also recognized the potential value of alternate fuel cycles and recommended continued research and development in that area. A recent separations workshop involving representatives of DOE's Offices of Science, Environmental Management, and Nuclear Energy and the National Nuclear Security Administration identified many areas of common interest and opportunities for improved program integration. Although many industrial-scale applications of advanced separations processes will not occur for several decades, some technologies under development may find near-term uses. Several will be identified and discussed in the presentation.

Separation Science and Technology in U.S. DOE Environmental Management

Mary Neu, Office of Environmental Management, U.S. Department of Energy, Washington, DC

Separations science was central to the Manhattan Project and the subsequent development of nuclear weapons and nuclear energy. Research, scale up and production in multiple nuclear application areas yielded the desired separated nuclear-related materials in the U.S. through the 1950s-1980s. Side products, waste streams, and contaminated facilities, equipment, and environmental media were co-produced on a massive scale. DOE's Environmental Management (EM) mission is to stabilize, store, process, dispose, and clean up those legacy byproducts and infrastructure. Separations and partitioning are clearly essential for specific mission elements; e.g. processing highly radioactive wastes stored in large tanks. Separations also have the potential to appreciably reduce the volumes of materials that must be disposed in most of EM's other mission areas. For example, technetium, mercury, and chromium in ground water, soils and subsurface environments; non-radioactive species in tank waste; transuranics in waste; actinides in spent fuel and complex materials. EM's restoration of sites can provide lessons and technologies for future sustainable nuclear cycles – from mining and production, to backend recovery and disposition.

Mining Uranium from Seawater

Sheng Dai, Oak Ridge National Laboratory, Oak Ridge, TN

For nuclear energy to remain a viable and sustainable energy source, there must be assurance that economical sources of nuclear fuels are available. Given the projected growth in nuclear power in the future, the goal of nuclear fuel research and development (R&D) activities is to evaluate the availability and accessibility of nuclear fuel resources and develop extraction technologies to enable a sustainable fuel cycle. The current R&D focus related to nuclear fuels resources in the United States Department of Energy (DOE) Office of Nuclear Energy is on extraction of uranium from the most challenging but highest-payoff unconventional resource: seawater. This talk will give a brief overview of the research efforts in this area through the Fuel Resources Program. The new fundamental understanding and the technology developed from these studies could also be used in extracting uranium from other resources, such as groundwater, and in extracting other metal ions of commercial value.

This work was supported by the United States Department of Energy (DOE) Office of Nuclear Energy.

Novel Approaches for Decorporation of Radionuclides

Tatiana G. Levitskaia, K. D. Thrall, J. M. Peterson, Pacific Northwest National Laboratory, Richland, WA

Recently acknowledged threats involving the potential of deliberate (terrorist activities) or accidental (nuclear power plan accident, occupational exposure, etc.) release of radionuclides into local environments now prompt new concerns and the need for improved methods of removing (decorporating) internally deposited radio-nuclides. Internal human contamination represents a serious health concern, and treatment strategies are focused on preventing the occurrence of acute health effects attributable to a large dose radiation exposure and/or restricting the likelihood of late stage health effects such as cancers in a prolonged chronic exposure to relatively low levels of radiation. To date, only a few standard treatments for certain radionuclide intakes exist, and in the event of a radiological and/or nuclear emergency available countermeasures to mitigate radiation damage within the body are extremely limited. Development and approval of new decorporation agents involve significant research investment in time, money and resources to gain fundamental understanding of the mechanism of radionuclide chelation in vitro and in vivo. In contrast, therapeutics that have already been developed and approved for other metal intoxication may offer at least a temporary solution, while more effective chelating

agents for human applications are being developed. Toward this goal, we are testing in vivo efficacy of Cuprimine and Syprine therapeutics, that are approved by the U.S. FDA to treat copper overload in Wilson Disease (a genetic defect in copper metabolism and transport), for decorporation of radioisotopes of cobalt. In alternative approach, we are exploring a potential of readily available and established for human applications natural chelators as decorporation agents for radionuclides.

The Role of a Transformed National Defense Stockpile in U.S. Strategic Materials Security

Richard A. Lowden, Oak Ridge National Laboratory, Oak Ridge, TN

The United States established a stockpile of strategic materials in 1939 beginning with a handful of ores and minerals which with time was expanded to include additional minerals, metals, chemicals, and other processed materials. The purpose of the stockpile was to preclude a dangerous and costly dependence by the United States upon foreign sources for supplies of scarce but important materials in times of national emergency. Although emphasis has traditionally been on the acquisition and retention of certain strategic and critical materials, the legislation includes provisions that encourage the conservation and development of resources and materials. The authors of the Stockpiling Act realized the value of recycling, improved separation techniques, and alternative methods for refining or processing of materials thus included language to address these issues. Since 1993 the Stockpile has been downsizing, selling off most of its assets, however, recent changes in the global marketplace and increasing risks associated with the supply of important materials such as the rare earths, interest in the stockpile has been renewed. The Stockpile is in the process of being transformed in a more flexible and dynamic strategic materials risk management (security) program with much broader scope and applicability with respect to the entire supply chains for important materials.

SESSION II – MEMBRANE SEPARATIONS

Water Containing Gas Stream Separations at High Temperature

J. R. Klaehn, C. J. Orme, F. F. Stewart, E. S. Peterson, Idaho National Laboratory, Idaho Falls, ID*

There is direct interest in high temperature gas separations (> 150 °C), especially for carbon dioxide (flue gas) or hydrogen (syn-gas). However, most industrially relevant high temperature gas separations involve water. At ambient temperatures, water vapor can permeate easily through most polymeric membranes, and possibly change (swell) the polymeric membrane. At higher temperatures, water vapor can be destructive to polymer membranes. Little data has been presented in the literature regarding how water vapor affects gas separations at high temperatures; therefore, investigations into water containing gas streams is important for indentifying a polymeric membrane's physical and gas separation properties. Previous INL studies have shown that polyimides are promising membrane candidates and gave interesting results for high temperature gas separations. Additionally, INL has found that polyimides can be blended with various polymers and several show excellent thermal stability with good gas permeabilities. This presentation will discuss polyimides that have been evaluated [like, Kapton®] for high temperature gas separations (up to 200 °C) with water containing gas streams.

Polyetherimide/ZIF-8 Asymmetric Mixed Matrix Hollow Fiber Membranes for Gas Separations

Y. Dai, J.R. Johnson, D. Sholl, W.J. Koros, Georgia Institute of Technology, Atlanta, GA*

In recent years, organic-inorganic hybrid (mixed matrix) membranes have been receiving increasing attention in the literature. These materials can potentially extend the separation performance of traditional polymeric materials. There have been few reported cases of these materials being successfully extended to the asymmetric hollow fiber morphology. In this work we report the first successful production of mixed matrix asymmetric hollow fiber membranes containing metal-organic-framework (MOF) fillers. Specifically, we have incorporated ZIF-8 into a polyetherimide (Ultem® 1000) matrix and produced dual-layer (composite) asymmetric hollow fiber members via the dry jet-wet quench method. The outer separating layer of these composite fibers contains 17vol% of ZIF-8 filler. These membranes have been tested over a range of temperatures and pressures for a variety of gas pairs. An increase in separation productivity for multiple gas pairs (e.g., CO_2/N_2, CO_2/CH_4) has been observed. Furthermore, these membranes were tested using humid gas feeds (representing flue gas) wherein additional increases in membrane efficiency were also observed. (Acknowledgement: This project is funded by the ARPA-E IMPACCT Program via award DE-FOA-0000208.)

Steam Reforming of Methanol in a Pd-composite Membrane Reactor

S. Ilias, D. Kuila, M.A. Islam, North Carolina A&T State University, Greensboro, NC*

Palladium-based membranes are being studied for simultaneous production and separation of hydrogen from reforming reactions in a single-unit operation by equilibrium shift. Although electroless plating (EP) has been the method of choice for fabrication of Pd and Pd-alloy membranes on microporous ceramic and stainless steel

(MPSS) supports, the conventional EP method is limited by the non-uniformity in depositions of Pd-grains on porous substrates, yielding defective films. The oxidation-reduction reactions in EP result in evolution of ammonia and nitrogen gas bubbles. These tiny gas bubbles hinder uniform Pd-film deposition when they adhere to the substrate surface and in the pores. To overcome these limitations, we investigated Surfactant Induced EP (SIEP) in deposition of defect-free Pd-film on MPSS support. The resulting membrane, with agglomerated finer grains, showed significant improvement in surface microstructures and film adhesion to the substrate surface with higher permeability and selectivity.

We used a Pd-MPSS membrane fabricated by SIEP technique in tubular configuration as fuel reformer to study the steam reforming of methanol (SRM) over Ni-Zn and Pd-Ni catalyst encapsulated in mesoporous silica. While Ni-Zn is commercially available, Pd-Ni was synthesized in our laboratory. The effect of steam to methanol ratio, temperature, and space velocity on methanol conversion, hydrogen yield, and carbon monoxide suppression was studied for the SRM in the membrane reactor. A two-dimensional, pseudo-homogeneous membrane-reactor model for the SRM reactions was developed to study the membrane reactor performance. Some of our experimental and modeling results of SRM in Pd-MPSS membrane reactor will be discussed in this paper.

Water Logistic Solution for Remote Locations: Membrane Separation of Water from Diesel Exhaust

M. Moses-DeBusk, B.L. Bischoff, J. Hunter, J. Klett, J. Conklin, C.S. Daw, Oak Ridge National Laboratory, Oak Ridge, TN*

Water transport logistics for locations where potable water is limited, such as combat zones, or the supply has been disrupted by natural or man-made disasters are costly and alternative solutions are energy intensive. Since potable water is a constant necessity for sustainable health, the supply must be continually replenished. In these situations, stationary generators and/or vehicles are typically present which produce exhaust containing ~10% water as a result of combustion of hydrocarbon based fuels.

This presentation will present a design for a multi-membrane module system which contains robust, tubular inorganic membranes capable of recovering the currently wasted water vapor from diesel exhaust with limited energy input. Working via capillary condensation, the membrane separation system can be used to reclaim the water at high efficiency at moderate temperatures. As the membrane pore size is reduced, efficiency is increased according to the Kelvin equation; however, maximizing the overall system efficiency must also be balanced with membrane permeance which typically decreases with decreasing pore size. Other important parameters include the membrane/vapor interface temperature and exhaust flow rate. Experimental results evaluating these effects will be addressed. In addition, an advanced cooling technology employing graphite foam for improving membrane temperature control for further enhancement of system efficacy will be discussed. Preliminary modeling data on the reclamation system's impact on generator operations will also be presented.

Research sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory (ORNL), managed by UT-Battelle, LLC for the U. S. Department of Energy.

New Composite Membranes for High Throughput Solid-Liquid Separations at the Savannah River Site

R. Bhave[1], M. R. Poirier[2], [1]Oak Ridge National Laboratory. Oak Ridge, TN and [2]Savannah River National Laboratory, Aiken, SC*

Solid-liquid separation is the limiting step for many waste treatment processes at the Savannah River Site. SRNL researchers have identified the rotary microfilter as a technology to improve the rate of solid-liquid separation processes. SRNL is currently developing the rotary microfilter for radioactive service and plans to deploy the technology as part of the small column ion exchange process. The rotary microfilter can utilize any filter media that is available as a flat sheet. The current baseline membrane is a 0.5-micron (nominal) porous metal filter (Pall PMM050). Previous testing with tubular filters showed that filters composed of a ceramic membrane on top of a stainless steel support produce higher flux than filters composed only of porous metal. The authors are working to develop flat sheet filter media composed of a ceramic membrane and/or ceramic-metal composite on top of a porous stainless steel support that can be used with the rotary microfilter to substantially increase filter flux resulting in a more compact, energy efficient and cost-effective high level radioactive waste treatment system.

Composite membranes with precisely controlled pore size distribution were fabricated on porous metal supports. High quality uniform porous metal (316SS) supports were fabricated to achieve high water permeability. Separative layers of several different materials such as ultrafine metal particles and ceramic oxides were used to fabricate composite membranes. The fabrication process involved several high temperature heat treatments followed by characterization of gas and liquid permeability measurements and membrane integrity analysis.The fabricated composite membrane samples were evaluated in a static test cell manufactured by SpinTek. The composite membranes were evaluated on several feed slurries: 1 wt. % strontium carbonate in deionized water, 1 wt. % monosodium titanate in simulated salt solution, and 1 wt. % simulated sludge in

simulated salt solution and deionized water. Flux as a function of feed flow rate and transmembrane pressure was measured for each of the above described feed slurries.

The authors will discuss the new membrane development efforts, waste slurry filtration performance evaluations and scale-up considerations.

Simulant Development and Validation Using Bench-Scale Cross-Flow Filtration

P.P. Schonewill, R.C. Daniel, R.L. Russell, R.W. Shimskey, C.A. Burns, J.M. Billing, R.A. Peterson, Pacific Northwest National Laboratory, Richland, WA*

In the past several years, cross-flow filtration has been studied extensively in a bench-scale system at Pacific Northwest National Laboratory using both actual tank waste from the Hanford site and waste simulants. One challenge when creating a waste simulant is duplicating the filtration behavior of real waste, in particular when the waste composition is not known with certainty. Based on mechanistic models and a systematic approach to filtration testing, it has been found that the solid components that dominate the filtration behavior can be identified. These solids components were combined with a supernate that is representative of the real waste and then the filtration performance was verified against real waste data. Along the way, PNNL is building a database of filtration performance for various solid species that can be used to quickly develop waste simulants in the future.

Electrophoresis of Proteins in Polyacrylamide/Montmorillonite Hydrogel Nanocomposites

J.W. Thompson[1], H. A. Stretz[1], P. E. Arce[1], H. Gao[2], H. Ploehn[2], J. He[3], [1]Tennessee Technological University, Cookeville, TN, [2]University of South Carolina, Columbia, SC, [3]Tulane University, New Orleans, LA*

Nanocomposite polymeric hydrogels represent a new tool for improved separations in clinical diagnostics among other biotechnological applications. However, the relationship between nanocomposite hydrogel structure and mass transport has not been systematically described. In this study, polyacrylamide (PAM) nanocomposites have been formulated in combination with sodium Montmorillonite (MMT). Random nano-platelet versus magnetized nano-platelet configuration were well characterized and related to effects on electrophoretic separation of two proteins, ovum serum albumin (OSA) and carbonic anhydrase (CA). The nanocomposite hydrogel morphologies were described using TEM, WAXD, SANS, SAXS and cryo-SEM. The effective electrophoretic mobilities of the two model proteins were determined using electrophoresis under a low applied electric field of 6.7 V/cm. These studies show that exposure during crosslinking to 2 Tesla magnetic field did not result in detectable alignment of the nanoparticles by diffraction/scattering techniques despite previous reports in epoxies that this alignment did occur, and this seeming discrepancy is attributed to localized bending of the platelets in the hydrogel cell walls. Morphology of the hydrogel cell structure was affected by this magnetic process, as observed using cryogenic SEM studies. Significantly improved separations were noted in the case of the magnetized nanocomposite hydrogel with selective reduction of mobility of OSA over CA. This is the first report of a nanocomposite hydrogel producing better electrophoretic protein separations. The improved separation can be explained as a combination of several factors, including sieving associated with larger number of cells encountered on the protein's path as well as at least two electrostatic contributions, affinity and electro-osmosis.

Methyl Acetate Separation by Pervaporation

T. Winkler, S. Lux, M. Siebenhofer, Graz University of Technology, Graz, Austria

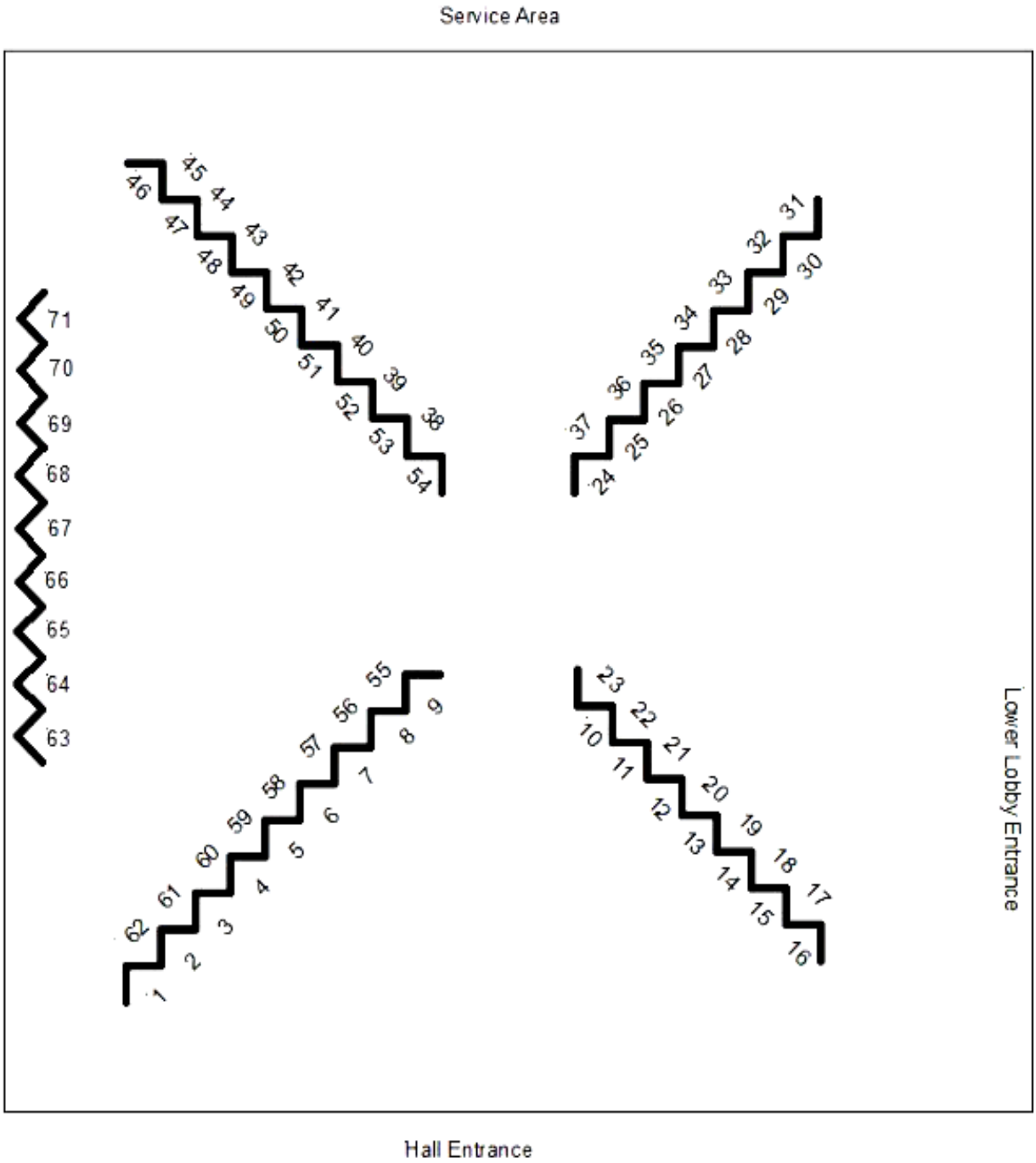
Aim of process intensification is to overcome limitations of mass and heat transfer, through new or different combination of technologies and/or process steps. Thermodynamic limitations and challenges in purification of the desired product are unavoidable when dealing with esterification reactions. Speeding up reaction kinetics of equilibrium reactions and elimination of azeotropes by adaptive configuration of reaction and separation steps was the basic strategy of this research activity. The synthesis of methyl acetate via esterification of acetic acid with methanol served as a model process. Methyl acetate forms low boiling azeotropes with methanol and water. The bulk product methyl acetate is produced in large quantities based on the established Eastman Kodak process.

This project deals with the investigation of alternative paths in the synthesis and purification of methyl acetate. Selective permeation is a promising route of azeotrope breaking. This unit operation can handle higher water contents than reactive distillation technology. Side reactions can be suppressed since operation temperatures are moderate. Esterification is carried out under acid limiting conditions. When using a hydrophilic membrane methanol and water can pass the membrane, whereas methyl acetate is kept in the retentate phase. In case of hydrophobic membranes methyl acetate is transferred into the permeate phase. Separation selectivity and permeate flux of several membranes of hydrophilic and hydrophobic surface properties were investigated. The influence of the operation parameters on the membrane performance was quantified and modeled via a solution-diffusion model. Process schemes for the acid limited reaction route were designed and validation experiments were conducted.

SESSION III – POSTER PRESENTATIONS

Poster abstracts are arranged sequentially beginning on the next page. Also refer to tri-fold brochure.

ARRANGEMENT



1. Phosphonium Carboxylate Ionic Liquids: Preparation, Characterization and Evaluation as Extraction Solvents

S.L. Garvey[*1], M.L. Dietz[1,2], I. A. Shkrob[2], T. W. Marin[2], [*1] University of Wisconsin–Milwaukee, Milwaukee, WI; [2]Argonne National Laboratory, Argonne, IL*

Ionic liquids (ILs) have recently been proposed as substitutes for the conventional organic diluents employed in liquid-liquid extraction processes for nuclear fuel and waste processing. An important but unresolved issue concerning the use of ILs in nuclear applications is the effect of radiolysis on their performance. Preliminary studies have suggested that phosphonium-based ionic liquids incorporating an appropriate aromatic anion should exhibit significant resistance to radiolytic degradation and thus, offer potential in the development of improved methods for actinide and fission product separations. With this in mind, a systematic examination of the synthesis, physicochemical properties (*e.g.*, water solubility), and performance as an extraction solvent of several trihexyl(tetradecyl)phosphonium carboxylates (*e.g.*, [$P_{666,14}$][benzoate]) before and after radiolysis has been undertaken. The results indicate that these solvents, in combination with a crown ether (*e.g.*, dicyclohexano-18-crown-6), can provide satisfactory extraction of radiostrontium at sufficiently high aqueous phase acidities. In addition, no appreciable deterioration of the solvent performance is observed upon radiolysis (*ca.* 200 Mrad). Finally, in contrast to imidazolium ILs, for which the acid dependency of metal ion extraction is often the result of a complex combination of pathways (*i.e.*, ion exchange and neutral complex partitioning), the behavior of these phosphonium ILs resembles that seen for a conventional organic solvent.

2. Taxonomy of the Electrostatic Potential in a Divergent and Convergent Channel for Separation in Microfludic Applications

P. Golbayani, A. Motamedilamouki, P. E. Arce, K. T. Seale, R. Sanders, *Tennessee Technological University, Cookeville, TN*

In modern times the flow in a divergent-convergent channel is of great interest in microfluidic devices for separation applications of relevance for miniaturized biological and chemical detection systems. The combined action of the micro-channel geometry with the particle (solute) properties (surface potential, shape, size, etc.) controls their motion, acceleration, and deceleration through the converging-diverging sections that allows, under favorable conditions, an enhanced separation efficiency.

In this study, based on the solution of the PBE under the Debye-Huckel approximation, for the first time a taxonomy of all physical situations for the electrostatic potential is presented by simply defining a parameter R (the ratio of wall potentials of the micro-channel) and using its values that lead to both limiting cases and a family of cases when R is varied within a given range. R controls the symmetrical/non-symmetrical aspects of the electrostatic profiles within the micro-channel. Two additional parameters complete the description of the electrostatic potential behavior: the angle of the divergent/convergent section (related to the walls of the channels) that handles the "magnitude" of the deviation with respect to a straight channel and the ratio of the width to the length that controls the "shape" of the channel section. Results of this study will be illustrated by using a series of portraits that capture the key behaviors of the electrostatic potential with respect to the three parameters described above. This study is critically needed to understand fluid motion inside the micro-channel to improve separation efficiency in microfluidic devices.

3. Insulator-based Dielectrophoretic Separation and Concentration of a Mixture of Particles

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Miniaturization is continuously presenting alternatives for Lab-on-chip (LOC) or micro-total analysis systems (μTAS) devices. Driven by advances in the fabrication of microdevices, new designs provide alternatives for different necessities. Dielectrophoresis is one of the main techniques being developed for a wide array of microscale applications. Insulator-based dielectrophoresis (iDEP) is the electrokinetic movement of particles due to polarization effects in the presence of non-uniform electric fields; where the field distortion is created by the inclusion of insulators between two electrodes. In the present work, a mixture of particles was separated and concentrated simultaneously in a two-section microdevice by means of DC-iDEP. Each section contains cylindrical insulating posts with different diameter to create two separated regions of dielectrophoretic strength by applying one electric potential across the entire microdevice. Each section has two side channels that are employed to collect the particles after immobilization by iDEP, this is achieved employing a secondary applied potential, allowing for purified and separated particles to be collected in different outlets using electroosmotic flow. By using DC electric fields the requirement of micropumps to move the fluid and particles is eliminated. In this manner, a mixture of 1 and 4 μm microspheres feed into the main inlet was dielectrophoretically manipulated,

achieving collection of the separated particles in their respective outlets. These results demonstrate the potential and flexibility of multisection devices for dielectrophoretic separation of mixtures of microparticles.

4. Effects of Cell Morphology on Dielectrophoretic Immobilization Employing Arrays of Insulating Structures.

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The need for more efficient and clean electrical power sources has led to the miniaturization of processes. This also increases the potential for sustainable and portable use of such energy sources. The study of microorganisms for the generation of sustainable electrical power as in micro bio-fuel cells has led to the need of manipulating bio-particles at a microscale level. Dielectrophoresis (DEP), defined as the motion of a dielectric particle due to polarization effects in the presence of a dielectric medium and a non-uniform electric field. One approach to create non-uniform electric fields is achieved by placing an array of insulating structures between two electrodes in order to distort the distribution of the electric field. This technique is known as insulator-based dielectrophoresis (iDEP), a novel DEP mode that has been proven as an efficient electrokinetic technique for the manipulation of bio-particles in microfluidic systems. In the present work, the performance of an iDEP microdevice to manipulate bioparticles with different geometry shape and size is evaluated. *Saccharomyces cerevisiae* cells with a spherical shape of diameter 5 μm, and Escherichia coli cells with a prolate ellipsoidal shape of 1.5 x 0.75 μm are employed in this work. A computational model is developed to predict and estimate the theoretical trapping zones in the microdevice due to the negative DEP response from the particles employed. Experimental and theoretical results are compared in the present study.

5. Separation of Hemicellulose from Alkaline Pulping Liquors

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Alkaline pulping liquors are concentrated by evaporation prior to combustion. Evaporator capacity is often the rate-limiting step in a pulp mill. By decreasing the organic content and viscosity of pulping liquors, separation of hemicellulose has the potential to increase the throughput of alkaline pulp mills by increasing both evaporator throughput and the final solids concentration of pulping liquors. Crude hemicellulose (which also contains lignin, salts, and extractives) can be precipitated and recovered at a number of different points in a mill using a continuous pulping process. Comparative neutralization, ash and volatiles contents, and desalting of samples from different pulp mill streams were evaluated at bench scale. Filterability improvement resulting from the use of crosslinkers was also evaluated. Downstream markets for crude, purified, and hydrolyzed hemicellulose precipitates, which include chemical and fermentation feedstocks, were profiled. Because the results indicate the possibility of recovering significant amounts of hemicellulose, recycling mill inorganic chemicals, and improving mill throughput, the process should be investigated at larger scale.

6. Kinetic study of DOTA as a Trivalent Ln/An Separations Agent in Advanced Fuel Reprocessing Schemes

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Trivalent lanthanide/actinide separation is an area of ongoing research interest for the development of advanced nuclear fuel cycles. Currently in the U.S. the front runner for this type of separation is the TALSPEAK process. Ongoing research in a number of institutions addresses the possible adjustments to this method to improve its separation performance. This study reports on the results of attempts to substitute the macrocyclic tetraaza complexant 1,4,7,10-tetraazacyclododecane-N, N', N'', N'''-tetraacetic acid (DOTA) for diethylenetriamine-N, N', N'', N''', N''''-pentaacetic acid (DTPA) as the trivalent actinide holdback reagent in an otherwise conventional TALSPEAK separation. DOTA is expected to provide increased actinide selectivity relative to DTPA. However, because of the macrocyclic arrangement of ligand donor atoms in DOTA, it is anticipated that kinetics may be an issue. The rate of complex formation for the Ln-DOTA series has been examined to better understand the effect that the ionic radius of the metal ion has on the rate of complexation. These studies have been conducted in an acetate buffer medium. The results indicate that acetate facilitates the complex formation reaction. Temperature studies have yielded activation parameters that demonstrate a changing mechanism of complexation across the lanthanide series. The combined results from the acetate study and temperature study suggest that DOTA is a viable candidate for application in lanthanide-actinide separations.

7. Washing Characteristics of Heavy Metals from Dredged Marine Sediments

J.C. Yoo, C.-D. Lee, K. Baek, *Kumoh National Institute of Technology, Republic of Korea*

In Korea, sediments in harbor have been periodically dredged to keep the sea water level, and a huge amount of dredged sediments have been dumped into far ocean without further treatment. Unfortunately, the dredged marine sediments had been polluted by heavy metals due to ships, dockyards, rivers and harbor facilities. Therefore, the sediments should be treated properly before final disposal because Basel convention

districts the ocean dumping. In this study, the feasibility of washing process was investigated to extract the heavy metals from dredged marine sediment by using various washing agents such as Na_2EDTA, NaCl, HCl, sodium citrate and HNO_3. Even though the general removal efficiencies of heavy metals were not high, sodium EDTA extracted most heavy metals compared to other agents. HCl extracted slightly more amount of heavy metals compared to HNO_3 because Cl^- formed complexes with heavy metals. This result was confirmed by Visual MINTEQ simulation. Fractionation analysis showed that the metals bound to organic and sulfide changed to exchangeable fraction through complexation reaction. As a result, the complexation or chelation is very important role to extract heavy metals from marine sediments. However, washing technique is not effective to remove metals exclusively from marine sediment, and additional treatment is needed to meet regulation levels. This work was supported by Basic Science Research Program through National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology.

8. Step-Wise Extraction of Metals from Dredged Marine Sediments

J.-C. Yoo, C.-D. Lee, K. *Kumoh National Institute of Technology, Republic of Korea*

Marine sediments have unique characteristics such as high alkalinity, content of fine particles, buffering capacity, and organic matter. Organic matters consist of humic and fulvic acids which combine with the heavy-metals strongly, therefore, they contribute to stabilize heavy metals. Additionally, anaerobic condition reduces sulfate to sulfide, which forms metal sulfide, a stable precipitates. Generally, large portion of heavy metals in marine sediments are fractionated in the form of organic and sulfide. In this study, the feasibility of step-wise extraction methods using various reagents was investigated to extract the heavy metals from dredged marine sediments. The experiments were the sequential extraction procedures (total 5 steps). The methods using HCl, Na_2EDTA/HCl, and Na_2EDTA/NaOH were relatively effective to remove heavy metals except for from the dredged marine sediments. In case of HCl, the heavy metals were gradually extracted compared to the others. When Na_2EDTA/HCl and Na_2EDTA/NaOH were used, most of heavy metals were extracted by EDTA, and HCl and NaOH showed limited effects. The heavy metals extraction was highly dependent on the equilibrium solution pH. Even though little amounts of metals were extracted from sediment by the procedures, this results indicates that EDTA and HCl might effectively remove heavy metals compared to other reagents because of ligand-complexation with metals. This work was supported by Basic Science Research Program through National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology.

9. Photovoltaic Powered Electrokinetic Restoration of Saline Soil

K.Baek, J.-M. Jung, S-U. Jo, D.-H. Kim, *Kumoh National Institute of Technology, Republic of Korea*

Electrokinetic technique has been applied to extract or remove contaminants from soils, sediments, and sludge. Energy cost accounts for 25% of total operation cost of the process. In this study, we investigated the photovoltaic powered electrokinetic system to remove salts from saline agricultural soils. We tested four different systems: solar-powered system (S1), solar-powered system + battery charged by solar panel (S2), normal direct current with power-on during daytime and power-off after sunset (S3), and normal direct current power (S4). There were no big differences in removal of chloride and nitrate, and more than 90% of chloride and nitrate were removed in all systems within 6 weeks. Additionally, more than 95% of exchangeable calcium, potassium, sodium, and magnesium were removed from soil in all systems. However, the average decrease in soil electrical conductivity (EC), an indicator of soil salinity, was 47.7%, 59.8%, 50.4%, and 55.5% for S1, S2, S3, and S4, respectively. The overall pattern of soil EC was very similar with the residual concentration of sulfate, which indicates that the residual sulfate is a major source of soil salinity after EK treatment. S2 showed highest removal of soil EC and other salts compared to other systems, however, S1 showed the lowest removal. The photovoltaic powered electrokinetic system provided a limited amount of electrical energy because the system could not generate any electricity during night time, but the system combined solar panel with rechargeable battery can be an excellent alternative for normal power supply to save energy cost in electrokinetic restoration. This work was supported by Korea Electrotechnology Research Institute.

10. A Pilot Scale Electrokinetic Remediation of Arsenic Contaminated Soil

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Metal contamination has been a serious environmental issue in Korea, especially abandoned mine sites and metal refinery plants. Arsenic is a most frequently observed contaminant, and it has different characteristics of oxyanions compared to other cationic metals. Metal contamination takes place in 50cm depth of soil from top at the sites near metal refinery plants. Electrokinetic remediation can be applied to remediate the metal contaminated soil as an in-situ, however, it is expected that ex-situ electrokinetic process is more effective after collecting the contaminated soil considering the depth of contamination. In this study, the effectiveness of ex-situ

EK technology was evaluated to treat actual As-contaminated soil in a pilot scale (W 1 m x L 1m x H 1.5 m). The average removal of As was 78% in two types of soil after 8 weeks, and the residual concentration met the Korean legal regulation level. Average removal rate was 1.06 mg/kg/day and 1.55 mg/kg/day, respectively, for paddy and dry field. Additionally, fractionation analysis showed that most other fractions and even large portion of residual fraction was removed after EK treatment. Ex-situ application provided more uniform electrolyte to the whole soils, therefore, there were no significant difference of As removal in depth of soil. Based on the results, ex-situ EK process can be an effective remediation technique for As-contaminated site.

This work was supported by Korea Environment Industry and Technology Institute (KEITI) through GAIA project.

11. Electrokinetic Extraction of Heavy Metals From Anaerobic Digestion Sludge: Influence of Pre-treatment Using Acid

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Electrokinetic technique has been applied to remove heavy metals from soil, sediments and sludges. However, the removal is highly dependent on the fractionation of metals in soil matrix. Metals fractionation in soil matrix are categorized into four forms: exchangeable forms (S1), portion bound to Fe/Mn oxides (S2), form bounds to organic matter and sulfide (S3), and residual (S4). It is more difficult to remove the metal in fraction as follows: S4 > S3 > S2 > S1. Acid treatment or redox manipulation might change the fractionation of metals. In this study, we investigated the effectiveness of acid pretreatment to enhance metal removal from anaerobic digestion sludge. Four different processing fluids were applied to evaluate the influence after pre-treatment. The pretreatment changes the fractionation of Cu and Zn from S3 to S1. Without pre-treatment using acid, Zn and Cu were not removed, and the concentration extracted by aqua regia increased a lot because the electrokinetic treatment changed the fractionation of metals. Pre-treatment enhanced metal removal from sludge, and EDTA showed highest removal of Zn upto 75% after 14 days. However, Cu was not removed and the extractability was increased by the treatment. Other processing fluids were not effective to remove Zn and Cu. Acid pre-treatment change the fractionation of Cu and Zn to more extractable forms, and EDTA forms metal-EDTA complexs. However, acid pre-treatment and EDTA circulation lowered the sludge pH to 3.5 – 5.5. After metal removal, pH adjustment is required to further reuse of sludge.

12. Role of Material Morphology on Electrophoresis of Biomolecules: Assesment of Convective-Diffusive Transport in Poiseuille Flows

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Research involving polymer gels with embedded nanoparticles of varying properties is quite attractive because of the multitude of potential applications, including separation of biomacromolecules for environmental proteomics in the assessment of contaminant impact on health issues; more effective and less time consuming clinical diagnostics, growth of tissue in synthetic or natural scaffold etc. Previously, analysis of the effects of the pore length and diameters on the transport of biomolecules was studied either analytically or computationally. In this research, we focus on computationally analyzing different pore models (associated with gel materials) and study the effect of geometry on the transport properties. In particular the role of the convective-diffusive transport via different values for the Peclet number will be assessed. Results will illustrate, for example, the role of pore-scale in conjunction with the effect of electrical fields in assessing different convective-diffusive regimes.

13. Electrochemical Transformation of Selenate in a Sand Column

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Oxyanionic forms of Se, selenate and selenite, are more mobile and more bioavailable than elemental Se and selenide. Selenite can be adsorbed onto ferric hydroxide or other metal oxides, but selenate cannot. Generally, selenate is reduced to selenite, after then it can be removed by co-precipitation method. In this study, sand-packed vertical flow columns were used in laboratory experiments to simulate in-situ electrochemical transformation of selenate in saturated zone. An upgradient iron anode and downgradient cathode, spaced 10 cm apart, was used to create a reducing condition for the reduction of selenate because the reactive anode oxidation prevented the evolution of oxygen which created to more reducing environment. The cathode generated hydroxide ions, and the ions and ferrous transported from anode formed precipitates of ferrous hydroxide, which contributed to transformation of selenate to selenite and elemental selenium. The removal of selenate was proportional to the applied current, but inversely proportional to the flow rate passed through the column. Longer residence time in the sand column resulted in the higher removal of selenate. This result suggests that the in-situ electrochemical system can be applied to treat Se-contaminated groundwater.

14. Removal of Anionic and Cationic Dyes from Water by Fe-Al Binary Oxide

H.-J. Hong, J.-S. Yang, E. J. Kim, Y.-J. Lee, J.-W. Yang, *KAIST, Republic of Korea*

Iron oxide is widely used as catalyst of heterogeneous Fenton reaction for removal of harmful organic pollutants. In this study, catalytic activity of iron oxide was enhanced by incorporating Al on iron oxide (Fe-Al binary oxide). Oxides with different Fe:Al ratios (10:0, 9:1, 7:3, 5:5, 3:7, 1:9, and 0:10) were synthesized and applied for removal of anionic (acid blue 25 [AB25], acid orange 7 [AO7]) and cationic dyes (methylene blue [MB], phenosaframine [PN]). Increase of incorporated amount of Al raised surface area of Fe-Al binary oxide and then improved dye contact with iron oxide. The highest dye removal efficiency was obtained by 5:5 and 3:7 Fe:Al ratio. AO7 which exhibited less complex chemical structure showed fast removal rate and high removal efficiency than the other dyes.

The effects of operation parameters such as Fe:Al ratio of binary oxide, solution pH, initial dye concentration and H_2O_2 concentration on degradation of AB25 were investigated in the presence of Fe-Al binary oxide (5:5 Fe:Al ratio). Dye removal rates were evaluated using first order reaction model. pH was the most important factor to affect the removal rate of AB25. Fe-Al binary oxide could be repeatedly used as a catalyst for dye degradation because little amount of (≈4 mg) Fe loss was observed from 1 g of Fe-Al binary oxide when 100 mg/L of AB25 was degraded completely. Recycled Fe-Al binary oxide exhibited similar AB25 removal efficiency to fresh Fe-Al binary oxide.

15. Effect of Pulse Power on Electrokinetic Removal of Salts from Saline Soil

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Electrokinetic (EK) separation is an emerging technology to control or remove various inorganic and organic compounds from porous media, especially with low permeability by inducing EK phenomena such as electromigration, electroosmosis and electrophoresis. The EK technique can be applicable to restoration of saline soils where a high concentration of salts causes adverse effects on crop growth. In this study, EK field tests were performed in a greenhouse to investigate the effect of pulse power on salts removal from the soil.

A pilot−scale EK test field (2.2 m × 10 m, W × L) consisted of 3 sections and EK test was separately operated in each section with DC or pulse (200 kHz) power mode. Initially, the electrical conductivity (EC) of the soil in the top layer was ranged in 11~18 dS/m and main ions were Ca^{2+}, Na^{+}, Cl^{-}, and SO_4^{2-}. After 1 month of the EK treatment, salts were significantly removed by electromigration, resulting in the reduction of the soil EC. While the soil EC was reduced to 56% in the EK−DC mode, the EK−Pulse mode showed similar results (55%) or even enhanced the EC reduction up to 72%. Besides, the EK−Pulse mode saved half of the electric power consumption of DC mode. Therefore, it is expected that the application of pulse power has advantages of the enhancement of salt removal as well as power saving in EK soil remediation.

16. Vacant

17. Microwave Assisted Extraction of Vanillin from Cured Vanilla Pods

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Conventional techniques of solvent extraction of plant materials are based on the consumption of huge quantity of solvents, heat and agitation to increase the solubility and mass transfer of the desired compounds, leading to enormous energy consumption. Keeping in pace with requirements for development of high performance rapid extraction methods, recent times has witnessed the use of novel extraction techniques with energy conservation concern. One such novel extraction method is the microwave assisted extraction (MAE) which has drawn significant research attention in the last decade.

In this research study, microwave-assisted extraction of vanillin from cured vanilla pods was carried out at lab scale using ethanol-water solvent system and Response Surface Methodology was used to optimize the various process parameters of extraction. Application of MAE dramatically reduced the extraction time by 50%. Maximum vanillin yield of 47.1 mg/g of vanilla pods was obtained from optimized conditions of Microwave power 30W, Irradiation time 90s and Soaking time of 30 minutes. The F-test and p-value indicated that both Microwave Power and Soaking time had highly significant effects on yield of vanillin, quadratic of all the parameters and their interactions also displayed significant effect. The experimental data were fitted in a steady state diffusion model proposed by Wongkittipong et al (2004). Higher diffusion coefficient values were obtained with irradiated material as compared to un-irradiated material, exhibiting that extraction of vanillin is an intra-particle diffusion controlled process and thus proving the feasibility of employing MAE as an efficient extraction technique for extraction of vanillin from cured vanilla pods.

18. Full-Scale Centrifugal Contactor Testing with Next Generation Solvent at the Savannah River Site

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In 2008, the Savannah River Site (SRS) successfully deployed a solvent extraction system for removal of cesium from stored waste from nuclear processing. Now, efforts are underway to qualify the Next Generation Solvent for this Caustic Side Solvent Extraction (CSSX) process. Researchers at multiple national laboratories are involved in this effort.

As part of the development effort, SRNL performed tests using the full-scale contactors that mimic the equipment used in the Modular Caustic Side Solvent Extraction (CSSX) Unit (MCU). The contactors were tested with the Next Generation Solvent, under extraction, scrub and strip conditions. Coalescing behavior and general hydraulic behavior were also studied. Phase carryover, decontamination factors and hydraulic behavior will be discussed.

19. Building Thermodynamic Models of Solution Mixtures to Support Predictive Modeling of Liquid-Liquid Distribution Systems

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Accurate characterization of some liquid-liquid distribution equilibria relies on proper consideration of non-ideal solution chemistry in aqueous electrolyte and non-aqueous solute mixtures. Examples of such metal partitioning systems will be presented. Quantitative description of chemical interactions in complex liquid phases may be realized through the process of thermodynamic parameterization of theoretically represented mixtures. The construction of such thermodynamic models allows for numerical representation of non-ideal solute behavior in aqueous and organic phase components of a liquid-liquid distribution. Here we describe a process of building such thermodynamic model for aqueous buffer: Eu^{3+} / H^+ / Na^+ / NO_3^- / H_2Mal / $HMal^-$ / H_2O, where Mal describes malonate, based on Pitzer ion-interaction theory. Progressive evolution of the model, supported by experimental inquiry of key chemical interactions, will be presented. Predictive description of the equilibrium set guiding the liquid-liquid distribution of Eu(III) between aqueous malonate solutions and mixtures of bis(2-ethylhexyl)phosphonic acid, HDEHEP, in n-dodecane, as afforded by a computational package SXFIT, will be illustrated. The program is an iterative fitting procedure, which allows the identification of an equilibrium model for the distribution of a solute in a liquid-liquid system. To account for solution non-idealities the program uses Pitzer ion-interaction theory to calculate activity coefficients in aqueous electrolyte mixtures. We will discuss the alterations to SXFIT calculations based on continuous improvements in the accuracy of the thermodynamic model for aqueous malonate mixtures.

20. Actinide Extraction by 2.6-Bis[(bis(2-N-octyl)phosphino)methyl]pyridine N,P,P`-trioxide TO(NOPOPO) from Nitrate and Thiocyanate Media

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A wide variety of organophosphorus solvent extraction reagents of varying basicity, geometric arrangement of donor groups and extractant types are known. In current applications and research on nuclear fuels reprocessing, the list of useful organophosphorus extractants ranges from tributyl phosphate (PUREX/UREX process) to various derivatives of carbamoyl(methyl)phosphine oxides (TRUEX, UNEX processes) and liquid ion exchangers like di-(2-ethylhexyl)phosphoric acid (TALSPEAK/DIDPA /GANEX/TRUSPEAK processes). The issues associated with managing phosphate wastes are balanced by the unique range of basicities, coordination geometries and general effectiveness of this class of reagents. As part of a continuing investigation related to minor actinide management, we have investigated the actinide/lanthanide extraction properties of 2.6-bis[(dialkyl)phosphino)methyl]pyridine N,P,P'-trioxide, T(R)(NOPOPO) derivatives. Previously reported results on selected actinide interactions with the tetra-ethyl(hexyl) derivative are here extended with a study of 2,6-bis[(bis(2-n-octyl)phosphino)methyl]pyridine N,P,P'-trioxide, TO(NOPOPO), which offers a distinct advantage (over TEH(NOPOPO)) of being readily purified by recrystallization. This work reports the result of investigations of the extraction capabilities of the trifunctional TO(NOPOPO) in toluene towards trivalent lanthanides and selected actinides; Am(III), Th(IV), Pu(IV), Np(V), and U(VI) from acidic nitrate and thiocyanate media. Initial results indicate that TO(NOPOPO) behaves as a classic, solvating extractant. The stoichiometry of the phase transfer reaction of the actinides into TO(NOPOPO) in toluene has been studied. The impact of nitric acid / nitrate and thiocyanic acid / thiocyanate systems on metal extraction was studied. Back extraction experiments of selected metal ions were performed. Current results indicate TO(NOPOPO) serves as a reasonable substitute for TEH(NOPOPO) for the solvent extraction chemistry of the certain actinides and in fact might offer some advantages over CMP/CMPO extractants.

21. Separation of Heavy Metals by Nitrogen-donor Multidentate Ligands Bearing Pyrazine Rings

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N,N,N',N'-tetrakis(2-methylpyridyl)ethylenediamine (TPEN) is a multidentate ligand, which consists of four pyridine rings and the framework of ethylenediamine. TPEN shows high coordination ability for various metals, especially for soft metals and many researchers studied the extraction separation of various metals by TPEN. However, it is difficult to extract metals in the pH range less than 2, because of the protonation of nitrogen donors. In this study, a new TPEN-type ligands bearing pyrazine rings instead of pridine rings, tpzen (N,N,N',N'-tetrakis(2-methyl-pyrazyl)- ethylenediamine), were synthesized according to the procedure of Karmazin et al. and the extractability and selectivity of heavy metals (Cd^{II} and Zn^{II}) in low pH range was studied. The protonation of tpzen and the the complex formation of Cd^{II} and Zn^{II} with tpzen were measured. Both the suppression of protonation and the improvement of the complex formation for CdII were observed by the titration method using aqueous solution dissolving a small amount of tpzen. The pyrazine-type TPEN derivatives are useful for the complexation with a soft metal in acidic solution. Next, hydrophobic tpzen derivatives with long alkyl groups were synthesized and applied to the solvent extraction tests of CdII and ZnII. These derivatives showed higher extractability and selectivity for CdII than the TPEN derivatives even in highly acidic solution less than pH1. These results suggest that the hydrophobic tpzen derivatives are applicable to the selective extraction of soft metals in acidic solution.

22. Developing Actinyl Force Field for Modeling Solvent Extraction Processes

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Aqueous separation processes are key to the development of advanced nuclear fuel cycle under the Global Nuclear Energy Partnership scheme. Despite significant advances in the field of molecular simulations we are unable to model these processes primarily due to the lack of accurate force fields for actinides. The lack of available experimental data for actinide systems (except for uranyl) precludes employing traditional methods of force field development wherein one refines force field parameters to match experimental thermodynamic or transport properties. To overcome this difficulty a number of research groups have developed force fields based on dimer potential energy surface generated via electronic structure calculations. In this poster we show that force fields developed based on dimer energetics grossly overestimate hydration free energies. We find that it is necessary to include first solvation shell to generate effective pair potentials for simulating condensed phase actinide systems.

23. Redox Chemistry of Third Phases Formed in the Cerium–Nitric Acid–Malonamide–n-Dodecane Solvent Extraction System

M. R. Antonio, L. D'Amico, R. J. Ellis, *Argonne National Laboratory, IL*

Since the early developments of original methods for the extraction and purification of cerium from the rare-earth-elements, the redox chemistry of trivalent and tetravalent Ce has figured prominently in the science of its solvent extraction (SX). The physical manipulations and chemical reactions in SX involving Ce(III) and Ce(IV) may lead to solutions with unanticipated valences, and to systems in which the valence of Ce is not evident. In particular, unexpected yellow colors of organic diluents arising from SX of colorless aqueous mineral acid solutions of $Ce(NO_3)_3$ can lead to speculative assignments of tetravalent Ce based upon its familiar and long-recognized color. Despite current practice and future prospects, there is a dearth of information about cerium valence and coordination chemistry with extractants in aliphatic diluents. This poster contains a selection of results collected from electrochemical, UV and X-ray absorption spectroscopies of the yellow and red third phases formed upon extraction of Ce(III) and Ce(IV), respectively, in nitric acid with the malonamide extractant known by the abbreviation DMDBTDMA at a concentration of 0.5 M in n-dodecane. These results – demonstrating electrochromism – stand at the intersection of two disparate fields: electroanalytical chemistry, on the one hand, and separations science, on the other, providing original insights into third phase phenomena in the SX system isotherms explained elsewhere at this conference (see R. J. Ellis, et al., Solvent Extraction Session, 26 October). This work is supported by the U. S. Department of Energy, Office of Basic Energy Science, Division of Chemical Sciences, Biosciences and Geosciences, under contract No DE-AC02-06CH11357.

24. Zirconium Masking in Actinide and Lanthanide SEParation Process (ALSEP)

E.O. Krahn, A.V. Gelis, *Argonne National Laboratory, Argonne, IL*

Separation of the minor actinides (Am, Cm) from the lanthanides at an industrial scale remains an important technical challenge for closing a nuclear fuel cycle. In proof-of-principle experiments using the TALSPEAK solvent (1M HDEHP/n-ddn) mixed with the neutral extractant N,N,N,N-tetra-2-ethylhexyl dyglycolamide (TEHDGA) TRU and Ln recovery and separation from fission products has been demonstrated. However, in this system there is also extraction of Zr from nitric acid into the organic phase. Once Zr is extracted it can be difficult to

strip, so various complexing agents were added to the aqueous phase in bench-scale experiments to try and inhibit its extraction. Data from these tests will be presented along with experiments at varying Zr concentrations in an effort to determine optimal conditions for Zr masking.

25. Temperature Dependence of Microscopic Structure Formed by Tri-n-butyl Phosphate and Zirconium ion in Extracted Solution

R. Motokawa, S. Suzuki, and T. Yaita, *JAEA(QuBS), Tokai, Japan*

In the solvent extraction of $Zr(NO_3)_4$-HNO_3/Octane-Tri-n-butyl phosphate (TBP), zirconic ions (Zr^{4+}) in aqueous phase are extracted to organic phase with involving a complex formation among Zr^{4+}, NO_3^-, and TBP, i.e., $Zr(NO_3)_4(TBP)_2$. In this solvent extraction process the organic phase is separated into two organic phases: light organic phase and heavy organic phase, which is in particular called as "the third phase", when the solution temperature deceases over a critical temperature. In this study, we investigated the temperature dependence of microscopic structure, formed by TBP, Zr^{4+}, and NO_3^-, in diluent by employing small-angle neutron and X-ray scattering (SANS and SAXS) techniques. As a result, we found that the correlation length of the thermal concentration fluctuation of the organic phase strongly contributes to the third phase formation with varying temperature.

26. Fundamental Investigation of the Next Generation Caustic Side Solvent Extraction (NG-CSSX) Process

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The Caustic Side Solvent Extraction (CSSX) process used at the Savannah River Site for the selective cesium removal from high-level salt waste has been markedly improved leading to the Next Generation CSSX (NG-CSSX) process. The NG-CSSX solvent involves the new and more soluble mono-crown calixarene extractant, MaxCalix. The solvent has a greater capacity for cesium due to the increased solubility and better hydraulics due to the decreased amount of modifier needed while yielding the required decontamination factor for Cs of over 40,000. To accurately predict the distribution of Cs (DCs) from a variety of waste compositions, an improved model of the NG-CSSX is required. To develop this predictive model the cesium distribution ratios were measured for simple aqueous solutions using the NG-CSSX solvent. An empirical equation has been developed, which predicts the distribution of Cs based on the [NO_3^-], [OH^-], [K^+], and [extractant]. The equation predicts DCs for waste simulants within a <±10% error. The program SXFIT has been applied to the distribution data to develop a chemically plausible model for the NG-CSSX process. The results of this study have led to a more solid understanding of this important liquid-liquid extraction.

This research was sponsored by the Office of Technology Innovation and Development, the Office of Environmental Management, and the U.S. Department of Energy.

27. Synergistic Extraction of Dy and La in a System Combining TBP and DBP

A. D. Braatz, T. Anderson, M. Nilsson, *University of California, Irvine*

In solvent extraction systems for the purification of spent nuclear material aggregation phenomena can interfere with the efficiencies of the processes. The predictability of these phenomena have been challenging due to the lack of a fundamental understanding of the mechanism that drives these aggregate formations. To investigate the aggregation more closely, tri-n-butyl phosphate (TBP) and dibutyl phosphate (DBP) in n-dodecane were chosen as the organic phase to be contacted with an aqueous phase containing a single metal ion from the lanthanide series. Lanthanum and dysprosium nitrate solutions at various concentrations between M and M were created in 2M or 0.2M nitric acid to be used as the aqueous phase for these studies. Neutron activation followed by gamma spectroscopy using a high purity Germanium detector was used to determine the distribution ratios under the various conditions and Karl Fischer coulometric titration and potentiometric titration were used to determine some physicochemical properties of the two phases in the system. Preliminary results from these experiments indicate that the same synergistic effect is not shown by the two trivalent metal ions from the lanthanide series when extracted with a combination of TBP and DBP. Possible explanations and future direction of this project will be presented.

28. Degradation Studies of CYANEX® 301

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Despite the numerous studies in the literature focusing on CYANEX® 301, very few explain its degradation in depth. To the best of our knowledge none has explained the inconsistency between the "common knowledge" of "CYANEX® 301 degrades into CYANEX® 272" (dithiophosphinic acid degrading into the corresponding phosphinic acid) and the 31P spectrum obtained by NMR of the degradation compound. The 31P {1H} NMR

analysis of a solution of CYANEX® 301 following prolonged contact with nitric acid shows a very complex spectrum, with resonances about 20 ppm downfield from what could have been expected assuming formation of CYANEX® 272.

The degradation product, which yields multiple resonances in the NMR spectrum that could be interpreted as a triplet of triplets, is actually a condensation product where two molecules of CYANEX® 301 are linked by a disulfide bridge. The explanation of the complexity of the spectrum comes from the comparison with the spectrum obtained for the degradation of a stereoisomerically-purified CYANEX® 301. This purification led to the removal of the [R;S] and [S;R] isomers from the initial mixture, and yielded a white crystalline solid proven to comprise exclusively [R;R] and [S;S] isomers by XRD analysis. It was determined that the chiral carbon induced an asymmetry of the phosphorus atoms upon condensation, leading to a wide combination of magnetically non-equivalent P-31 nuclei. These non-equivalent P-31 nuclei exhibit different coupling through the S-S bond. The complete interpretation of the NMR spectra was established and corroborated by elemental analysis.

29. Separation of Americium from Europium using Pyridine-based Receptors

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Spent nuclear fuel consists of four primary categories of waste: short-lived isotopes, short-lived fission products, long-lived actinides, and long-lived fission products. Of these, the long-lived actinides are particularly difficult to separate from the shorter-lived lanthanide fission products. Yet, the isolation of the minor actinides from the lanthanides significantly reduces the volume of long-lived nuclear waste, and also allows transmutation of the actinides to isotopes with shorter half-lives. Alternatives to the TALSPEAK process for the selective separation of minor actinides, particularly americium and curium, from lanthanides in actual spent fuel are being investigated.

One class of compounds with selectivity for americium and curium under the necessary conditions is pyridine-based receptors. These nitrogen-based BTP/BTBP/BTPhen ligands are desirable for both separation ability and for being incinerable, and can remove pH control and aqueous complexants from the extraction process requirements. This poster will highlight several ligands in this class which were analyzed for their respective stability, solvability in Cs-7SB/Isopar L, and separation ability when in contact with both nitric and hydrochloric acid. In particular, a relatively stable ligand in this class was synthesized in house, characterized via NMR, and studied for extraction ability in this solvent/modifier system.

30. Coordination and Separation Behavior of Actinides, Lanthanides, and d-transition Metals with Phenanthroline Amide (PTA)

T. Yaita, T. Kobayashi, K. Akutsu, S. Suzuki, H. Shiwaku, Japan Atomic Energy Agency

N-alkyl, N-tolyl-1,10-phenanthroline-2-carboxyamide (PTA), which includes O, N as donor atom, is the ligand to respond selectively to the ion having f electron, and effectively works for the separation of tri- and tetra-valent actinides, An(III) and (IV), from the trivalent lanthanides, Ln(III), and the other d-transition metal ions. It is already known in our previous work, in particular, that this selectivity for An(III) and An(IV) arises from the property of which the actinides form the unique chemical bond between actinide 5f and nitrogen 2p orbitals. Regarding the distribution of Pu(IV), Am(III) and Cu(III), the distribution ratios of these ions showed sufficient extractability, namely these were about 200 and the separation factors from Ln(III) were about 50 at pH 2. Exceptionally, the distribution ratio of Pu(IV) above 1M HNO_3 increased linearly. It means that PTA worked as oxygen donor ligand like monoamide only for Pu(IV). On the other hand, the d-transition metal ions except for Pd(II) showed similar separation behavior to Eu(III), while the distribution ratio of Pd(II) gradually increased with an increase in acidity of aqueous solution but it was sufficiently lower than that of An(III) and An(IV) in the extraction from the aqueous solution of pH 2 to 1M HNO_3 solution. Accordingly, the PTA would work as useful extractant for actinides in the spent fuel solution in the acidic region.

In this presentation, we will also discuss about coordination properties of actinides, lanthanides, and the other d-transition metal ions based on X-ray crystallography and EXAFS studies.

31. The Effects of Sky Spectrum on Photovoltaic (PV) Modules

I. B. Karki, †D. Faiman, *J. J. Nakarmi, ‡S. Chatterjee, *Tribhuvan University, Nepal; †Ben-Gurion University, Israel; North Bengal University, Siliguri, India*

In this study, we analyzed the effects of changing spectrum after noon time to till sunset on the three most common types of PVs - polycrystalline silicon (p-Si), single crystal silicon (c-Si), and amorphous silicon (a-Si). Each panel's current, voltage, fill factor and maximum power output were adjusted to STC using corresponding temperature coefficient parameters. We observed, the spectral sensitivity functions (SSFs) for the current and power, increases with increase in pressure corrected airmass for poly and mono crystalline silicon modules, and

in the case of amorphous modules, it seems to be opposite. This means that PV modules are influenced by the sky spectrum.

32. Prediction of Separation Characteristics of Multicomponent Systems for Energy-Efficient Processing

P. Mair-Zelenka, T. Wallek, A. Reiter, M. Siebenhofer, *Graz University of Technology, Austria*

Energy efficiency in separation processes is a high priority task. About 3% of all worldwide energy is needed for distillation purposes. Especially in the field of distillation a strong focus is on crude oil processing. In this project modelling and prediction of boiling point characteristics of crude oil is in operation. State-of-the-art technology in modelling boiling point characteristics of crude oil is the derivation of pseudo component mixtures from boiling point curves. Although pseudo components provide quick support in distillation they are not of much help in the prediction of substance/mixture properties such as cold flow properties.

Our approach is to specify the boiling characteristics of crude oil with real components following an algorithm, which will briefly be presented. The algorithm enables the derivation of the composition of the multicomponent mixture from the True-Boiling-Point (TBP) curve and density characteristics based on the specification of real substances (approx. 100). The main advantage of this approach is the prediction of product properties based on the specified molecular information (e.g. cold flow properties). Further the modelling of different reaction equipment (e.g. hydrodesulfurization, isomerization) based on real components and therefore based on real instead of formal kinetics is possible. Based on the fundamental knowledge of molecular information the specific energy consumption of the overall process and the process steps can finally be kept at minimum.

33. Study and Modeling of High-Level Waste Simulant Slurry Filtration Dynamics

R.C. Daniel, P.P. Schonewill, R.L. Russell, R.W. Shimskey, C.A. Burns, J.M. Billing, R.A. Peterson, Pacific Northwest National Laboratory, Richland, WA

Prediction and control of High-Level Waste (HLW) filtration rates are necessary to maintain waste throughput rates during HLW treatment. Nuclear wastes are complex, having a broad range of dissolved and undissolved solids at high concentrations (~35% total solids by weight) with insoluble solid particle sizes ranging from 0.1 to 100 μm or greater. Given the complex nature of the waste chemistry and the difficulties associated with working with radioactive wastes, filtration data on which predictive models can be based are limited, especially with respect to filtration times relevant to full-scale waste treatment operations, which are on the order of 100 hours. The current study evaluates the rate of filter flux decline during filtration of a Hanford tank waste slurry simulant using a 2-foot-long, 0.5-inch diameter Mott Grade 0.1 sintered stainless steel filter element. The impact of operational parameters such a filter transmembrane pressure, crossflow velocity, and ratio of solids mass to filter surface area on the rate of increase and overall extent on irreversible and reversible fouling are examined. In addition, the efficacy of filter backflush operations at maintaining filter flux is determined. The results of these filtration studies are used to develop predictive models for use in optimizing filter throughput for long-time (~100 hour) filtration operations.

34. Processing Macrobatches 3 and 4 at the Savannah River Site Integrated Salt Disposition Process

T.B. Peters, R.A. Pierce, F.F. Fondeur, M.W. Geeting, S.D. Fink, Savannah River National Laboratory, Aiken, SC*

The Savannah River Site (SRS) is currently removing liquid radioactive waste from the tanks in its Tank Farm. To treat waste streams that are high in ^{137}Cs, ^{90}Sr, and actinides, SRS developed the Actinide Removal Process (ARP) and the Modular Caustic Side Solvent Extraction (CSSX) Unit (MCU). The ARP contacts SRS salt solution with monosodium titanate (MST) to sorb strontium and select actinides. After MST contact, the resulting slurry is filtered to remove the "loaded" MST and entrained sludge. The filtrate is transferred to the MCU for further treatment to remove cesium. The solid particulates then are transferred to the Defense Waste Processing Facility (DWPF) for vitrification. The CSSX process extracts the cesium from the radioactive waste using a DOE EM developed solvent to produce a Decontaminated Salt Solution (DSS), and strips/concentrates the cesium from the solvent with dilute nitric acid.

Currently, SRS is processing the third batch of material (Macrobatch 3). SRNL personnel performed tests using actual radioactive samples of this waste batch for processing prior to treatment. Testing included MST sorption to remove strontium/ actinides and CSSX batch contact tests. The poster will describe the current processing results compared against pervious processing campaigns and will also discuss the qualification efforts for the next campaign, Macrobatch 4.

35. Aluminum Solubility: Experimental Studies in Mixed Sodium Salt Solutions

L. T. Smith, R. K. Toghiani, Y. Xia, and J. S. Lindner, Mississippi State University, Mississippi State, MS*

Large quantities of aluminum are present in the defense wastes located at Hanford. Current technologies call for removal of aluminum in order to reduce cost and overload for HLW vitrification facilities. Dissolution of

either gibbsite ($Al(OH)_3$), or boehmite (AlOOH), through formation of the aluminate ($Al(OH)_4^-$) anion, will require significant additions of caustic. The increased sodium from these additions would impact downstream processing requiring dilution before radionuclide removal and subsequently impact aluminum solubilities. Extensive solubility studies on sodium salts found within Hanford tank wastes have been performed in these laboratories leading to the creation of the ICET V7DBLSLT database. This database has been incorporated into the MSE platform of the Environmental Simulation Program (ESP, OLI Systems, Inc.) and has led to improved model predictions for many of the double salts found during processing tank wastes. A test plan was designed and implemented to investigate aluminum solubilities with selected sodium constituents over a set range of temperatures and caustic loadings in order to examine the amount of caustic required to enable retrieval of the aluminum. Results from these tests and the resulting data regressions for ESP incorporation efforts will be presented.

36. Raman Based Process Monitoring Methods for Continuous Real-Time Analysis of High Level Radioactive Waste

S. A. Bryan, and T. G. Levitskaia, Pacific Northwest Laboratory, Richland, WA*

Raman spectroscopy can be used as a means to determine mineral and chemical species present in waste tank heels in situ. Raman spectroscopy is a vibrational spectroscopic method that provides information on molecular structure, which in turn can be applied to identifying specific species present in a sample material. In this respect, each mineral or chemical compound that has Raman-active vibrations will display a characteristic "fingerprint" in the Raman spectrum.

Modern fiber optic technology makes it possible to measure Raman spectra from remote locations. Indeed, such technology has been developed to monitor the concentration of oxyanions in static HLW supernates at SRS and under flow conditions during the retrieval of tank waste liquids at Hanford. This presentation gives an overview of the process monitoring efforts performed by our group at PNNL directed toward Hanford tank wastes. We will give an overview of the Raman based on-line monitor used for various Hanford tank waste applications, including: real-time analysis of salt-cake dissolution, deployment as a quantitative analytical method for the Pretreatment Engineering Platform (PEP), deployment during treatment operations of continuous sludge leaching (CSL) processing, and development of a telescopic Raman monitor for in-situ analysis for in-tank deployment.

37. A Water Activity Data Assessment for Hanford High-Level Tank Waste

J.G. Reynolds, R. Carter, R.S. Disselkamp, D.A. Greer, Washington River Protection Solutions, Richland, WA*

Water activity is one of the most important thermodynamic parameters governing many separation processes used for treating high-level waste stored in tanks at the Hanford site. Water activity is important for predicting the crystallization of solids that have waters of hydration, such as $Na_2CO_3{\cdot}H_2O$, and $Na_2SO_4{\cdot}10H_2O$. Models are currently being developed to predict water activity in the multi-component, highly concentrated Hanford waste liquids. These models must be fit to experimental data. Most water activity data is scattered throughout the literature and reported in different units. Some data compilations smooth the data, which obliterates the opportunity to evaluate regression statistics when fitting models to the data. Much water activity data is measured by the isopiestic technique, and it has not been clear if the reference electrolyte data is consistent with other data in the reported in databases. This present study compiles a self-consistent water activity database as a function of concentration and temperature for Hanford relevant electrolytes. This study recalculates the water activity from the raw data, thus forcing self-consistency amongst all of the systems and studies. A comparison of data reported across studies indicates that most studies are consistent with each other, but notable differences were observed in some cases. This study found ample data at 298.15 K, but data was sparse at other temperatures for many electrolytes.

38. Sulfate-binding Cages for Separation Applications in Moderately to Highly Alkaline Solutions

A. Rajbanshi, B.A. Moyer, R. Custelcean, *Oak Ridge National Laboratory, Oak Ridge, TN*

Recent breakthrough results on selective sulfate separation from competitive aqueous solutions as found in the radioactive waste stored at Hanford will be presented. Our approach involves the selective crystallization of cages self-assembled from a simple urea-functionalized tripodal receptor L1. The appropriately placed hydrogen bonding groups in L1 coordinate strongly to the sulfate anion within the rigidified cavity of the cage, isolating it from the outer aqueous environment. In addition, the excellent fit of sulfate inside the cage, via the formation of 12 complementary hydrogen bonds, ensures the preferential encapsulation of this anion against competing anions in solution. Further studies led to the optimization of the sulfate crystallization with L1 in the presence of different coordinating metal cations (Mg^{2+}, Na^+, K^+), leading to the development of different separation cycles tailored for various pH conditions. The use of magnesium as a coordinating cation works exceptionally well in

mildly alkaline solutions (pH < 9.5), whereas the sodium cation is well-suited for highly alkaline solutions (pH = 14). This presentation features the study of these two metal-coordinated systems to: (i) probe the stability, efficacy, and recyclability of the receptor L1 in the crystallization of the magnesium-based systems, and (ii) explore the sulfate separation process via crystallization of the sodium coordination cages under more realistic conditions analogous to Hanford waste. The utilization of these two metal-coordinated systems highlights the flexibility of the process with potential applications in selective sulfate separations from alkaline solutions of varying pH. This research was sponsored by the Office of Technology Innovation and Development, Office of Environmental Management, U.S. Department of Energy.

39. The Effect of Temperature on the Dissolution of Lignocellulose in Ionic Liquids

S.A. Morton III; A.J. Placido; A.R. Sharits; L.A. Morton; *University of Kentucky, Lexington, KY*

A significant hurdle for the sustainable development of lignocellulosic derived alternative fuels and co-products is that current strategies do not effectively utilize the lignin portion of available biomass. Ionic liquids have been proposed as a potential solution to this dilemma. These novel compounds have been shown to be promising solvents for the dissolution and/or separation of lignocellulosic biomass into constitutive fractions. Using a thermal-stage equipped optical microscope in tandem with high performance liquid chromatography, we have investigated the effects of temperature and ionic liquid composition on the dissolution of cellulose, hemicellulose, and lignin as well as whole lignocellulosic biomass in selected ionic liquids. Our results have demonstrated that moderately elevated temperature combined with simple changes to the composition of the ionic liquid can have a profound impact on the rate and extent of dissolution of the biomass and its components. Moreover, the capacity of these ionic liquids to dissolve specific components of the whole biomass has the potential to dramatically affect the accessibility of the lignin for further thermochemical conversion. In this presentation we will discuss new developments, potential applications, and remaining challenges for the use of ionic liquids as solvents for the dissolution and utilization of lignocellulosic biomass.

40. The Apparent Solubility of Aluminum(III) in Hanford High-Level Waste Tanks

J. G. Reynolds, Washington River Protection Solutions, Richland, WA

The solubility of aluminum in Hanford nuclear waste impacts many separation processes. For many years, Hanford staff has anecdotally noted that aluminum appears to be considerably more soluble in Hanford waste than the simpler electrolyte solutions used as analogues. There has been minimal scientific study to confirm these anecdotal observations, however. The present study determines the apparent solubility product for gibbsite in 50 tank characterization samples. The ratio of aluminum to hydroxide in the liquid phase for the samples is calculated, and plotted as a function of total sodium molarity. Total sodium molarity is used as a surrogate for ionic strength. These results were compared to the simple $NaOH$-$NaAl(OH)_4$-$H2O$ system, and the $NaOH$-$NaAl(OH)_4$-$NaCl$-H_2O system data retrieved from the literature. The results show that gibbsite is apparently more soluble in tank waste samples than in the simple systems whenever the sodium molarity is greater than 2. This apparent enhanced solubility cannot be explained solely by differences in ionic strength, because the change in solubility with ionic strength in simple systems is small compared to the difference between aluminum solubility in Hanford waste and the simple systems. The reason for the apparent enhanced solubility is unknown, but could include kinetic factors or thermodynamic factors that are not present in the simple systems.

41. Sensitivity Analysis of the Capital Costs of an All Vanadium Redox-Flow Battery

M. Moore, J.S. Watson, T.A. Zawodzinski, and R.M. Counce, *University of Tennessee, Knoxville,TN*

Interest in the development of redox-flow batteries (RFBs) for large-scale grid storage is growing. The VRB has similar system design considerations to both batteries and fuel cells, and considerable investments have been made into the research and development of RFBs over the past few decades. Unfortunately, practical implementation has been hampered by various cost and performance issues typical of an immature state of development.

One critical factor for the competitiveness of this technology is the installed, or capital, cost. ARPA-e has provided an aggressive target of $100/kWh installed, which is a difficult goal to reach. In this work, we incorporate recent developments in all-vanadium RFBs research and present an analysis of the associated cost factors. We previously analyzed VRB systems using chemical process engineering design strategies. The major variables affecting installed cost are identified and varied to determine their sensitivity.

We will elaborate this study in detail to provide a snapshot of the state of the art and to elucidate possible fruitful paths forward. Key findings include high sensitivity of system cost to purity of vanadium and substantial fractions of the cost associated with perflurorosulfonic acid membranes currently used for proton transport.

42. Extraction Chromatographic Clean-up of Potentially Acidic Hanford Wastes Containing $Al(NO_3)_3$ using Tri-n-octyl Phosphine Oxide

J. C. Braley, M. D. Ogden, J. Sulakova, K.L. Nash, *Washington State University, Pullman, WA*

As the Hanford site undergoes remediation, significant economies could be realized if aluminum and chromium are kept from High Level Waste glass produced at the Hanford Waste Treatment Plant (WTP). An acidic scrub of the Hanford sludge could enhance Al removal, although such treatment could lead to the mobilization of transuranic elements. If mobilization were minor, a chromatographic secondary cleanup of the acidic waste stream may be preferred to allow preconcentration of radionuclides prior to processing through the Hanford WTP. This study examines tri-n-octyl phosphine oxide impregnated resins as a chromatographic means for the removal of transuranics from a secondary waste stream. Results indicate >99% of the radioactive material present from an acidic sludge leach may be recovered using extraction chromatography; providing an effective avenue for high aluminum content tank pre-treatment.

43. Thiosemicarbazone and Semicarbazone Chelating Resins and their Use in Environmental Applications

A. J. Crook, D. D. Ensor, E. C. Lisic, *Tennessee Technological University, Cookeville, TN*

The Resource Conservation and Recovery Act (RCRA) was passed in 1976 and is used to regulate the presence of heavy metals in the environment. The presence of metals in the environment is increasing and an effective means for removing harmful metals from the environment is proposed through the use of thiosemicarbazone (TSC) and semicarbazone (SC) chelating resins. These resins are synthesized by attaching the TSC or SC ligand onto a resin bead by ion exchange. The ability to chelate radioactive tracer metals out of aqueous solutions at environmental pH values is being considered. Resin loading data is also being studied to determine the amount of exchange sites occupied by the ligand when placed onto the resin bead. The ability of naphthoquinone sulfonic acid (NQSA), isatin sulfonic acid (ISA), and formyl furan sulfonic acid (FFSA) TSCs and SCs to adsorb radioactive tracer metals $^{63}Ni^{2+}$, $^{109}Cd^{2+}$, and $^{57}Co^{2+}$ is determined by a batch technique at various pH values. Dry-weight distribution, D_w, values are calculated and presented for the various chelating resins.

44. Adsorption Characteristics of As(III) and As(V) onto Sludge from Water Purification Facility

Y-S Kim, S-M Park, J-S Yang**, K. Baek, *Kumoh National Institute of Technology, Republic of Korea, **KIST-Gangneung Institute, Republic of Korea*

Aluminum (Al) has been used as a coagulant to purify water, and the usage generates huge amount of sludge (Alum sludge). The sludge has been treated by ocean dumping or landfill, however, ocean dumping is prohibited, and landfill site is limited in Korea. Therefore, recycling or reuse of this sludge is required. Additionally, it is well known that the material containing Al has adsorption capacity for arsenic (As). In this study, the adsorption characteristics of As(III) and As(V) were investigated to evaluate the potential of Alum sludge to remove arsenic species from water. Adsorption kinetic data was fitted with pseudo-second order kinetic models. The adsorption reaction of As(III) was equilibrated within 1 hr at a initial concentration of 100 mg/L, while the adsorption of As(V) reached an equilibrium within 5 hr at the same initial concentration. The maximum adsorption capacity for As(III) and As(V) was evaluated to 8.8 mg/g and 5.1 mg/g, respectively, at 293 K, and the adsorption and affinity increased in temperature. The adsorption of As(III) decreased with increasing solution pH to around pH 6, after then it increased to around pH 11, but decreased sharply above pH 11. The As(V) adsorption decreased dramatically with increased in solution initial pH. The presence of sulfate did not affect the adsorption of As(III) at the range of 0 – 400 mg/L, however, phosphate decreased dramatically As(III) adsorption because of competition. NaOH extracted 20-30% of As(III) and As(V) adsorbed onto alum sludge. Based on the experimental results, the sludge can be used as an adsorbent for the both of As(III) and As(V). This work was supported by Basic Science Research Program through National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology.

45. Removal of As(III) and As(V) Using Iron-Loaded Sludge From Treatment Plant of Acid Mine Drainage

Y.S. Kim, J.-S. Yang**, K. Baek, *Kumoh National Institute of Technology, Republic of Korea,**KIST-Gangneung Institute, Republic of Korea*

Acid mine drainage (AMD) contains heavy metals and high concentration of ferric ions because of oxidation of iron-bearing minerals. Active treatment plant neutralizes AMD, generates huge amount of iron-loaded sludge, and the disposal of the sludge is an another environmental issue in Korea. Iron mineral and precipitates is well known as excellent adsorbent for As(III) and As(V). We investigated the feasibility of the sludge for an adsorbent for arsenic removal through batch kinetic and isotherm adsorptions and column study. The adsorption followed pseudo second order kinetic models and Freundlich adsorption isotherms. The maximum adsorption capacity was 21.5 mg/g for As(V) and 66.8 mg/g for As(III) at 293 K, respectively. The huge adsorption capacity of the

sludge indicates that the sludge can be used as an adsorbent for As. Additionally, the reuse of iron-loaded sludge as an adsorbent can solve the problem of sludge treatment in the plant.

This work was supported by Basic Science Research Program through National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology.

46. Mn-Fe-CO_3 Layered Double Hydroxide for New Adsorbent of As(III) and As(V)

K. Baek, E. Otgonjargal, J.-S. Yang**, *Kumoh National Institute of Technology, Republic of Korea, **KIST-Gangneung Institute, Republic of Korea*

Arsenic pollution in drinking water or surface water has become a worldwide environmental issue and threatening to human health seriously. As (III) is more toxic than As (V), and the removal of As (III) is more difficult than that of As (V). In this study, Mn-Fe-CO3 layered double oxides (LDOs) were prepared by the co-precipitation methods for As (III) and As (V) removal from solutions. The samples were characterized using X-ray diffraction (XRD), X-ray photoelectron spectrum (XPS) and scanning electron microscopy (SEM). The oxidation process of As (III) and ion exchange process of As (V) into Mn-Fe LDOs were determined by batch and column experiments. Isotherm study in the temperature range of 283-323K was also investigated and the thermo-dynamic parameters were calculated. Adsorption kinetic and isotherm experiments followed a pseudo-second order model and Langmuir isotherms, respectively. NaOH and Na_2CO_3 are very efficiently used for desorption with regeneration regents. Adsorption capacity of As (III) and As (V) was calculated as 1.37, 0.86 mmol/g and column studies obtained values of 70.76, 26.33 mg/g, respectively. The large adsorption capacities of the synthetic adsorbent for As(III) and As(V) indicates that the adsorbent can be used to remove As(III) and As(V) from the contaminated water streams. However, further research is needed to be separated easily after application. This work was supported by KEITI through GAIA project.

47. Optimization and Evaluation of Uranium Sorptive Bio-materials

C. S. Griggs, S. L. Larson, J. H. Ballard, P. S. Barber, and R.D. Rogers, *University of Alabama, Tuscaloosa, AL*

Apatite ($[Ca_{10}(PO_4)_6(OH)_2]$) can be used to immobilize cationic soluble species such as UO_2^{2+} by forming insoluble PO_4^{3-} salts. Raw fish bones, a mechanically-produced byproduct of the fishing industry, is highly microporous and provides a readily available and reactive source of soluble phosphate to react with dissolved metals. Of the raw fish bone material obtained from the fishing industry, 40% consists of residual organics, primarily in the form of collagen. Removal of the residual organics and surface modification provides for increased reactive surface area and enhanced uranium sorption. Introduction of the untreated apatite to density-based fluidized bed reactors, followed by oxidation and thermal treatment steps can produce a sorbent with a high affinity for uranium. Untreated apatite provides a partitioning coefficient (K_d) value of 1,821 mg/Kg. Fully processed apatite provides a K_d value of 23,074 mg/Kg (more than 12 times that of the untreated apatite). This increased uranium partitioning is attributed to the surface area increase from 7.4 m^2/g in the untreated to 87.4 m^2/g processed. Current research to move beyond the dissolution precipitation mechanism provided by apatite, is focused on chitin-derived biomaterials functionalized with selective ligands for preferential complexation of uranyl ion derivatives. Coordination chemistry and sequestration rates from tailored ligands as a function of pH and resulting speciation, offer important design considerations for permeable reactive barriers (PRB) to selectively remove uranium from solution. This presentation will discuss the challenges with apatite based barriers, and current efforts to optimize sequestration by appending uranium selective ligands to chitin polymers.

48. Enhancement of Ion Transport in Carbon Electrodes using Low-Amplitude, High-Frequency Electrical Signals

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Electrosorption of ions by a charged surface submerged in an aqueous electrolyte solution is important in desalination of saline water via capacitive deionization (CDI) and in energy storage devices, such as supercapacitors. Self-assembled mesoporous carbon (MC) materials synthesized at ORNL are promising materials for such applications. CDI experiments have shown that ions transport faster into MC electrodes when a low-amplitude, high-frequency alternating-current (AC) signal is applied. In-situ neutron imaging experiments reveal information on kinetics of ion transport in pores of MC electrodes. Ion permeation experiments through a MC membrane showed an effect of the AC signal on the transport rate of ions.

49. Uptake of Uranium from Seawater: Testing of Sorbents

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Uranium can be found in terrestrial ores and in seawater. This project focuses on harvesting uranium from seawater, where the concentration of uranium is 3.3 parts per billion. Sorbents based on polyethylene fibers functionalized with amidoxime, a proven sorbent for uranium from seawater, are employed for this task. In

adsorption experiments, amidoxime scavenges uranium from 19 L of seawater. Seawater is used as obtained from a location 250 miles east of Savannah, Georgia, and 210 m deep. Initially, two experiments were performed in parallel: in the first experiment, the sorbent contained fibers made by Japanese scientists and in the second, the sorbent contained fibers prepared at Oak Ridge National Laboratory (ORNL). The two sorbents were made of similar materials. Two seawater containers, each containing 19 L of seawater and 5 mg of one of the sorbents, were continuously mixed for 30 days at 24 °C. Samples from each container were taken daily and analyzed by ICP-MS to determine the amount of uranium and other ions present in solution. Results from these two experiments were analyzed to determine how the ORNL adsorbent compared to the Japanese adsorbent, in terms of the rate of uranium uptake. Initial results indicate that the rate of uranium uptake is 0.04 mg per day per gram of sorbent for both sorbents. In a second set of experiments, improved sorbents synthesized at ORNL performed much better than the Japanese sorbent. Sorption results will be compared and discussed with respect to sorbent preparation methods with the objective to develop guidelines for the synthesis of improved sorbents. This research was sponsored by the Fuel Resources campaign in the Fuel Cycle Research and Development program of the Office of Nuclear Energy, U. S. Department of Energy.

50. Speciation Behavior of Americium Higher Oxidation States for the Separation of Americium From Curium in Nuclear Fuel Cycle Separations

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Many countries are currently expanding nuclear energy as a method for the safe generation of carbon free energy. Closed fuel cycle technologies may be key to waste reduction and a sustainable nuclear energy future and in order to support this effort, characterization of key actinides is at the for front of separations research. Characterization of higher oxidation states of americium (Am) has been performed using spectroscopy methods which have recently shown promise for determining Am speciation in these states. Americium in the formal oxidation states of Am(V) and Am(VI) have been prepared by oxidation of Am(III) in acid solution and determined by X-ray absorption fine structure spectroscopy (XAFS), consisting of EXAFS (extended X-ray absorption fine structure spectroscopy) and XANES (X-ray absorption near-edge spectroscopy) analysis. Initial experiments were performed using sodium bismuthate as the oxidizing agent and the oxidized Am species was evaluated using XAFS at Argonne National Laboratory Advanced Photon Source (APS). XAFS was used to examine stereochemical arrangements of atoms in close proximity to Am in different oxidation states. Various methods of Am(V) and Am(VI) characterization are described, including preparation of a stable crystalline complex of oxidized Am for evaluation using single crystal X-ray crystallography. This research will lead to a better understanding of the behavior of this actinide species in both complexed and uncomplexed forms in the stages prior to, during and post separation as well as the separation of trivalent actinides from the lanthanides.

51. Recycle of Zirconium from Used Nuclear Fuel Cladding - an Economic and Waste Reduction Incentive

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Advanced fuel cycle studies are in progress to develop a process and design chemical reactors for the recovery of zirconium from used nuclear fuel (UNF) cladding, containing 98+% hafnium-free zirconium, which has a market value of $40–$80/kg. The cladding is the second largest mass component in UNF assemblies, on average ~25 wt %. The current U.S. generation rate is over 700,000 kg/year, and significant growth is expected in the future. If not recycled, the cladding is a contaminated waste material requiring high level waste disposal in a geologic repository. Therefore, the recycle of the zirconium represents a significant economic and waste reduction incentive for the nuclear energy fuel cycle. Feasibility tests of the recovery process which uses iodine as a recycled reactant is a modification of the "hot wire" process developed by van Arkel and de Boer. Tests were performed during the past year using nonradioactive samples of Zircaloy that are typically used for nuclear fuel cladding. Test results confirmed that zirconium can be recovered in high yield and with sufficient purification from the nonradioactive alloy metals, tin and niobium. R&D studies have progressed to initiate reactor design for the formation of volatile ZrI_4, and subsequent decomposition of the iodide to zirconium metal, and to the removal of volatile SnI_4 from the iodine reagent. Batch reactor design and fabrication for radioactive tests with actual UNF cladding samples are the focus of current studies. Design and testing of continuously fed reactors will complete the project.

52. The Behavior of Nitrous Acid in the HNO_3/TBP Extraction System

M. Precek, A. Paulenova, Oregon State University, Corvallis, OR*

Nitrous acid (HNO_2) is an important redox-active compound significantly influencing the extraction behavior of neptunium and plutonium during separation processes based on extraction of these actinides from tri-n-

butylphosphate (TBP) from aqueous nitric acid (HNO_3) solutions. High nitrous acid content in the aqueous phase acts as a stabilizer of extractable tetravalent plutonium but also leads to the reduction of a significant portion of neptunium to its inextractable pentavalent state.

Analysis of extraction and radiolytic production and extraction behavior of HNO_2 in the HNO_3/TBP system has been performed. Nitrous acid was found to be well extracted (log D ≈ 1), while HNO_2 radiolytic yields from HNO_3 in the organic phase are significantly higher than from HNO_3 present in the aqueous phase that it the organic phase is in contact with. This is explained as a result of much smaller presence of nitrite-scavenging intermediate species produced by the radiolysis of water (such as are the hydroxyl radical or hydrogen peroxide).

53. Optimization of Centrifuge Extraction Operation by Visualization of Oil-water Countercurrent Flow

**M.Nakase, R.Makabe, K.Takeshita, H.Kikura, *Tokyo Institute of Technology, Tokyo, Japan*

The authors are developing an oil-water countercurrent centrifuge extractor with an inner rotor and an outer stable cylinder. Aqueous and organic phases are flowed counter-currently through the gap between the inner rotor and the outer cylinder. When the coquette flow of aqueous phase by rotating the inner rotor reaches to a critical Ta number, Taylor vortices are formed in the aqueous phase. Then the organic phase is dispersed by the shearing force on the rotor surface and flowed up in the Taylor vortices of aqueous phase. The stable countercurrent flow of oil and water is maintained by the formation of Taylor-vortex flow. High extraction efficiency between oil and water with multiple theoretical stages is attained.

In this study, the relation between the extraction rate and the countercurrent flow is examined. The extraction of Zn with D2EHPA was tested in the extractor and the oil-water countercurrent flows are visualized by the UVP (Ultrasonic Velocity Profiler) method. Axial flow rate of aqueous phase and rotating speed of the inner rotor were changed in the ranges of 3 to 20 cc/min and 800 to 1500 rpm, respectively. As a result of the UVP measurement, the Taylor-vortex flow of the aqueous phase was classified into 3 types, such as (A) ascending vortexes, (B) stationary vortexes and (C) unstable turbulent vortexes. The flows of (A) and (B) were observed in lower rotating speed range of the inner rotor below 1200 rpm and the flow (C) in higher rotating speed. The extraction efficiency of Zn was increased with increasing the rotating speed of the inner rotor, because of the improvement of the oil dispersion and the increase of the oil residence time with increasing the oil hold-up. However, in the flow range of (C), the extraction efficiency was reduced due to the increase in the axial mixing effect with the instability of oil-water counter-current flow. These results indicate that the optimal centrifuge extraction operation can be decided visually by the UVP measurement of oil-water countercurrent flow.

54. Separation Characteristics of Manganese as a Surrogate for Americium during the Distillation Operations of Pyroprocessing

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The loss of americium metal during the pyroprocessing of used nuclear fuel has long been a concern due to its high vapor pressure relative to the operating conditions of the process. In particular, the actinide products containing as much as 5 wt. % of americium would be affected by evaporative losses during the process. Of the two high temperature vacuum operations (distillation and casting) performed during pyroprocessing, the distillation operation would incur significantly more americium losses by at least an order of magnitude. The distillation operation is required for the removal of both cadmium and salt from the actinide products. Thus, a series of tests were initiated to investigate the evaporative characteristics of manganese as a surrogate for americium during distillation operations.

Although the use of manganese as a surrogate for americium vaporization is well established, an assessment will be provided that compares the efficacy of manganese to americium in terms of their thermochemical properties. The results for the separation of manganese will be presented from the test program and compared against modeled data. Modeled data will also be shown for americium evaporation and adjusted for the differences noted. It is anticipated that less than 5 wt. % of the americium will be lost during the distillation operation of actinide products during the pyroprocessing of used nuclear fuel.

55. Modeling of Metal Ion Transport in TALSPEAK-Like Extraction Systems

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Modeling of extraction equilibria is critical for predicting the transport behaviour of metal ions under varied liquid-liquid extraction conditions. This report describes our initial method development directed toward assembling a library of the thermodynamic parameters (i.e., Pitzer ion interaction parameters) required to

accurately model liquid-liquid extraction data involving non-ideal aqueous electrolyte solutions. In this work, complex liquid-liquid extraction schemes such as the Trivalent Actinide-Lanthanide Separation by Phosphorus reagent Extraction from Aqueous Komplexes (TALSPEAK) and related TRUSPEAK (that combines the Transuranic Extraction process extractant, CMPO, with the TALSPEAK solvent) serve as model processes. Preliminary results of the SXLSQI modeling of the extraction behavior of the Na^+, Nd^{3+}, and Eu^{3+} metal ions by HDEHP with and without CMPO are discussed.

56. N-Donor Ionic Liquids as Unique Environments for f-Element Chemistry

S. P. Kelley, E. L. Stoner, R. D. Rogers, *University of Alabama, Tuscaloosa, AL*

The interaction of soft Lewis bases with lanthanides and actinides has been a research focus for many years. Although lanthanide and actinide cations are both considered hard Lewis bases, trivalent actinides are known to show a greater affinity towards soft donors than trivalent lanthanides of similar size-to-charge ratio. This is one of the only effective ways of separating these elements. The mechanism behind this is disputed but often cited to be due to greater availability of actinide 6d and 5f electrons for back-bonding. However, a detailed study of f-element interactions is made difficult by the fact that most solvents used in metal coordination chemistry are themselves hard Lewis bases and will readily bond to f-elements. ILs, defined as salts with melting points below 100°C and whose melts consist solely of ions, have already received attention as replacement solvents in extraction of f-elements for a number of reasons. We are interested in studying the interactions of f-elements with ILs containing soft Lewis basic anions. These ILs can offer an environment consisting entirely of free, soft basic anions with no other solvents to cause interference. Our group has prepared classes of ILs and IL precursors which can be used for this purpose such as ILs based on the azolate ion. In this poster we present our studies on the interactions of these moieties with f-element salts, including the crystal structures of uranyl complexes with N-donors grown from ILs.

57. Application of Ionic Liquids for Separations in the Thorium Nuclear Fuel Cycle

E.L. Stoner, S.P. Kelley, R.D. Rogers, *University of Alabama, Tuscaloosa, AL*

Ionic liquids (ILs) have shown promise in the area of separations and are currently being explored as a means of replacing volatile organic solvents and providing new avenues for liquid-liquid extractions such as in nuclear waste reprocessing applications. Despite a limited number of high-grade uranium ore deposits and the possibility that the U.S. will have to rely on an imported supply of fuel to maintain widespread nuclear power production from a ^{235}U cycle, the U.S. currently utilizes the once-through uranium nuclear fuel cycle. Most IL research in this particular arena, therefore, has focused on the use of ILs to address separation challenges associated with the consumption of ^{235}U. The thorium based nuclear fuel cycle offers certain benefits over the once-through uranium cycle including lower a) operating costs, b) dependence on a foreign fuel supply and importation, and c) proliferation concerns. The use of thorium as nuclear fuel, however, is also associated with a number of separation challenges on both the front and back ends of the nuclear fuel cycle. The study of ILs and the thorium based nuclear fuel cycle offers a unique opportunity to address these challenges and integrate the use of ILs throughout the reactor cycle as it is developed. Continued study of thorium in ILs will also help further the understanding of fundamental thorium chemistry. This presentation will provide an overview of our motivation for this research, our current results, and our future challenges.

58. Pilot Test for Separation of Sr^{2+} and Nd(III) from HLLW Using TiBOGA

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A pilot test for the separation of strontium and trivalent lanthanides/actinides, using Nd(III) as surrogate, from a simulated acidic high level waste (HLW) has been performed with a 10-mm centrifugal contactor pilot plant using N,N,N'N'-tetra-iso-butyl-3-oxa-glutaramide (TiBOGA) as extractant. The test shows that Sr^{2+} and Nd(III) can be co-extracted from HLW and then separated from each other by step stripping. The results indicate that 99.99% Sr^{2+} and Nd(III) can be removed from HLW, and less than 0.01% of Nd(III) remains in Sr^{2+} product stream and 0.1 of Sr^{2+} in Nd(III) stream. The hydraulic performance of HNO_3 solutions –0.2 M TiBOGA in 40% n-octanol/kerosene system and the mass transfer stage efficiencies of HNO_3 and Sr^{2+} have also been studied on a single-stage 10-mm centrifugal contactor.

59. Thermal Stability of Formohydroxamic Acid

F. F. Fondeur and T. S. Rudisill, *Savannah River National Laboratory, Aiken, SC*

Formohydroxamic acid (FHA) was evaluated as a replacement for acetohydroxamic acid (AHA) in the uranium extraction (UREX) process to prevent the extraction of Pu and Np into the tributyl phosphate solvent. The replacement of AHA with FHA eliminates acetic acid from the UREX waste stream which is produced by

acid hydrolysis. Both of the FHA decomposition products (formic acid and hydroxyl amine nitrate) readily decompose to gaseous products and water. Following the procurement of FHA for use in the UREX evaluation, the Savannah River National Laboratory was notified by the manufacturer that a bottle of FHA from the same lot of material had generated sufficient pressure to break the cap and expel material from the bottle while stored at ambient conditions. Prior to evaluating the use of FHA in the UREX process, the thermal stability of the material was examined by accelerating rate calorimetry. Experimental assessments were performed using the solid material and 1 M solutions of FHA dissolved in water and 1 M nitric acid. Preliminary data from the thermal stability studies demonstrated that the FHA could be used in the UREX process evaluation without undue concern; however, the thermal stability of the solid material was a concern above approximately 60 °C. Based on this data, additional studies were performed using differential scanning calorimetry and thermal gravimetric analysis. The data from the thermal decomposition studies are reported and recommendations for storage conditions which minimize the potential for gas generation or thermal decomposition of the FHA are provided.

60. Design and Coordination of f-Elements with Amidoxime-Functionalized Ionic Liquids

P.S. Barber, S. Kelley, R. D. Rogers, *University of Alabama, Tuscaloosa, AL*

Of the 20-30 tons of spent nuclear fuel (SNF) waste produced for every year of nuclear power generation, only one weight percent is highly radiotoxic and considered a long-term hazard. If this material could be efficiently separated from bulk, it would reduce the waste storage time from several thousands of years to a few hundred years. Current efforts for the separation and reprocessing of SNF involve the use of volatile organic solvents. Ionic liquids (ILs) are a class of organic salts with melting points below 100°C that are currently being investigated for their interesting properties and the ability to replace traditional and highly volatile solvents. While ILs make suitable replacements for traditional solvent, they also have potential to revolutionize SNF reprocessing through the tunability of their physical prosperities and the ability to incorporate solvent and extractant as one material. ILs also offer radiation stability that rivals traditional solvents. Our current efforts in this field include the design and synthesis of an amidoxime [R(-NH2)(=NOH)] functionalized IL. Amidoximes have been shown as effective ligand for the coordination of transition metals and uranium, but have not been studied as ionic liquids. Incorporation of this ligand into an IL may allow new avenues of extraction and tunable selectivity. Here we present our results towards designing an amidoxime-functionalized IL for investigating the coordination of this functional group to f-elements.

61-62. Vacant

63. Value Added Products from Lignocellulose Based Biochar

R.Feiner, N. Schwaiger, S. Lux, M. Siebenhofer, *Graz University of Technology, Austria*

New complementary technologies are required to meet the directives of the European Commission to increase the amount of biofuels within the field of motor fuels to 10% until 2020. Gasification of the feedstock and liquefaction by Fischer-Tropsch-Synthesis is an established way. Another promising route of producing liquid energy carriers from biomass is Liquid-Phase-Pyrolysis. Beside biocrude condensibles of medium quality combustion properties biochar is a major product of Liquid-Phase-Pyrolysis with a broad field of applications. The specific surface area of biochar gives access to chemical modification even including intermediates for fuel synthesis.

Liquefaction of biochar by catalytic hydrogenation is carried out in a batch reactor of 1100 ml volume. The reactor can be operated at a maximum pressure of 20 MPa and a maximum temperature of 400 °C. Batch size is 25g to 50g of biochar dissolved in n-alkane carrier. Prior to liquefaction biochar is carefully mixed/impregnated with the catalyst (5 wt% at maximum) and dried to minimize physically dissolved water. Overall kinetics of liquefaction is deduced from monitoring hydrogen consumption.

With molybdenum based catalysts and hydrogenation at T=370 °C and P = 18 MPa the formation of a wide range of alkanes <C30 as well as cycloalkanes is observed. Latter substances are assumed to be derivatives of the lignin structure. Tar like liquids, supposed to be asphaltenes, also have been detected but are still subject of investigations. Asphaltenes seem to be an intermediate during conversion of coal to oil by hydrogenation.

64. Nitrophenol Hydrogenation Using Pd Immobilized on Ionic Liquid-Alginate Spherical Resins

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Alginate was used for the immobilization of an alkylphosphonium ionic liquid (IL, Cyphos IL111, Cytec). The IL-alginate resin served for Pd(II) binding from HCl solutions. After chemical reduction of Pd(II), the composite was tested for the hydrogenation of nitrophenols (NPs) using sodium formate or formic acid as the hydrogen donor in

batch system. The influence of agitation speed, particle size, type and concentration of hydrogen donor (HD) and pH have been evaluated for 2-NP, 3-NP, 4-NP and 4-NA. The agitation speed does not interfere on hydrogenation kinetics: the film diffusion is not the rate limiting step. The pH influences the catalytic efficiency and the kinetics: a pH close to 2-3 appears better than pH 1. The concentration of the HD does not influence kinetic profiles above 0.25 M. The modeling of kinetic curves depends on experimental conditions: zero-order rate equation at pH 1, and variable order reaction rate or reversible reaction rate for other pHs, depending on HD concentration and type. In the last section of the manuscript a new conditioning of alginate-Il-Pd support was tested in column system (with feed solution recycling) under similar conditions (HD, etc.). Highly porous monoliths have been prepared while immobilizing the IL in the biopolymer matrix. The feed solution is circulated through the porous network and the reaction occurs on the globules that contain the IL and Pd nano-crystals, at the surface of the polymer structure (SEM-EDAX analysis). This new conditioning of the catalyst and its application in dynamic and recycling mode allows fast conversion of the substrate (about45-60 minutes versus 3-4 hours with spherical resinsn batch system).

65. Modeling Oil-in-Water Coalescing Behavior on Polyphenylene Sulfide Fibers: Experiments Versus Computations

F. F. Fondeur, S. D. Fink, Savannah River National Laboratory, Aiken, SC*

Since 2008, the Savannah River Site has decontaminated more that 1.5 million gallons of supernate waste using solvent extraction driven by centrifugal contactors. At times the success of that campaign has been limited by the coalescing performance of a cartridge of fibrous polyphenylene sulfide (PPS) that improves the oil separation from water in decanters. During processing, the pressure differential across the coalescer steadily increases beyond operational limits prompting cessation of operations, cleaning procedures and limited reuse of the coalescer. Analysis of spent coalescers revealed the effectively irreversible trapping of inorganic material on the fibrous beds as well as some sorption of components from the solvent. This work modeled the hydrodynamics and coalescing efficiency of a fibrous bed using PPS surface energy (from wetting angle measurements) to predict modifications of the oil particle size distribution. The model was used to predict the effect bed length, fiber diameter, temperature, and fluid velocity on coalescing behavior. The model predicted a maximum in coalescing performance with bed length as well as with fluid velocity. The model also includes an oil-on-fiber sorption isotherm (irreversible sorption) to model the effect of plugging. The same method was applied to model heterogeneous nucleation on the PPS fibers when a supersaturated solution of aluminum and silica flows through the coalescer bed. The model has been used to predict the coalescing behavior of other surface energies (other materials) that could be used to maximize coalescing and minimize heterogeneous precipitation.

66. The Chemical and Radiation Resistance of Polyphenylene Sulfide under Solvent Extraction Conditions

F.F. Fondeur, M.R. Poirier, D.T. Herman, T.B. Peters, S.D. Fink, Savannah River National Laboratory, Aiken, SC*

The Savannah River Site (SRS) has processed more than 1.5 million gallons of supernatant waste. Using solvent extraction driven by centrifugal contactors. The process uses cartridges of fibrous polyphenylene sulfide (PPS) to supplement the oil separation from aqueous solutions in downstream decanters. Success of that campaign has resulted in part due to the resiliency and durability of PPS fibers used in coalescers to the severe conditions of radioactive liquids containing large number of different compounds. This work shows the degree of resistance of PPS to the simultaneous application of chemical (including supersaturated solutions of aluminum) and radiation stress. The work shows the pathway decomposition of PPS under radiation in air and in presence of caustic solutions saturated in aluminum. The data predicts the lifetime of PPS in contact with radioactive supernate and explain the resiliency of PPS under this environment.

67. A Step by Step Design for Membraneless and High Energy Density Redox Flow Battery

M Zhang, T.A. Zawodzinski, R.M. Counce, J.S. Watson, University of Tennessee, Knoxville, TN*

Large-scale electrical energy storage (EES) has been considered as an effective method to utilize the fluctuating electricity from sustainable energy. It can smooth input power to stabilize the electrical grid and can be used for peak load shaving. Among various EES technologies, redox-flow batteries (RFBs), such as the all-vanadium RFB system (or VRB), are being pursued as a promising direction based on their electrochemical performance and efficiency. Though multi-MWh VRB systems have been demonstrated, three significant limitations constrain its wide deployment. First, high cost, high purity vanadium solution comprises up to 45% of the total system building cost. Secondly, an expensive ionic exchange membrane is required and electrolyte cross-over decreases energy efficiency. Thirdly, the inherently low energy density leads to the need for a large volume of tanks to store electrolytes.

To solve the above limitations, an active energy material might be utilized to replace vanadium electrolyte in redox-flow battery, such that more electrons can be produced/consumed in electrochemical reactions. In certain designs, the cell contains a single electrolyte compartment, eliminating the membrane and circumventing self-discharging. We used a hierarchical decision procedure to design this conceptual flow battery to achieve high energy density. The building cost of this conceptual battery in each step can be predictable to offer optimization suggestions. Sensitivity analysis considering battery performance parameters was applied to evaluate the cost limiting factors. Optimization and development of the conceptual flow battery could accelerate the progress of electrical energy storage techniques.

68. Modeling Water Activities for Aqueous Sulfuric Acid

D. R. Caldwell, R.M. Counce, J.S. Watson, T.A. Zawodzinski, University of Tennessee, Knoxville, TN

The purpose of this research is to develop a simple model to predict the activities of water for aqueous sulfuric acid solutions. Data of the partial pressure of water is given at various temperatures ranging from 0° to 310° C at different concentrations of sulfuric acid in the literature This data is then modeled to predict the activity of water from a given temperature and concentration of sulfuric acid within a specified range. This model is then tested against limited data of the binary system to measure its ability to predict the activities of water. The Stokes Robinson-Brunauer Emmett Teller (BET) model is used to determine a relationship between temperature, concentration, and water activity. The Stokes Robinson BET model is typically useful for concentrated ionic solutions. This paper discusses the application of Stokes-Robinson-BET model to the sulfuric acid – water system.

69. A Step by Step Methodology for the Design of a Base Case Redox-Flow Battery

M. Moore, R. M. Counce, J.S. Watson, T.A. Zawodzinski, University of Tennessee, Knoxville, TN*

The growing demand for energy and the resulting strain on the electrical grid has exposed the vulnerabilities of our decades old electrical power production and distribution system. As renewable energy sources are added, fluctuations of electricity supply and demand are larger. A possible solution to fluctuations and shortages in electrical generating capacities is the use of flow batteries for energy storage. These devices can store electrical energy when generating capacity exceeds the demand for electricity and release the electrical energy during periods of high demand. Flow batteries have only recently moved from the laboratory to industry, however, and more information is needed for design and evaluation of flow batteries. Adding to this difficulty, the handful of companies building flow batteries today often consider this information proprietary and do not always release sufficient information for independent evaluations. This paper presents a procedure to generate a base case design for a redox-flow battery that can be used to explore the effects of selected design and operating parameters on battery cost and performance. This approach uses an evolutionary procedure where the major components of a redox-flow battery are added to the flow sheet at discrete decision levels. The method provides a profitability analysis at each decision level so that more profitable alternatives and directions can be indentified before additional time and effort is expended on an impractical design. This paper shows results for a base case and illustrates how the resulting program can be used to assess parameters in battery design and performance.

70. Tank Type IIIa Analysis and Cleaning Protocol

F. F. Fondeur, T. L. White, L. N. Oji, C. J. Martino, W. R. Wilmarth, Savannah River National Laboratory, Aiken, SC*

Solid residues on two sets of thermowell pipe samples from the D2 riser in SRS Tank 48H were characterized. The residue thickness was determined using the ASTM standard D 3483-05 and was found to be three order of magnitudes below the 1mm thickness estimated from an earlier video of the tank cooling coil inspection. The residues appear to consist primarily of potassium tetraphenylborate (39.8 wt% KTPB) and dried salt solution (33.5 wt% total of nitrates, nitrites and oxalate salts), although ~30% of the solid mass was not accounted for in the mass balance. A residue leaching protocol was determined, successfully implemented, and Tank 48H was returned to operation.

SESSION IV – ADSORPTION AND ION EXCHANGE

Application of Molecular Mechanics and CSTR Experiments to Study Metal Adsorption by Oxalate-modified Activated Carbons

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This paper presents a novel approach to the study of metal adsorption on modified carbon adsorbents by combining molecular mechanics and adsorption experiments. Initially, a peat-based activated carbon (AC)

having a well characterized surface was used to establish the adsorption capacities of heavy metal cations in acidic and neutral solutions. Thereafter, the peat-based AC surfaces were immobilized with oxalate ($C_2O_4^{2-}$) molecular groups and then applied to adsorb several heavy metal ions from the bulk solution using fixed-bed and CSTR reactors. Experimental results showed that negatively charged oxalate-modified ACs adsorbed heavy metals more than native ACs and the results were modeled.

In addition, adsorption of oxalate on activated carbon was studied using molecular mechanics. The COMPASS force field was used since previous calculations of molecular adsorption on activated carbon showed that this force field yields structures and adsorption strengths that are in good agreement with first principles results. Initial calculations were performed in the absence of water and showed that the oxalate adsorbs strongest to carboxylic acid functional groups (adsorption energy -34.8 kcal/mol) compared to ester (-28.4 kcal/mol), ketone (-26.4 kcal/mol) and ether (-18.3 kcal/mol) functional groups. Since carboxylic acid groups are the dominant type of functional groups on activated carbon, and since the binding energy of oxalate to the bare surface is very small (-5.0 kcal/mol), the calculations suggest that these functional groups dominate the adsorption of oxalate to the activated carbon surface. Addition of water to the carboxylic acid – oxalate complex does not break the intermolecular bond but acts to hydrate the entire complex. On the basis of molecular mechanics and experimental data, new adsorbents were synthesized using saw dust precursors.

Rapid Removal of Mercury from Aqueous Solutions Using Thiol Functionalized Biosynthesized $Zn_{0.6}Fe_{2.4}O_4$ Nanoparticles,

F.He, W. Wang, J.-W. Moon, L. Liang, Oak Ridge National Laboratory, Oak Ridge, TN*

Zn-doped magnetite nanoparticles ($Zn_{0.6}Fe_{2.4}O_4$) were synthesized through biofermentation and functionalized with mercaptopropyl-trimethoxysilane (MPTS), and then used as a high-capacity and collectable adsorbent for mercury removal. FTIR characterization confirms the attachment of MPTS on the nanoparticle surface. X-ray Diffraction (XRD) showed that the crystalline size of $Zn_{0.6}Fe_{2.4}O_4$ particles is 17.7 nm, while the scanning electron microscope (SEM) and dynamic laser scatting (DLS) analysis revealed that the particles aggregated in aqueous solution and form aggregates with average hydrodynamic size of 826±32 nm. The $Zn_{0.6}Fe_{2.4}O_4$ particles have a calculated saturation magnetization of 90.7 emu/g and can be simply separated from water within a minute using a magnet. Sorption of mercury to the nanoparticles was much faster than other commercial mercury sorbents and the mercury sorption isotherm in an industrial wastewater follows Langmuir model with a maximum capacity of 416 mg/g. The $Zn_{0.6}Fe_{2.4}O_4$ particles were stable in a range of solutions, from contaminated water to acid/base solutions.

Evaluation of Potential Eluants for Non-Acid Elution of Cesium from Resorcinol-Formaldehyde Resin

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This is a continuation of the Part I study, which used batch contact sorption equilibrium tests to screen 36 potential non-acid eluants. It was followed by actual sorption (loading) and elution confirmation tests of the top candidate eluants via batch contact sorption and quasi column caustic wash/water rinse/elution.

This Part II study seeks to optimize the elution process using the typical sRF-cesium ion exchange column process (i.e., loading, caustic wash, water rinse, and elution) on two potential eluants – ammonium carbonate and ammonium acetate. Parameters of interest are concentration, pH, eluant combinations, and temperature.

The data gathered so far indicate all the eluants (including nitric acid - the benchmark eluant) are promising cesium eluants. At the end of 22 hours (about 25-31 bed volumes [BV]) of elution, each of the eluants regardless of concentration, pH, eluant combination, and temperature had attained virtually 100% cesium elution. The percent elution at the end of 6 hours (about 7-9.3 BV) of elution for some of the eluants are relatively high to infer that 100% elution will occur closer to the 6th hour than the 22nd hour.

Ion Exchange Kinetics Testing with SRF Resin

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Ion exchange using the Spherical Resorcinol-Formaldehyde (SRF) resin has been selected by the U.S. Department of Energy's Office of River Protection for use in the Pretreatment Facility of the Hanford Tank Waste Treatment and Immobilization Plant (WTP) and for potential application in an at-tank deployment for removing 137Cs. Recent proposed changes to the WTP ion exchange process baseline indicate that loading may include a broader range of sodium molarities (2 to 8 M) and higher temperatures (50°C) to alleviate post-filtration precipitation issues. Therefore, it is important to understand the behavior of SRF resin performance under the conditions expected with the new equipment and process changes.

This research examined the impact of linear load velocity (4, 6, 8 cm/min), initial sodium concentration (2, 5, 8 M), initial sodium-to-cesium ratio (1.4E+05, 2.1E+05, 2.8E+05 mol/mol), initial sodium-to-hydroxide ratio (2.0, 3.0, 4.0 mol/mol), and high free hydroxide on resin degradation during extended solution flow using elevated temperature (45°, 50°, 55°, 60°, 65°, 75°C). Testing was performed using an ~1mL column packed

with resin with feed flowing through it in an up-flow pattern. Samples were taken at set intervals and the data analyzed to help understand the impact of these conditions on the SRF resin performance.

It was found that the kinetics were all good under these test conditions and the velocity of the flow was the most important variable in the determination of the loading.

Platinum(IV) recovery from HCl solutions using Amberlite XAD-7 Impregnated with a Tetraalkyl Phosphonium Ionic Liquid

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An ionic liquid (IL) (Cyphos IL-101; tetradecyl(trihexyl)phosphonium chloride, Cytec) was immobilized in Amberlite XAD-7 for preparing extractant impregnated resins (EIR). The IL content was varied in the resin between 59 and 586 mg IL g-1. The EIR were used for Pt(IV) recovery from (0.01 – 8 M) HCl solutions. Platinum sorption efficiency increased with IL loading (>99% for EIR with 586 mg IL g-1 in 0.01 M HCl) but slightly decreased with HCl concentration (84% in 8 M HCl). Metal ions were extracted by an ion exchange mechanism involving the binding of the chlorocomplex ($PtCl_6^{2-}$) to IL phosphonium cation. SEM-EDX analysis showed that IL and platinum were homogeneously distributed in the whole mass of the EIR. Sorption isotherms were fitted with the Langmuir equation and maximum sorption capacity increased with extractant loading, reaching values up to 74.6 mg Pt g-1, for an EIR with 291 mg IL g-1 in 0.01 M HCl solution. Sorption kinetics were not affected by the agitation speed indicating that the resistance to film diffusion is not the limiting step. Uptake kinetics were controlled by the resistance to intraparticle diffusion. The intraparticle diffusivity coefficient slightly increased with temperature but decreased with increasing IL loading. Platinum desorption from EIR and resin recycling can be performed using a number of eluents including HNO_3 (1, 3, and 5 M), $HClO_4$ (1 and 3 M) and thiourea (1 M in 0.5 M HCl).

Minor Actinide Separations using Ion Exchangers

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Meeting future energy demands in the US will require the development of advanced nuclear fuel cycles. A critical need in developing closed or modified open fuel cycles is a simple and efficient separation of the transuranic or minor actinides from lanthanides and other fission products. Benefits of such a separation include making the fuel more proliferation resistant, recovery of the energy value of the minor actinides, reduction in waste volume requiring disposal in a repository, elimination or significantly reducing radiotoxic elements from the waste, and reducing long-term actinide heat generation in geological repositories.

Newly initiated studies at SRNL seek to determine if minor actinide separations can be accomplished effectively using the inorganic-based ion exchange materials sodium nonatitanate (SrTreat®) and monosodium titanate (MST), both of which are commercially available. Uptake of trivalent ions onto the ion exchanger has proven to be near quantitative at pH 6. This presentation will present recent findings combining the strategic use of complexing agents, oxidizing agents, or both under mildly acidic conditions with two titanium-based ion exchangers to facilitate an effective separation of minor actinides, in particular Am, from the lanthanides. Attempts to recover materials adsorbed to the selected ion-exchangers will also be discussed.

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Improved Titanate Sorbents for Strontium and Actinide Separations

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High-level nuclear waste produced from fuel reprocessing operations at the Savannah River Site (SRS) requires pretreatment to remove ^{137}Cs, ^{90}Sr, and alpha-emitting radionuclides (i.e., actinides) prior to disposal onsite as low level waste. The baseline material for ^{90}Sr and alpha-emitting radionuclide removal at SRS is monosodium titanate (MST), $NaTi_2O_5H$, which is produced by a sol-gel process. A titanate sorbent has recently been prepared by the treatment of MST with hydrogen peroxide to form a peroxotitanate material (modified MST or mMST) which has improved Sr and Pu removal performance compared to the baseline material. Both of these materials are suitable for use in batch contact processes, in which the loaded material is separated by filtration after contacting the contaminated solution for a set period of time. To evaluate these materials for possible use in a column configuration, engineered forms of the two materials have been prepared, with particles sizes of approximately 300-600 μm. This paper will discuss recent results from testing with both the mMST and engineered forms of both MST and mMST.

Modeling Adsorption Processes for Direct Capture of CO_2 from Ambient Air

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Post combustion CO_2 capture technologies currently focus on large point source emitters that account only for about one third of total CO_2 emissions. Direct capture of CO_2 from air is an approach that can, if technically and economically feasible, account for emissions from all possible sources. The economic and technical feasibility of air capture is an intensely debated topic because of the high projected energy costs associated with absorption based air capture processes. Recent CO_2 adsorption studies by our group have shown that amine oxide hybrid materials, specifically silica supported hyperbranched aminosilicas and related materials can capture CO_2 selectively at 400 ppm gas phase concentrations with as little as a 2.2 factor decrease in capacity as compared to flue gas capture; despite the 250 fold decrease in gas phase concentration. It seems possible that a temperature swing adsorption process using similar highly selective materials can be used to capture CO_2 directly from air. In this work, two novel equilibrium adsorption processes are presented that use diurnal temperature swing and low pressure steam as driving forces for sorbent regeneration. Using real annual temperature data of six different locations from the United States, our calculations show that product CO_2 purities of 32% and 80% are obtainable for different processes. The energy requirement ranges from 1600 to 3000 MJ/t CO_2 for the thermal energy required for desorption and the mechanical energy associated with moving air thorough the contactor.

SESSION V – NOVEL SEPARATIONS

Evaluation of Hydroxyalkyl-Functionalized Imidazolium-Based Ionic Liquids as Solvents for the Extraction of Metal Ions

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As part of a broader effort to evaluate the suitability of a variety of ionic liquids (ILs) as solvents for the extraction of actinides and fission products, a series of new ILs containing a (1-hydroxyalkyl)-functionalized imidazolium cation have been prepared and characterized. Although certain of their physicochemical properties (e.g., density) remain largely unaffected vs. their N,N-dialkylimidazolium analogs by hydroxyl-functionalization, other characteristics, such as their hydrophilicity and ability to solubilize extractants, are measurably altered. In addition, this functionalization has been found to alter the "balance of pathways" among the various routes by which a metal ion may partition between aqueous nitric acid solutions and ionic liquids containing a neutral extractant. Specifically, the presence of the hydroxyl group is accompanied by a greater tendency toward ion exchange as the predominant mode of partitioning. The implications of these differences for the design of improved metal ion separation processes using ionic liquids are examined.

Ionic Liquids for Radioisotope Separations Involving Thorium and Actinium

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The solvent extraction of Th-227 and Ac-225 from the aqueous phase into ionic liquids (ILs) was investigated by using N,N,N',N'-tetraoctyldiglycolamide (TODGA) or di(2-ethylhexyl)phosphoric acid (HDEHP) as an extractant. Four ILs, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C_4mim][NTf_2]), 1-butyl-3-methylimidazolium bis(perfluoroethanesulfonyl)imide ([C_4mim][BETI]), 1-butyl-2,3-trimethyleneimidazolium (trifluoromethanesulfonyl)imide ([BuI5][NTf_2]), and 1-benzyl pyridinium bis(trifluoromethanesulfonyl)imide ([$PhCH_2Py$][NTf_2]) were used in this study as extraction solvents for the separation of Th-227 and Ac-225. Excellent extraction efficiencies and selectivities were found for Th-227/Ac-225 when HDEHP was used as an extractant in these ILs. The effects of different extractant concentrations in ILs and different aqueous phase acidities on extraction efficiencies and selectivities of Th-227/Ac-225 were also studied. Ionic liquid systems for separating Th^{4+}/Ra^{2+} and Ac^{3+}/Bi^{3+} will also be presented.

High Solubility of CO_2 in an Ionic Liquid with the Tetracyanoborate Anion – An Insight from Molecular Simulation

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Recently, it was found that 1-ethyl-3-methylimidazolium tetracyanoborate [emim][$B(CN)_4$] shows greater CO_2 solubility than several popular ionic liquids of different anions including [emim] bis(trifluoromethylsulfonyl) imide [Tf_2N]. In this work, both classical molecular dynamics simulation and quantum mechanical calculations were performed to understand the high solubility of CO_2 in the [emim][$B(CN)_4$] IL. We found that the solubility is dominated by the cation-anion interaction, while the CO_2-anion interaction plays a secondary role. The atom-atom radial distribution functions (RDFs) between cation and anion show weaker interaction in [emim][$B(CN)_4$] than in [emim][Tf_2N]. A good correlation is observed between gas-phase cation-anion interaction energy with CO_2 solubility at 1 bar and 298 K, suggesting weaker cation-anion interaction leads to higher CO_2 solubility.

Based on site-site RDFs, we found that CO_2 in the ILs is closer to the anion than to the cation and that it exhibits a stronger peak with $[B(CN)_4]$ than with $[Tf_2N]$. Moreover, a higher volume expansion is observed in [emim] $[B(CN)_4]$ than in [emim]$[Tf_2N]$ at different mole fractions of CO_2. These results indicate that $[B(CN)_4]$, a small and highly symmetric anion is unique in giving a high CO_2 solubility.

Recovery of Minor Actinide from Spent Fuel by Extraction Chromatographic Technique using Immobilizing TPEN-gels

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A series of separation experiment was performed in order to study a recovery process of minor actinide, such as americium and curium, from actual spent fuel using extraction chromatographic technique. N,N,N',N'-tetrakis(2-pyridylmethyl)ethylenediamine (TPEN) which was immobilized chemically in a polymer gel was developed by Tokyo-Tech, and the TPEN-gels was used as new extraction chromatographic agents in this experiment.

The mixed oxide fuel highly irradiated in the experimental fast reactor "JOYO" was used as a reference spent fuel to demonstrate the recovery of minor actinides. The MOX fuel including 29.9 wt.% plutonium was irradiated up to 119 GWd/t. The irradiated fuel was further sliced into pieces of 5mm in length, and the sliced specimen was placed in a flask mounted with reflux condenser and dissolved in 28 ml of an 8M HNO_3 solution by heating for 6 h at its boiling temperature.

Firstly, actinides, uranium and plutonium, were separated by ion-exchange method (AG 1×4 100-200 mesh), and then platinum group elements were removed by CMPO (TRU-Resin 50-100 μm : TR-B50-S) to obtain mixed solution of minor actinide and lanthanides. The TPEN-gels was immerged in 0.01M $NaNO_3$ solution, and pH was adjusted to 4. Then extraction column (□6.5, 25 mm height) was made by packed with 1.0 ml TPEN-gels and was rinsed by 5 column volume of 0.1M $NaNO_3$ (pH4). A 0.02 ml aliquot of sample solution prepared from spent fuel was passed through the column. The column was washed with 41 column volumes of 0.01M $NaNO_3$ (pH4) at the flow rate of 0.1 ml/min and effluent was taken as a sample fraction for gamma-ray spectrometry and ICP-AES analysis. Europium was detected at the former fraction of effluent. Then the effluent was changed to 12 column volumes of 0.01M $NaNO_3$ (pH2) at the flow rate of 0.1 ml/min to strip minor actinide from the column. As main nuclides, americium and curium were detected in the effluent.

These results prove that the proposed recovery process of minor actinide has a reality as a candidate for future reprocessing process based on the extraction chromatographic technique.

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Self-Assembled Capsule Receptors for Sulfate Recognition and Separation

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Self-assembled urea-functionalized capsules have been employed as novel sulfate separation vehicles in competitive aqueous solutions. The motivation for sulfate separation is two fold. First, separation of this anion represents a fundamental challenge, as sulfate is very difficult to extract from aqueous media due to its strong hydrophilicity. Second, from a practical perspective, sulfate is a problematic component of legacy nuclear wastes, particularly those stored at Hanford, as it interferes with the vitrification process selected for waste disposal, increases the volume of waste forms that must be produced and stored, and reduces their geologic performance.

After exploring a number of potential sulfate separation methods, the most promising approach found to date involves selective crystallization of self-assembled capsule receptors functionalized with urea hydrogen-bonding groups. Similar to the naturally occurring sulfate-binding protein, these capsules completely sequester the sulfate anion from the aqueous solvent by encapsulation inside well-defined and rigid cavities lined with complementary binding groups, thereby ensuring excellent selectivity based on shape and size recognition. Furthermore, the cages were found to persist in various crystalline environments, allowing for fine-tuning of their structure and selectivity, as well as for optimization of the crystallization process for the conditions found in nuclear wastes. Of particular promise was found to be a Na-based capsule, which displayed efficient and selective sulfate encapsulation from aqueous alkaline $NaNO_3$ solutions. We recently demonstrated a closed separation cycle based on these crystalline capsules, which provides the basis for a potential breakthrough technology for sulfate separation from the Hanford waste.

Electrosorption of Ions by Novel Mesoporous Carbon Materials

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The formation of an electrical double layer (EDL) near a charged surface has important implications in various processes, such as desalination of water by electrosorption and energy storage in supercapacitors. Electrosorption of ions from aqueous solutions is used in the capacitive deionization (CDI) technology for water treatment. Mesoporous carbon materials are suitable electrodes for CDI, as they have a high specific surface area and high electrical conductivity. The objectives of the present work are to (1) synthesize durable and efficient mesoporous carbon electrodes for CDI, (2) test their application at various conditions in the CDI process, (3) better understand the mechanisms of electrosorption, and (4) develop a mechanistic model to describe and predict the performance of the CDI process. Progress in all the project objectives will be reported. Novel mesoporous carbon materials have been developed via a self-assembly method and attracted industrial interest. CDI results obtained so far suggest that mesoporous carbon synthesized at Oak Ridge National Laboratory performs better than the conventional carbon aerogel. In-situ neutron-imaging and scattering experiments provide a better understanding on ion transport in the pores of mesoporous carbon electrodes. The influence of elevated temperature on the sorption of ions is also investigated, as it has implications in the treatment of produced water from the oil industry. A predictive transport model will be also discussed.

Electrochemical Studies of Cation-cation Complexes Involving UO_2^+ and UO_2^{2+} in Chloride and Perchlorate Aqueous Systems

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Cation-cation complexes are known to be important in a number of chemical equilibria. These complexes exist in reaction intermediates, hydrolysis products, dimer formation and undergo self-association in aqueous solutions. Cation-cation complexes may have significance when processing used nuclear fuel on an industrial scale. There is a lack of literature data pertaining to the systematic study of actinyl-actinyl complexes. In this study, the equilibrium constants (K/Γ) of cation-cation complex formation pertaining to the reaction: $UO_2^+ + UO_2^{2+} \leftrightarrows [UO_2 \cdot UO_2]^{3+}$ in chloride and perchlorate aqueous media have been determined. The K/Γ values were determined over a range of ionic strengths (μ=0.5 – 9.0M) using electrochemical techniques, such as: cyclic voltammetry, normal pulse voltammetry, and double-potential step chronoamperometry. Heterogeneous activation parameters for the reaction $UO_2^{2+} + e^- \leftrightarrows UO_2^+$ indicate a change in the electron transfer process as μ increases. A secondary anodic wave is observed when this mechanism change occurs, indicative of a different UO_2^+ environment. An ECE mechanism and calculated parameters: $E^{o\prime}$, α, k_s, K/Γ, and D_o were successfully used to simulate voltammograms and predict the electrode-solution interface chemistry of these reactions. The influence of temperature, ionic strength, supporting electrolyte and hydration on the formation of actinyl cation-cation complexes in aqueous solutions is discussed

SESSION VI – NUCLEAR FUEL CYCLE SEPARATIONS

Separation of Am(III) from Eu(III) Using Polymer Gels Cross-Linked with Nitrogen-Donor Ligands

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N,N,N′,N′-tetrakis(2-pyridylmethyl)ethylenediamine (TPEN) is one of the podand-type ligands with six nitrogen-donors and recognize the slight difference in the softness between Am(III) and Eu(III). We have tried to synthesize a novel extraction chromatographic agent, which exploit such feature of TPEN. The use of a polymer gel as a support of the extractant can be expected to keep the flexibility of extractant and suppress the effluence of the extractant. *N,N,N′,N′*-tetrakis-(4-propenyloxy-2-pyridylmethyl)ethylenediamine (TPPEN) which is a TPEN analog introducing polymerizable group to pyridine rings was used as a cross-linker of acrylic monomers. We have synthesized polymer gels from various acrylic monomers, such as *N*-isopropylacrylamide (NIPA), acrylic acid (AAc), methyl methacrylate (MMAc), *N,N*-dimethylacrylamide (DMAAm), and diacetoneacrylamide (DAAAm). The NIPA- and the DMAAm-TPPEN gel were swollen at room temperature, whereas the volume change of the AAc-, the MMAc-, and the DAAAm-TPPEN gel were not observed. The adsorption tests of 241Am(III) and 152Eu(III) by these gels were carried out. In the pH range of 4.5 to 6.0, the NIPA- and the DMAAm-TPPEN gel had the high separation factors of Am(III) over Eu(III) (*SF*Am/Eu), which were evaluated to be 26 and 18, respectively. These *SF*Am/Eu value are sufficient for the chromatographic separation of MA. The *SF*Am/Eu for AAc-, MMAc-, and DAAAm-TPPEN gel were lower than those for the NIPA- and the DMAAm-TPPEN gel. These results indicate that the swollen gels, such as the NIPA- and the DMAAm-TPPEN gel are suitable for Am/Eu separation.

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Probing Ligand Exchange Kinetics in Solvent Extraction Systems using ^{31}P NMR

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Solvent exchange reactions on metallic cations constitute a fundamental step in complex-formation reactions and can be successfully probed using Nuclear Magnetic Resonance (NMR) spectroscopy. NMR studies of small solvent molecule exchanges (H_2O, DMF, DMSO, etc.) have been widely developed and reviewed. In the case of lanthanide cations, water exchange rate is decreasing from gadolinium to ytterbium as the ionic radius decreases and $\Delta S^{\ddagger}$ is negative indicating an associative mechanism. However, similar NMR investigations have been more rarely applied to stronger and bulkier ligands used in organic phases of extraction systems. ^{31}P NMR presents advantages compared to other NMR techniques: only singlet peaks are observed when proton is decoupled, simplifying the analysis and the quantification of exchange rates; the analyzed sample doesn't need to be prepared in a deuterated diluent. Organophosphorus extractants are widely used in the field of actinide separation. Nevertheless, few NMR studies of these ligands have been published in the literature and are reviewed in this paper. ^{31}P NMR was investigated to probe the kinetics of monoacid organophosphorus ligands exchange reactions (HDEHP, [HEH]EHP, Cyanex 272) in 1,3-diisopropylbenzene with several lanthanide cations. Exchange rates and activation parameters were calculated at different temperatures by performing a complete band shape analysis using M. T. Rogers and J. C. Woodbrey general equations.

Development of a Simplified Soft Donor Approach to Trivalent Actinide/Lanthanide Separations

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One of the most effective ways of partitioning of the trivalent lanthanides and actinides is the application of soft donor molecules in organic extractants such as dithiophosphinic acids or aqueous phase complexants like DTPA in the TALSPEAK process. However, both these types of processes require pH regimes that are not conducive for industrial applications, further the TALSPEAK process in particular has a complex aqueous phase. In an attempt to simplify such processes we have begun to investigate the usefulness of amino acids in the separation of the trivalent actinides (An^{3+}) and lanthanides (Ln^{3+}) in a solvent extraction process. Amino acids have the benefit that they can buffer extraction systems if necessary at pH values ~2 and also have soft donor atoms within their molecular structure, this feature may ultimately allow for the removal of a complexant from a system like TALSPEAK. In this presentation we will discuss the initial results of solvent extraction investigations into the separation of the lanthanide elements from americium with L-alanine as a buffer system.

Interaction between HDEHP and CMPO in Combined TRUEX-TALSPEAK Extraction System

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One of the options currently being investigated for the separation of trivalent actinides from the trivalent lanthanides is the combination of two extraction processes TRUEX and TALSPEAK. It has been previously reported that in this mixed process, two extractants interact together creating a system with complex extraction behavior. To better understand these interactions FT-IR spectroscopy in combination with solvent extraction was employed in this work. The data show that in the presence of CMPO, HDEHP dimer breaks and interacts with CMPO through the hydrogen bonding with phosphoryl group of CMPO. The formation constant for a new HDEHP···CMPO adduct ($\log\beta=3.4$) was determined by examination of the FT-IR spectra for various mixtures of HDEHP and CMPO. The distribution ratios of Ln(III) decrease significantly with nitric acid concentration, and point to acidic properties of this mixed extractant. The data presented suggest that several species containing HDEHP···CMPO adduct, HDEHP dimer and/or nitrate are formed upon extraction of Ln(III) by the mixture of HDEHP and CMPO.

From TALSqueak to TRUSqueak: Application of Aqueous Ternary Species

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The recently developed TALSqueak (Trivalent Actinide Lanthanide Separation using quicker extractants and aqueous komplexes) separations process utilizes 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester acid (HEH[EHP]) and N-(2-hydroxyethyl)ethylenediamine triacetic acid (HEDTA) as the organic extractant and holdback reagent, respectively, to perform TALSPEAK-type separation of the lanthanides from the actinides. TALSqueak appears to offer several benefits over conventional TALSPEAK, including: improved the predictability of process performance based on available thermodynamic data, decreased interphase miscibility, faster kinetics, a nearly flat extraction trend across the lanthanide series, and a flat dependence of metal extraction on pH. Many of these desirable characteristics are enhanced by the introduction of a secondary aqueous complexing

agent, dipicolinic acid (DPA). Utilization of aqueous ternary HEDTA-DPA-metal species allows this system to provide separation factors between americium and the least extracted lanthanide greater than 100 at pH $\geq$ 3.7. The ultimate objective is to apply this chemistry to a mixed-extractant (TRUSqueak) organic phase containing octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide (CMPO) and HEH[EHP. The transfer from TALSqueak to TRUSqueak chemistry will be greatly facilitated through a strong fundamental understanding of chemical interactions throughout the system. This presentation will describe the characteristics of the metal-DPA-HEDTA ternary species and introduce preliminary TRUSqueak capabilities.

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Separation and Recovery of Uranium and Group Actinide Products from Irradiated Fast Reactor MOX Fuel via Electrolytic Reduction and Electrorefining

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A series of bench-scale tests was conducted with irradiated fast reactor MOX fuel to separate and recover both refined uranium and group actinide products via pyroelectrochemical techniques. Irradiated fast reactor MOX fuel was separated from its cladding by mechanical (crushing) and pyrochemical (high temperature oxidation) means, yielding fuel particulate. The particulate was loaded into five permeable stainless steel baskets, and each was successively immersed in a pool of molten LiCl – 1 wt% Li_2O at 650 °C and electrolyzed to convert the mixed oxide fuel to metal (electrolytic reduction). Each basket of reduced fuel was then successively electrorefined in LiCl-KCl-UCl_3 at 500 °C, yielding refined uranium metal product. After completely electrorefining uranium from the five baskets of reduced MOX fuel, two additional electrorefining experiments were performed in which actinides (i.e., uranium, neptunium, plutonium, and americium) were recovered as a group. Pre- and post-test samples of the MOX fuel and salt following each of the unit operations were analyzed to characterize the conversion and partitioning of fuel constituents in the prescribed pyroelectrochemical processes.

Spectroscopic On-Line Monitoring for Process Control and Safeguarding of Radiochemical Streams

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There is a renewed interest worldwide to promote the use of nuclear power and close the nuclear fuel cycle. The long term successful use of nuclear power is critically dependent upon adequate and safe processing and disposition of the spent nuclear fuel. Liquid-liquid extraction is a separation technique commonly employed for the processing of the dissolved spent nuclear fuel. The instrumentation used to monitor these processes must be robust, require little or no maintenance, and be able to withstand harsh environments such as high radiation fields and aggressive chemical matrices. In addition, the ability for continuous online monitoring allows for numerous benefits.

This paper reviews application of the absorption and vibrational spectroscopic techniques supplemented by physicochemical measurements for radiochemical process monitoring. In this context, our team experimentally assessed the potential of Raman and spectrophotometric techniques for on-line real-time monitoring of the U(VI)/nitrate ion/nitric acid and Pu(IV)/Np(V)/Nd(III), respectively, in solutions relevant to spent fuel reprocessing. Both techniques demonstrated robust performance in the repetitive batch measurements of each analyte in a wide concentration range using simulant and commercial dissolved spent fuel solutions. Static spectroscopic measurements served as training sets for the multivariate data analysis to obtain partial least squares predictive models, which were validated using on-line centrifugal contactor extraction tests. Satisfactory prediction of the analytes concentrations in these preliminary experiments warrants further development of the spectroscopy-based methods for radiochemical process control and safeguarding. Current research in our laboratory will be discussed in this paper.

Secondary Rare Metals by Separation and Transmutation of Fission Products – From Adv.-ORIENT Cycle to Après ORIENT

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Rare metals are inevitable in the leading industries and thus hold the national GDP. Industry-oriented rare, such as RE (Nd, etc) and PGM (Ru, etc) etc, metals are extremely localized in the earth and/or must be exhausted within two hundred years. They are strategic material like oils at producing countries. Nuclear fission reaction will create 31 rare metals in spent fuel (SF) as well as energy. Thus, the SF should be considered as not wastes but new artificial ores. Hydrometallurgical, *soft* and *salt-free*, separation processes have been under developed in the flame of *Adv.-ORIENT Cycle* during the period of FY2005-2010. A hybrid separation system of ion exchange chromatography (IXC) and catalytic electrolytic extraction (CEE) in HNO_3/ HCl media was found to be promising for deep separation of *f*-elements and rare metal fission products. Electrocatalytic abilities of micro co-deposits of PGM, Tc and Re are significant for H_2 production in either alkali solution or sea water.

Nuclear creation/transformation of actinides and fission products will be newly evaluated with special attention of non-proliferation and resourceability points of view in the flame of *Après ORIENT* research since this year. This presentation will highlight the calculation results of

$$ {}_{Z}FP^{A}\ (n,\gamma)\ {}_{Z}FP^{A+1} \xrightarrow{\beta-} {}_{Z+1}FP^{A+1} $$

reactions, specifically for Rh and Nd, etc production as representitative of 5th and 6th period FP elements. Their production yields, radioactive properties by each isotopic compositions will be discussed based on the FBR cycle conditions.

SESSION VII – SOLVENT EXTRACTION

Solute Partitioning and Lanthanide Speciation in TALSPEAK Media

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As a means of separating trivalent actinides from lanthanides in advanced nuclear fuels recycling, the TALSPEAK process has repeatedly been a focus of attention during the past four decades. Engineering scale demonstrations of the basic interactions of a cation exchanging extractant (HDEHP) in either aliphatic (dodecane) or aromatic (1,4-diisopropylbenzene) diluents in contact with a concentrated carboxylic acid buffer solutions (lactate, citrate, among others) containing an actinide-specific aminopolycarboxylate holdback reagent (DTPA) have been conducted in several different guises around the world. After this repeated examination, TALSPEAK remains a viable approach to accomplishing this difficult separation and several variants have been proposed for application, though none has been put into operation. Collectively, the technological application studies have established both the utility and the limitations of the process. As a solution chemistry problem, TALSPEAK has so many interesting facets that basic studies of the fundamental interactions have proven to be an irresistible challenge. Recent research has addressed some of the more fundamental chemistry that underpins this process, with the combined objectives of 1) improving predictability and control of the process, 2) explaining anomalous behavior that is not predicted by the best available thermodynamic data relevant to process conditions and 3) expanding the basic concept to different separation systems. Developing appropriate thermodynamic modeling information is in fact one of the most difficult challenges of TALSPEAK research, as the conditions required to support a functional separation system are far from the standards of "ideality". In this report, the results of a multi-technique attempt at explaining the anomalous pH dependence of TALSPEAK are reported. Work supported by the U.S. Department of Energy, Office of Nuclear Energy, Fuel Cycle Research and Development program, Sigma Team for Minor Actinide Separations and Nuclear Energy University Programs.

Gamma Radiolysis of TBP/n-dodecane in the Presence of Nitric Acid Using the INL Radiolysis Test Loop

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Design and installation has been completed for a state-of-the-art radiolysis/hydrolysis test loop system. The system is used to evaluate the effects of gamma radiolysis and acid hydrolysis on the stability and performance of solvent extraction process solvents. The test loop is comprised of two main sections; the solvent irradiation and hydrolysis loop and the solvent reconditioning loop. In the solvent irradiation and hydrolysis loop, aqueous and organic phases are mixed and circulated through a gamma irradiator until the desired absorbed dose is achieved. Irradiation of the mixed phases is more representative of actual conditions in a solvent extraction process. Additionally, the contact of the organic phase with the aqueous phase will subject the solvent components to hydrolysis. This hydrolysis can be accelerated by controlling the system at an elevated temperature. At defined intervals, the organic from the irradiation/hydrolysis loop will be transferred to the solvent reconditioning loop where the solvent is contacted with scrub, strip, and solvent wash solutions which simulate process flowsheet conditions. These two processes are repeated until the total desired dose is achieved.

Since all viable solvent extraction components in an advanced fuel cycle must exhibit high radiolytic and hydrolytic stability, this test loop is not limited to any one solvent system but is applicable to all systems of interest. Also, the test loop is not limited to testing of process flowsheets. It is also a valuable tool in support of fundamental research on newly identified extractants/modifiers and the impact of gamma radiation on their stability in a dynamic environment. The investigation of the radiolysis of a TBP/n-dodecane process solvent in contact with aqueous nitric acid has been performed. These studies were intended to confirm/optimize the operability of the test loop system. Additionally, these data are directly applicable to numerous other solvent extraction processes containing TBP that are being developed to support advanced aqueous separations processes. Initial experimental results are consistent with existing literature reports regarding TBP/n-dodecane radiolysis. Additionally, the gamma dose rate has been characterized within the test loop and analytical methods have been developed for the characterization and quantification of radiolytic degradation products.

Ionic Liquids: Unique Environments for f-Element Chemistry

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There is a tremendous need for fundamental scientific insight and the development of research capabilities in actinide chemistry and radiochemistry in the United States and around the world. At the same time, there is a growing recognition that the study of ionic liquids (ILs, salts with melting points below 100 °C, many of them even liquid at room temperature and below) offer an opportunity for new insight, science, and technology which has to date been unavailable using other media. While the high temperature molten salt chemistry of 5f-elements has been studied in detail for many years, there is virtually no information on the behavior of actinides in totally ionic media at room temperature and below. Given the technological relevance of these elements in today's society, this represents a fundamental science gap which requires detailed study.

The advantages that ILs offer over conventional solvents in the context of actinide chemistry, arise from a combination of properties including a) wide liquidus range extending from ca. -80 °C to 350 °C, b) accessible large electrochemical windows, c) designable low volatility and nonflammability, and d) an impressive range of tuneability with relatively modest adjustments to the chemistries of either ion. Nonetheless, to move beyond the current Edisonian approach to using ILs and achieve the unique promise of such materials for new actinide chemistry, more fundamental information which predicts the chemical and physical properties of the combinations of these anions and cations with f-block metals is needed to inform decision-making in the development of specific ILs for the solubilization and derivatization of actinide compounds. *This leads to the main challenge in IL design - understanding the complementary structural features of the cation and anion that can provide IL solvation of actinides and also allow additional ligand coordination and chemistry to occur.*

There are several properties that are general among ILs yet uncommon in molecular liquids. The most well-known property is the low vapor pressure shown by most ILs, however ILs also possess other properties such as unusual solvating power, short range order, and a tendency to resist crystallization on cooling which can result in both novel findings and unforeseen challenges when ILs are newly applied to a field. One such field from which ILs have received much attention is the processing of spent nuclear fuel. In much of this work hydrophobic ILs have been used as nonaqueous phases in extractions, but there has been less research into the fundamental chemistry of actinides in ILs. Because the environment in an IL consists solely of ions, ILs are particularly interesting for metal chemistry. The metal ion can interact with counterions without the interference of solvents. However it can be a challenge to access this chemistry because metal salts are often insoluble in ILs. Furthermore traditional evaporation-based crystallization techniques are not usable with ILs. This presentation will discuss our research into the reactivity of ILs with f-elements, including crystal structures of the first uranyl dicyanamide and uranyl imidzole complexes to be synthesized from an ionic liquid.

Investigations on the Synergistic Effects in Solvent Extraction Systems Combining TBP and DBP

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During treatment of spent nuclear fuel by the PUREX (Plutonium URanium EXtraction) process the main active component tributyl phosphate (TBP) may degrade to dibutyl phosphoric acid (DBP). This degradation and the effects have been extensively studied and observations indicate that DBP result in increased extraction of metal ions in spent nuclear fuel, complicating stripping. Furthermore DBP may cause precipitation in combination with high loading of certain metal ions. TBP is known to aggregate and produce a third phase at high metal loading and high nitric acid concentration causing unwanted effects in process. Compared to TBP the coordination of metals by DBP is not promoted by high acid but by a low acid concentration and similar effects are not anticipated. In this study we have investigated what effect combining TBP and DBP has on metal, acid, and water extraction. In addition, small angle X-ray scattering (SAXS) was carried out at Argonne National Lab to study possible structural organization in the organic phase. We observed a non-linear, non-additive effect in the extraction behavior and the results from the SAXS show that system behaviors with mixed TBP+DBP extractants are not simple arithmetic averages of the responses for the two extracting reagents, TBP and DBP on their own. The observations made and possible explanations will be presented and discussed.

Ce(III) Extraction by Aliphatic Malonamide: A Micro- and Macro-Molecular Structural Study

R. J. Ellis, L. D'Amico, M. R. Antonio, *Argonne National Laboratory, IL*

Associations of solutes in solvents driven by ion-ion and dipole-dipole forces as well as by ion-dipole ones, and influences of the solvent itself on solute interactions impact processes in separations science, possibly none more important than SX. Our research is designed to lead to a fundamental understanding of self-assembly and supramolecular behaviors, such as ion-pairing, micellization, and third-phase formation, in bulk media—aqueous and organic alike—and to correlate the structural aspects of microemulsions in advanced SX system chemistry with solute partitioning.

The amphiphillic alkyl-functionalized malonamide reagents used for the separation of trivalent lanthanides and actinides in the DIAMEX (DIAMide EXtraction) process are known to form such supramolecular aggregates in aliphatic solvents. A variety of methods were used to probe the local and macromolecular environments in the extracted assemblies in loaded organic, light organic and third phases formed from the extraction of Ce(III) from nitrate media. A 'zoom-out' approach was used, combining spectroscopic and electrochemical techniques, to study local structure within the reverse micelle and X-ray scattering techniques to investigate the macro-molecular structure of the aggregate assemblies. Both neutral and acidic Ce(III) extraction systems were investigated to assess the role of acid in extracted assemblies. The results show that the organization of extractants in non-polar diluents mediates the distribution of target solutes in ways that are only now being understood. This work is supported by the U. S. Department of Energy, Office of Basic Energy Science, Division of Chemical Sciences, Biosciences and Geosciences, under contract No DE-AC02-06CH11357.

Synergistic Extraction of Americium and Europium Using bis-(o-trifluoromethylphenyl)-dithiophosphinic Acid and Neutral Donors

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The separation of minor actinides, such as Am (III), from light lanthanides remains one of the more difficult technical challenges in the nuclear fuel cycle. These trivalent elements possess few differences in chemical characteristics that are necessary for an efficient separation process. Current efforts have focused on the use of compounds containing soft donor (i.e., N and S) atoms which show a preference for binding Am (III). This study reports the combination of a soft donor acid, *bis*-(*o*-trifluoromethylphenyl)-dithiophosphinic acid (BFDPAH), with neutral donors to extract these elements. The synergistic effect of the combination of TOPO and BFDPAH was significant with separation factors (SF = Am/Eu) of over 300 observed in extractions of Am (III) from 0.10 M HNO_3. Investigation of the overall extraction mechanism using synergistic mixtures by the slope analysis method illustrated that the mechanism was different for the extraction of Am (III) compared to Eu (III). The implication of this system for improved separation of these elements will be discussed.

Functionalized Dipicolinic Acid Derivatives for Trivalent Actinide and Lanthanide Complexation

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Dipicolinic acid complexes have been widely studied and a wide variety of information is all ready known about their behavior including a large data base of metal stability constants. However, one factor that inhibits the utility of dipicolinic acid in separations applications is its limited solubility in acidic media. This research focuses on two main goals 1) overcoming the limited solubility in acidic media and 2) addressing gaps in the thermodynamic literature database by characterizing dipicolinate complexes with actinide ions. To address the first issue, several dipicolinic acid analogues have been synthesized include 4-(hydroxymethyl) pyridine-2,6-dicarboxylic acid (4-HMDPA), 1-(2, 6-dicarboxypyridin-4-yl)-N, N, N-trimethylmethanamonium chloride and (DCPTMMA), [2,2'-bipyridine]-6, 6'-dicarboxylic acid (BPDCA). Complexes of these dipicolinate derivatives and the parent compound (pyridine-2,6-dicarboxylic acid, Dipic) have been characterized using spectrophotometry and solvent extraction techniques. It was intended that functionalization of dipicolinic acid at the 4-position would have limited effect on the binding pocket of the ligand. It has been seen in this research that even slight modifications show substantial changes in the behavior of the ligand and its interaction with metal centers. The results of these studies will be discussed in this report.

Work supported at WSU and at PNNL by the U.S. Department of Energy Office of Nuclear Energy Science and Technology Fuel Cycle Research and Development program Sigma Team for Minor Actinide Separations.

Cooperativity in Liquid-Liquid Anion Exchange by Lipophilic Quaternary Ammonium Salts in Combination with Neutral Anion Receptors

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Although liquid-liquid anion exchange (LLAE) is a venerable technique for separation of anions, it is limited by a persistent selectivity order termed the Hofmeister bias, meaning that the selectivity order is controlled by anion hydration just as in Hofmeister's first observations of salting-out ability. Typically, LLAE relies on simple alkyl ammonium salts that are sufficiently lipophilic to remain highly partitioned to a water-immiscible organic solvent even when the counter-anion is highly hydrophilic. This anion, often chloride, is easily exchanged for less hydrophilic anions. Our idea has been to enhance LLAE selectivity by adding a neutral lipophilic anion receptor to an organic solvent containing a lipophilic quaternary ammonium salt, usually chosen to be in the chloride or nitrate form. The resulting synergism or antagonism may be related to the affinity of the anion receptor for either the anion of the quaternary ammonium salt or the competing anion in the aqueous phase. But does the

structure of the quaternary ammonium cation play a decisive role? A survey of ten aqueous anions using either of two anion receptors combined with either of two quaternary ammonium chloride salts was performed. It was found that the enhancement of exchange tends to favor the smaller, more charge-dense anion, an expected anti-Hofmeister bias. Enhancement was not impressive except in the case of calix[4]pyrrole (C4P) combined with Aliquat 336 (methyltri-C_8,C_{10}-ammonium chloride), in which case the extraction preference for chloride exceeded that of the more lipophilic anions bromide and nitrate. This selectivity reversal is attributable to the known ability of C4P to act as an ion-pair receptor, in this case with chloride receiving hydrogen bonds from C4P and the methyl group of Aliquat 336 occupying the cup of the C4P in the cone conformation. The remarkable cooperativity found exclusively for C4P combined with Aliquat 336 shows that the structure of the cation may indeed play a decisive role in synergistic anion-exchange systems.

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SST Banquet Session

Non-Traditional Materials Research at ORNL: From Rare Earths and Actinides to Stainless Steel Crystals

Lynn Boatner, Materials Science and Technology Division and ORNL Center for Radiation Detection Materials and Systems, Oak Ridge National Laboratory, Oak Ridge, TN

ORNL has enjoyed a long history of original, frequently non-traditional, materials research in which unique combinations of the capabilities of the Laboratory have been successfully applied. These capabilities have included, among others, the availability of actinide isotopes produced at the HFIR Reactor and then separated and purified at the TRU Facility - as well as enriched stable isotopes separated using the Calutrons at the Y-12 Facility. At one point, the ORNL capability for growing single crystals of transuranic-containing elements (a capability that has now been lost) was essentially unique in the world. Examples will be given of some of the materials research at ORNL in which actinides or rare earths played an important role - and of other non-traditional materials science research such as the growth and application of stainless steel single crystals to the science of welding or the use of ion implantation to form "smart" nano-composite surfaces.

Biographical Information: Lynn Boatner received a Ph.D. degree in physics from Vanderbilt University. He is currently an ORNL Corporate Fellow and Battelle Distinguished Inventor in the ORNL Materials Science and Technology Division. Lynn is a Fellow of: the American Physical Society, the American Ceramic Society, the Mineralogical Society of America, the Materials Research Society, the American Association for the Advancement of Science, ASM International, and the Institute of Materials, Minerals, and Mining of the UK. He has received a number of awards for his research, including: R&D 100 Awards in 2010, 1996, 1985, and 1982; The AACG Crystal Growth Award of the American Association for Crystal Growth, (2003); and the Frank H. Spedding Award for Excellence in Rare Earth Research, (2002).

Session VIII – Department of Energy Applications

Vacuum Salt Distillation for the Removal of Chloride and Fluoride Salts

R.A. Pierce, T.D. Caldwell, and D.J. Pak, *Savannah River National Laboratory, Aiken, SC*

Vacuum distillation of chloride salts from plutonium oxide (PuO_2) and simulants for PuO_2 has been previously demonstrated at Department of Energy sites using kilogram quantities of chloride salt. The application of this technique is of particular interest to the HB-Line Facility and the MOX Fuel Fabrication Facility at the Savannah River Site. Both facilities are involved in efforts to disposition excess fissile materials. Many of these materials contain chloride and fluoride salt concentrations which make them unsuitable for dissolution without prior removal of the chloride and fluoride salts.

Between September 2009 and January 2011, the Savannah River National Laboratory (SRNL) and HB-Line designed, developed, tested, and successfully deployed a system for the distillation of chloride salts. Subsequent efforts are attempting to adapt the technology for the removal of fluoride. Fluoride salts of interest are less-volatile than the corresponding chloride salts. Consequently, an alternate approach is required for the removal of fluoride without significantly increasing the operating temperature.

Data from the use of *in situ* reactions to remove less-volatile chloride and fluoride salts, including plutonium fluorides, will be presented. Emphasis will be placed on how hydroxide salts can perform an exchange reaction with fluoride to form a product that is suitable for distillation.

Treat and Transfer Testing of Actual K Basin Sludge at 1 wt% and 2.5 wt%

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The Sludge Treatment Project (STP), managed for the U.S. Department of Energy by CH2M Hill Plateau Remediation Company, is designing systems for loading K Basin sludge into Sludge Transport and Storage Containers (STSCs). The STP is considering adding a flocculating polymer during sludge transfer to improve settling rates in the STSCs. CH2M Hill personnel previously tested approximately 30 flocculants and simulated K Basin sludge to determine the best flocculant for the testing with actual K Basin sludge samples. Based on this prior work, the Pacific Northwest National Laboratory has tested flocculant addition to sludge samples using an apparatus and test regime designed by CH2M Hill personnel to mimic the pump and treat process and the recirculation loops which are currently proposed for the STP sludge retrieval and transfer process. A non-radiological sludge simulant was used for shakedown testing of the apparatus, followed by 16 tests with actual sludge slurries. Turbidity in most of the slurry samples was reduced to less than 50 nephelometric turbidity units (NTU) by addition of < 1.5 mg flocculant per liter of slurry (mg/L). In one case the turbidity was reduced from > 1600 NTU to < 15 NTU by addition of a total of 1.2 mg/L. The settling of the flocculated solids from all the sludges tested was measured over several months to assess the long-term behavior.

The successful completion of the tests provides the data and experience necessary to move the testing to the pilot scale, and to eventual application to sludge transfer operations.

Near-Tank Treatment of Hanford Tank Waste: Pilot-Scale Testing

P.P. Schonewill, M.K. Edwards, R.W. Shimskey, R.A. Peterson, C Smith, R Tranbarger, *Pacific Northwest National Laboratory, Richland, WA*

In order to reduce the number of high level waste canisters that will have to be produced by the Hanford Tank Waste Treatment and Immobilization Plant, supplemental waste treatment technologies are being investigated. One such technology is the Near-Tank Treatment System (NTTS), which uses continuous sludge leaching, filtration, and ion exchange to process the waste in a simple, compact system. The NTTS is ideally suited for handling Hanford tanks with large amounts of boehmite, a difficult aluminum phase to dissolve. A pilot-scale NTTS was constructed and tested with a boehmite and iron oxyhydroxide waste simulant to evaluate the robustness and effectiveness of the system. The data from the pilot-scale tests were also used to assess scale-up from previously performed bench-scale tests.

Real Time Raman Analysis of Near Tank Treatment System Process Streams

M.K. Edwards[1], P.P. Schonewill [1], R.W. Shimskey[1], C.M. Niver[1], S.A. Bryan[1], R.A. Peterson[1], C. Smith[2], R. Tranbarger[2], *Pacific Northwest National Laboratory, Richland, Washington; [2]Parsons Infrastructure and Technology Group, Inc., Pasco, WA*

Periodic determination of various ionic species in sludge extract is required to sufficiently assess the effectiveness of sludge treatment operations during continuous sludge leaching (CSL) processing. The current laboratory analytical method, ICP atomic emission, requires a significant turnaround time during which species of interest could potentially precipitate. A much more rapid and frequent analysis is required to better understand, optimize, and monitor sludge processing operations. Furthermore, multivariate modeling work is necessary to develop a reliable and robust method for quantifying the ionic species of interest in sludge extract: hydroxide (caustic), aluminate, nitrate and nitrite. Raman spectroscopy, which is based on inelastic scattering of monochromatic light and used to study vibrational, rotational, and other low-frequency modes in a system, was identified as a rapid analytical technology that could adequately provide the reliable and timely results the CSL processing would require. During the integrated Near Tank Treatment System (NTTS) pilot demonstration, a Raman spectrometer was coupled in-line with the permeate stream exiting the reaction vessel. The data provided by the spectrometer was used to generate a real-time chemometric analysis to yield a quantitative analytical measurement of the process stream. The Raman proved to be a promising in-line technology and will be discussed as well as its comparison to external analytical measurements.

Development of the Next-Generation Caustic-Side Solvent Extraction (NG-CSSX) Process

L. H. Delmau, J. F. Birdwell, Jr., P.V. Bonnesen, N. B. Ladd, B.A. Moyer, E. L. Stoner, D. L. Lee, F. V. Sloop, Jr., *Oak Ridge National Laboratory, Oak Ridge, TN*

The Next-Generation Caustic Side Solvent extraction (NG-CSSX) process now represents the culmination of two decades of basic and applied research in perfecting the application of calixarene-crown ether chemistry in the removal of cesium from alkaline nuclear waste. Original efforts in the USA focused on the development of CSSX chemistry that could achieve a decontamination factor (DF) of 40,000 with a concentration factor (CF) of

15 in the removal of cesium from waste stored in underground tanks at the U.S. Department of Energy (US DoE) Savannah River Site (SRS). Using a calixarene-crown ether extractant, called BOBCalixC6, a 33-stage flowsheet was successfully demonstrated in 2-cm centrifugal contactors with actual waste and subsequently adopted for use in the SRS Salt Waste Processing Facility (SWPF) to begin processing SRS salt waste in 2014. The Modular CSSX Unit (MCU), a pilot-scale facility at the SRS, has been in operation since 2008, treating over 7.4 million liters (2 Mgal) of low-curie waste feed through September 2011. A recent goal has been to provide the technical basis for extending the life of the MCU by developing a next-generation CSSX chemistry that will allow the 18-stage MCU configuration to achieve DF = 40,000 and CF = 15, the same performance goals as SWPF. A major throughput increase could also be achieved by implementation of NG-CSSX in the SWPF, and a modular Hanford facility is feasible.

Results are presented toward the development of the NG-CSSX process for the removal of cesium from alkaline high-level nuclear waste. Employing a new calixarene-monocrown ether called MaxCalix and improved stripping chemistry, dramatically improved overall performance is obtained, including greater decontamination power, better resistance to third-phase formation, tolerance to high potassium feed concentrations, and likely higher throughput.

Synthesis and Evaluation of Guanidine Suppressors Used in the Next Generation Caustic Side Solvent Extraction (NG-CSSX) Process

N. C. Duncan, A. Rajbanshi, N. J. Williams, B. Roach, P. V. Bonnesen, B. A. Moyer, *Oak Ridge National Laboratory, Oak Ridge, TN*

Under funding from the DOE-EM Office of Technology Innovation and Development, recent laboratory efforts are being directed toward developing the NG-CSSX process for cesium removal from alkaline tank wastes. In support of EM's drive to accelerate processing of tank wastes at the SRS and Hanford site, laboratory efforts have sought increased performance of NGCSSX, both in decontamination efficiency and waste-processing rate. This presentation will highlight the role of one component of this process, dicyclohexylisotridecylguaninide (DCITG), the suppressor in the system, which is critical to the stripping of cesium from the loaded organic solvent. The synthesis of this compound will be reported, as well as its performance in the solvent extraction system with regards to its ability to aid stripping, long-term thermal and radiolytic stability, and effect of impurities and degradation products on its ability to perform at acceptable levels. Three variations of DCITG synthesized from different feedstocks and having different isomeric ratios have been studied and are compared to each other and to other potential guanidine candidates for use in the final solvent system. Future work in this area will include the synthesis and evaluation of other guanidine candidates, whose structures will be based on the results of this study.

Performance Testing of the Next-Generation CSSX Solvent with Actual SRS Tank Waste

R. A. Pierce, T. B. Peters, S. D. Fink, *Savannah River National Laboratory, Aiken, SC*

In 2008, the Savannah River Site (SRS) successfully deployed a solvent extraction system for removal of cesium from stored waste from nuclear processing. Now, efforts are underway to qualify the Next Generation Solvent for this Caustic Side Solvent Extraction (CSSX) process. Researchers at multiple national laboratories are involved in this effort.

As part of the effort to qualifying the Next Generation Solvent, SRNL has performed a number of tests at various scales. First, SRNL conducted a series of batch Extraction-Scrub-Strip (ESS) tests. These test used ~30 mL of Next-Generation solvent and either actual SRS tank waste, or waste simulant solutions. The cesium mass transfer results from these small scale tests are used to predict solvent behavior under planned facility operations.

At a larger scale, SRNL assembled a series of twelve, 2-cm centrifugal contactors. This rack of contactors is structurally very similar to one tested in 2001 during the demonstration of the original CSSX process. SRNL performed a non-radiological test using 40 L of cesium-spiked caustic waste simulant. The contactor assembly was then placed into a shielded-cells facility and tested with a comparable volume of actual tank waste. We will report the results from the ESS and the 2-cm centrifugal contactor tests. As appropriate, comparisons will be made between the 2001 and the 2011 data.

Investigation of Catalytic Pathways and Separations for Lignin Breakdown into Monomers and Fuels

J. McFarlane, J.A. Gluckstein, M. Z. Hu, M. Kidder, C.K. Narula, M.R. Sturgeon,*Oak Ridge National Laboratory, Oak Ridge, TN*

Lignin is currently burned for heat and power in industrial processes, but its aromaticity and high energy content make it a promising source for liquid fuels, fuel additives, and chemical feedstocks. Success in conversion of lignin has been achieved in the laboratory, however processing lignin poses technical barriers, particularly in the selectivity of the conversion reactions and requirements for separations both before and after processing of

the material. The project to be discussed here includes the experimental evaluation of a number of different catalytic pathways for the decomposition of lignin into small molecules, the evaluation of flowsheets for lignin decomposition in terms of thermodynamic efficiency, costs of separation, and the technical feasibility of each process.

Lower temperature conversions and more rapid processing may be possible with the use of nanocatalysts in lignin breakdown. In addition, if high temperatures can be avoided, it is expected that aromatic moieties will remain intact. Simplicity and thermodynamic advantages can be gained relative to syngas production and reconstitution of breakdown fragments, along with less char formation. Conversely, separations prior to and during lignin conversion are complicated when handling more complex and highly functionalized feedstocks that are present at lower temperatures. Flowsheets to achieve conversion under less extreme conditions were compared with conventional gasification and pyrolysis, to identify areas where catalysis could play a major role in increasing the feasibility of lignin conversion.

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