30TH ACTINIDE SEPARATIONS CONFERENCE

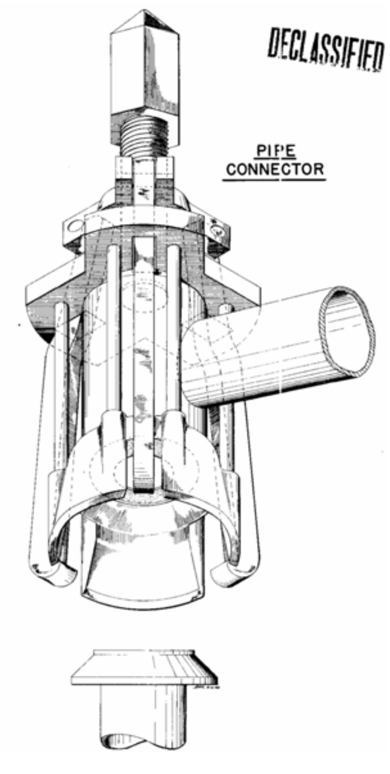
May 23-25, 2006

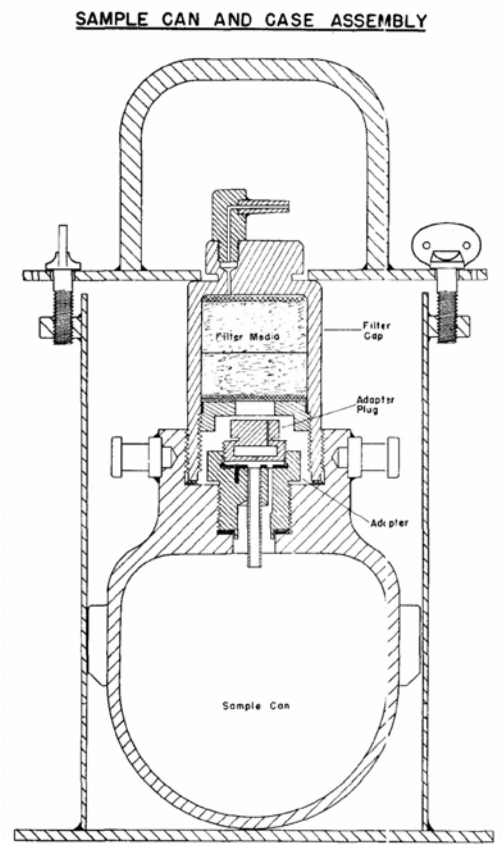
PNNL-SA-50126

The cover shows an overhead view of the Hanford Site's PUREX canyon and of process equipment used to implement actinide separations from dissolved irradiated uranium fuel.

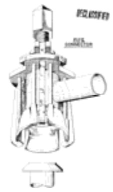
The ability to remotely operate and maintain the Hanford chemical processing facilities, such as the PUREX Plant, in high radiation fields, and the capability to modify and improve the process equipment, were made possible with the Hanford connector. The Hanford connector, shown below (left), on the cover as its successor, the PUREX connector, and in the headings of this Program's pages, is "a special device by which pipes, conduits or instrument leads can be connected together by tightening a single nut" according to the Hanford Technical Manual. The connector was opened and closed by an impact wrench slung from an overhead crane. The crane operator, who sat in a heavily shielded cab separated from the process canyon by a thick concrete wall, viewed his work by two adjustable periscopes and by television. The Hanford connector and the early use of television were two of the many adroit technical innovations implemented in the Manhattan Project.

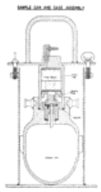
The product of the Hanford Site during the Manhattan Project was plutonium nitrate produced "as a viscous or semi-rigid cake for shipment" to Los Alamos. A diagram of the container used to transport the paste to Los Alamos is shown below (right) and in the page headings of this Program.





Many of you, the participants in the 30th Actinide Separations Conference, will see yet another marvel of Manhattan Project ingenuity, the B Reactor, during the week's activities. We welcome your participation in this year's Conference and thank you for describing your own technical advances in actinide and chemical separations.





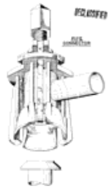
Welcome to the 30th Actinide Separations Conference

Welcome to the 30th Actinide Separations Conference, hosted this year by the Pacific Northwest National Laboratory. With your active participation and papers on many interesting topics, we look forward to a valuable and informative technical interchange. We are pleased to enjoy at this Conference the contributions of scientists and engineers from the US Department of Energy, Savannah River, Oak Ridge, Argonne, Los Alamos, Idaho, Berkeley, Livermore, and Hanford, from private firms, from France and the United Kingdom, and from academia, including a significant number of students from Washington State University.

The complexities of actinide and separations chemistry are reflected in both the diverse subjects of the technical program and in the physical realities of the Hanford Site and B Reactor to be seen by many of you during the Conference's Wednesday afternoon program. We encourage you to take advantage of the Conference to learn not only more about your particular areas of expertise but also to learn of advances in areas perhaps different than your immediate research interests. The success of this Conference ultimately is because of you, the scientists and engineers willing to share information, ask questions, and engage actively in discussion.

We thank the Pacific Northwest National Laboratory for providing the venue and for administrative support, the Department of Energy for allowing the Conference and the Site tour, Washington Closure Hanford, with the DOE, for opening and hosting the B Reactor visit, and Fluor Hanford, the B Reactor Museum Association, and Michele Gerber for providing expert commentary for the Site and B Reactor tours. We also thank Jim Chatters for his presentation at the Seaborg Awards Banquet. We especially thank you, the participants in the 30th Actinide Separations Conference, for your involvement. We hope you enjoy the Conference.

Chairman	Cal Delegard
Technical Program Co-Chairs	Sergei Sinkov Joel Tingey
Administration	Tracy McFall
Refreshments and Arrangements	Debbie Krisher
Budget and Finance	Kathy Harris
Bookkeeping	Dixie Iwan, Peggy Gillard, and Sue Williams
Hanford Tour and B Reactor Visit	Carolyn Ballard, Lori Huntley, Brenda Herrington, and Richard Romanelli



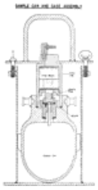
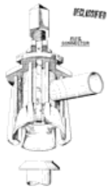
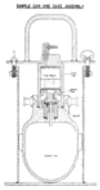


Table of Contents

Presentation Summaries





Actinide Separations Conference Advisory Board Members

Elizabeth A. Bluhm
Los Alamos National Laboratory

Calvin H. Delegard
Pacific Northwest National Laboratory

Karen D. Dodson
Lawrence Livermore National Laboratory

L. Kevin Felker
Oak Ridge National Laboratory

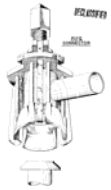
Mark P. Jensen
Argonne National Laboratory

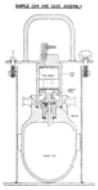
Alice M. Murray
Savannah River National Laboratory

Kenneth L. Nash
Washington State University

Robert T. Paine
University of New Mexico

Terry A. Todd
Idaho National Laboratory





Conference Agenda

Tuesday, May 22, 2006

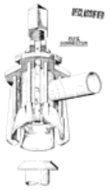
Registration	7:30 - 8:15 a.m.
Welcome	8:15 - 8:25 a.m.
Opening Session:	8:25 – 9:15 a.m.
Technical Session I: Medical Isotopes	9:15 - 10:05 a.m.
Technical Session II: Complexation	10:20 a.m. - 12:00 p.m.
Lunch Break	12:00 - 1:30 p.m.
Technical Session III: Plutonium Processing	1:30 - 4:50 p.m.
Poster Session (Heavy hors d'oeuvres will be served)	7:00 - 9:00 p.m.

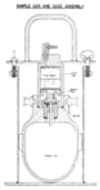
Wednesday, May 23, 2006

Registration	7:30 - 8:15 a.m.
Technical Session IV: Facilities	8:15 - 9:05 a.m.
Technical Session V: Actinide Storage	9:05 a.m. - 12:00 p.m.
Lunch Break	12:00 - 1:00 p.m.
Hanford Site Bus Tour & Visit to the B Reactor	1:00 - 4:30 p.m.

Thursday, May 24, 2006

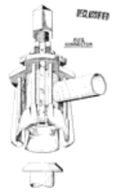
Registration	7:30 - 8:15 a.m.
Technical Session VI: Fuel	8:15 - 9:55 a.m.
Technical Session VII: Tank Waste	10:20 a.m. - 12:00 p.m.
Lunch Break	12:00 - 1:30 p.m.
Technical Session VII: Tank Waste (Cont.)	1:30 – 1:55 p.m.
Technical Session VIII: Solvent Extraction	1:55 – 4:50 p.m.
Banquet/Seaborg Award Presentation	7:00 - 9:00 p.m.

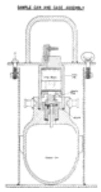




The Glenn T. Seaborg Actinide Separations Award

1984	Glenn T. Seaborg, *University of California at Berkeley*
1985	Don E. Ferguson, *Oak Ridge National Laboratory*
1986	Larned B. Asprey, *Los Alamos National Laboratory*
1987	Wallace W. Schulz, *Westinghouse Hanford Company*
1988	Lawrence J. Mullins, *Los Alamos National Laboratory*
1989	Gregory R. Choppin, *Florida State University*
1990	Donald A. Orth, *Westinghouse Savannah River Company*
1991	David O. Campbell, *Oak Ridge National Laboratory*
1992	E. Philip Horwitz, *Argonne National Laboratory*
1993	Earl J. Wheelwright, *Pacific Northwest Laboratory*
1994	Leslie Burris, *Argonne National Laboratory*
1995	Robert R. Penneman, *Los Alamos National Laboratory*
1996	David G. Karraker, *Westinghouse Savannah River Company*
1997	Major C. Thompson, *Westinghouse Savannah River Company*
1998	Walter D. Bond, *Oak Ridge National Laboratory*
1999	Jack L. Ryan, *Pacific Northwest National Laboratory*
2000	John L. Swanson, *Pacific Northwest National Laboratory*
2001	George F. Vandegrift, *Argonne National Laboratory*
2002	Leonard W. Gray, *Lawrence Livermore National Laboratory*
2003	Kenneth L. Nash, *Argonne National Laboratory*
2004	Emory D. Collins, *Oak Ridge National Laboratory*
2005	Terry A. Todd, *Idaho National Laboratory*





2006 Glenn T. Seaborg Actinide Separations Award

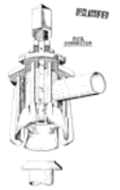
Renato Chiarizia

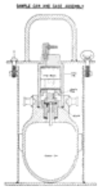
Renato Chiarizia began studying actinide chemistry as a PhD student in Inorganic Physical Chemistry at the University of Rome, Italy during the early 1960s. On completion of his degree in 1966, Renato became a staff Scientist and eventually a Senior Scientist at the Industrial Chemistry Laboratory of the Casaccia Nuclear Center of the Italian Atomic Energy Commission, now known as the Italian Agency for Energy, Environment and New Technologies (ENEA). During his years at Casaccia, he became known for his investigations of the chemistry of lanthanide and actinide complexes relevant to separations systems in both aqueous and biphasic systems, the kinetics of metal ion extraction in liquid-liquid systems, transport processes in liquid membranes, and the development of solvent extraction processes for hydrometallurgical and nuclear waste applications.

In 1981, Renato began the first of four appointments as a Visiting Scientist at various times over the next eleven years in the Chemistry Division at Argonne National Laboratory. During this time, Renato was an active member of the Separations Group where he applied his expertise in separations to the development of important aspects of the chemistry of the TRUEX process, as well as investigations into liquid membrane systems for actinide separations from nuclear waste and the development of new ion exchange and extraction chromatographic materials for actinide separations. He received an R&D 100 Award in 1994 for his work as a co-inventor of the Diphonix ion exchange resin.

Continuing his association with the Separations Group, Renato joined the Chemistry Division at Argonne in 1992 as a full staff member, and is now a Senior Scientist. Since that time, his scientific work has focused on the development of alkylsubstituted diphosphonic acids as actinide separations agents, investigations of the importance of extractant aggregation in solvent extraction systems, and providing the first quantitative descriptions of the mechanism and energetics of third phase formation in TBP solvent extraction systems. Over this time Renato also served as the co-Editor of the journal *Solvent Extraction and Ion Exchange* (1993-2001) and is now its Editor Emeritus.

To relax from the burdens of his scientific work, Renato enjoys opera, yoga, and, when the Chicago weather cooperates, long swims and bicycle rides.



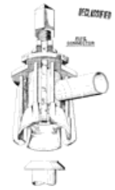


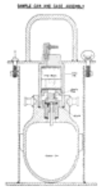
Opening Session

Session Chair: Cal Delegard, PNNL

8:25 a.m. Actinide Separations Research Supported by DOE Office of Basic Energy Sciences
Lester R. Morss and William S. Millman*

8:50 a.m. Tracing the Steps of Illicit Civil Plutonium
Leonard W. Gray, Bartley B. Ebbinghaus, Jor-Shan Choi, Patrick Epperson, Jim Lawson, Doug Manatt, Les Nakae, Darrell Pugh, and Paul Yap-chiongco*





May 23, 2006

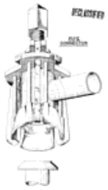
Technical Session I
EMSL Auditorium

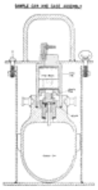
Medical Isotopes

Session Chair: Dennis Wester, PNNL

9:15 a.m. Recovery and Purification of Ac-225 from LWBR Fuel Sources
D. H. Meikrantz, T. A. Todd, T. J. Tranter, J. P. Henscheid, L. C. Lewis, E. P. Horwitz, and D. A. McAlister*

9:40 a.m. Recent Advances in the Extraction and Purification of ^{225}Ac
E. Philip Horwitz, Daniel R. McAlister, and David H. Meikrantz*





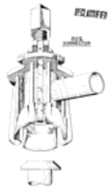
May 23, 2006

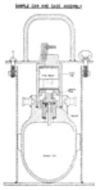
Technical Session II
EMSL Auditorium

Complexation

Session Chair: Sergei Sinkov, PNNL

10:20 a.m.	Understanding Actinide Chemistry: Combining Computational Modeling and Experiment *W. A. de Jong*, J. Li, T. L. Windus, and H. M. Cho*
10:45 a.m.	Application of Liquid Waveguide Capillary Cell Based Optical Absorbance Spectroscopy for Enhanced Actinide Speciation and Complexation *Sergei I. Sinkov* and Gregg J. Lumetta*
11:10 a.m.	Comparative Stability of Uranyl Amide Complexes *Gary S. Groenewold*, Garold L. Gresham, and Michael J. Van Stipdonk*
11:35 a.m.	Coordination Chemistry of Technetium Under Solvent Extraction Conditions *Bruce McNamara*, Herman Cho, Wibe A. de Jong, and Lanée Snow*
12:00 p.m.	Lunch Break





May 23, 2006

Technical Session III
EMSL Auditorium

Plutonium Processing

Session Chair: Joel Tingey, PNNL

1:30 p.m. Uranium Plutonide-Possible Formation During Aging of Plutonium Metal and Some Reactor Fuels
Roberta N. Mulford

1:55 p.m. An Improved Method to Dissolve Plutonium Residues
*Danièle Cardona-Barrau *, Patrick Vedrenne, Laurent Pescayre, and Hervé Chollet*

2:20 p.m. Separation of Metallic Beryllium from Plutonium by Selective Ammonium Fluoride Dissolution
*Fausto G. Bajao, Walt Close, Karen Dodson, Andrea Goins, Oscar Krikorian, and Richard A. Torres**

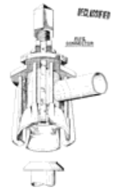
2:45 p.m. Electrochemical Deoxidation of Mixed CaO-$CaCl_2$ Residues
Séverine Ched'Homme

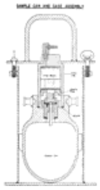
3:10 p.m. Break

3:35 p.m. Chloride-to-Nitrate Solution Conversion
Robert A. Pierce and Ann E. Visser*

4:00 p.m. A Kinetic Model for Predicting Hydroxylamine Nitrate Chemical Stability in Plutonium Process Solutions
G. Scott Barney and Marc A. Vial*

4:25 p.m. Development of a CO_2 Cleaning Technology for the Removal of Plutonium Contamination on Highly-Enriched Uranium Metal Surfaces
Michael S. Blau





May 23, 2006

Poster Session
EMSL Lobby
7:00 - 9:00 p.m.

Poster Session

Session Chair: Cal Delegard, PNNL

Thermodynamic of Cs/Sr Isolation in the UNEX Process: Calorimetric Study
Peter Zalupski, Ken Nash, Terry Todd, Scott Herbst, and Dean Peterman*

Thermodynamic Studies of Actinyl Carbonate Interactions with Hydrogen Peroxide
Tom Shehee, Leigh R. Martin, and Kenneth L. Nash*

Removal of Radioactive Residues from $Al(NO_3)_3$ by Solvent Extraction
Ryan Harrington and Kenneth L. Nash*

Synthesis and Characterization Of N, N'-Bis(2-Methylpyridyl)Piperazine Extractant for Trivalent Actinide Partitioning
Mark D. Ogden and K. L. Nash*

Thermodynamic Features of Lanthanide and Actinide Interactions with α-Hydroxyisobutyric Acid
Maria Kriz and Kenneth L. Nash*

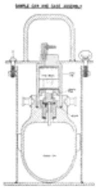
Kinetics of Lanthanide Complexation Reactions with Aminopolycarboxylates in Lactic Acid Media
Aymeric Martin and Kenneth L. Nash*

Hydraulic and Mass Transfer Testing of Commercial 5-cm Annular Centrifugal Contactors at the INL
T. G. Garn, D. H. Meikrantz, N. R. Mann, J. D. Law, and T. A. Todd*

Modular CSSX Unit
Ryan McNew

Development of Custom Processing Flowsheets for Unique Actinide-Bearing Residues
G. F. Kessinger, A. E. Visser, and W. D. Rhodes*

Separation of Ac-225/Bi-213 from Un-Irradiated Light Water Breeder Reactor Fuel
T. J. Tranter, T. A. Todd, D. H. Meikrantz, J. P. Henscheid, and L. C. Lewis*



Characterization of Trans-Dioxotechnetium (V) Excited States and Spectroelectrochemical Detection of Pertechnetate
Samuel A. Bryan, Andrew S. Del Negro, Zheming Wang, Timothy L. Hubler, William R. Heineman, and Carl J. Seliskar*

Actinide Sorption by an Extraction Chromatography Resin Containing an Alkyl-Substituted Kläui Ligand
Tatiana G. Levitskaia, Gregg J. Lumetta, and Sergei I. Sinkov*

Spectrophotometric Studies on the Complexation of NpO_2^+ and PuO_2^{2+} with Dicarboxylic Acids
Guoxin Tian and Linfeng Rao*

Plutonium/Americium Solubility Studies Using Simulated Savannah River Site Waste Solutions
Tracy S. Rudisill, David T. Hobbs, and Thomas B. Edwards*

Disposition of Sources, Standards and Miscellaneous Nuclear Material At PFP
T. J. Venetz

Tantalum Corrosion with Pu-Ti Alloys
T. J. Paget and R. F. Watson*

S-Functionalized Cysteine Ligands for Complexation with $M(CO)_3^+$ (M=Re, ^{99m}Tc) for Diagnostic Applications
Brienne N. Bottenus, Glenn A. Fugate, and Paul Benny*

In Situ Formation of Tridentate Ligands in Aqueous Media from 2, 4-Pentanedione to Form Imine Complexes around $M(CO)_3^+$ (M=Re, Tc) Centers
Glenn A. Fugate, Brienne N. Bottenus, and Paul Benny*

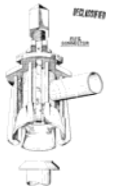
Surface Charge of Layered U(VI):Silicate Solids
Samuel W. Chen, Sarah E. Pepper, Laurence C. Hull, and Sue B. Clark*

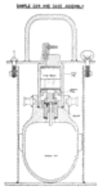
Adsorption of Lanthanum to Goethite in the Presence of Oxalate
François Marsal, Sarah E. Pepper, and Sue B. Clark*

Surface Charge in Montmorillonite
Sarah E. Pepper, Francois Marsal, Laurence C. Hull, and Sue B. Clark*

Improved Milling and Grinding Process
John Stong, Richard Salazar, Anthony Lupinetti, and Cynthia Kowalczyk*

MOX Fuel Fabrication: New Requirements Will Enhance Safety
Archie Nixon, D. Garcia, J. Roybal, J. Valdez, Y. Martinez, and J. Brock*



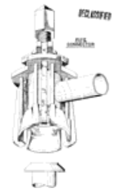


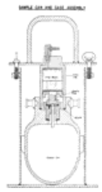
MOX Fuel Fabrication: Where We've Been, Where We Are, and Where We Hope to Be
Devin Gray and Archie Nixon*

The LLNL Heavy Element Facility: Facility Management, Authorization Basis, and Readiness Assessment Lessons Learned in the Heavy Element Facility (B251) Transition from Category II Nuclear Facility to Radiological Facility
Leonard Gray, Brian Anderson, Mark Mitchell, and Erik Brown*

Development of Capillary Electrophoretic Methods for Preconcentration and Separation of Trivalent Lanthanides and Actinides
Erin Finn, Colt Heathman, Judah Friese, and Sue Clark*

Update on Los Alamos National Laboratory Chemistry and Metallurgy Research Facility Replacement Project (NOTE – contains UCNI; poster in EMSL Board Room)
T. R. Leckbee, L. Schulte, V. Hatler, B. T. Martinez, W. Smyth, and Z. Svitra*





May 24, 2006

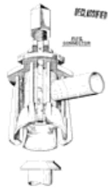
Technical Session IV
EMSL Auditorium

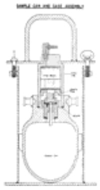
Facilities

Session Chair: Kevin Felker, ORNL

8:15 a.m. Chemistry and Metallurgy Research Replacement (CMRR) Project Update
L. D. Schulte, V. A. Hatler, T. O. Nelson, S. D. Dinehart, T. R. Leckbee, B. T. Martinez, W. D. Smyth, and Z. Svitra*

8:40 a.m. Update of Fuel Cycle Development Activities at the Radiochemical Engineering Development Center
L. K. Felker, P. D. Bailey, D. E. Benker, E. D. Collins, R. J. Vedder, and E. A. Walker*





May 24, 2006

Technical Session V
EMSL Auditorium

Actinide Storage

Session Chair: Ron Livingston, SRNL

9:05 a.m. Failure Analysis of Breached Container 38621
David Kolman, Paul Blumberg, Vince Garcia, and Kirk Veirs*

9:30 a.m. Preparation of Material for the Surveillance and Monitoring Large Scale Corrosion Studies and Initial Results
Obie W. Gillispie, Elizabeth E. Kelly, Annabelle S. Lopez, Joshua E. Narlesky, Dennis D. Padilla, Leonardo A. Trujillo, D. Kirk Veirs, Edward L. Wilson, and Laura A. Worl*

9:55 a.m. Break

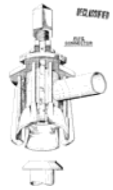
10:20 a.m. Prompt Gamma-Ray Analysis of Plutonium Oxide Inventories at the Plutonium Finishing Plant
J. M. Tingey, S. A. Jones, C. H. Delegard, and D. M. Fazzari*

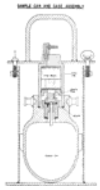
10:45 a.m. Accurate Calculation of NDA Gamma Spectroscopy Correction Factors
Thurman D. Cooper

11:10 a.m. Neptunium Oxide Moisture Concerns at SRS
Jeff Jordan and Paul Palmer*

11:35 a.m. Evaluation of Expanded Neptunium Oxide Production
*Steve Hensel, Robert Watkins, and Ron Livingston**

12:00 p.m. Lunch Break





May 25, 2006

Technical Session VI
EMSL Auditorium

Fuel

Session Chair: Tracy Rudisill, SRNL

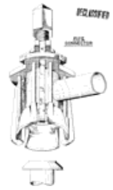
8:15 a.m. Remote Hot-Cell Fabrication of Actinide-Aluminum-Cermet Targets at the REDC for Heavy Element Production
R. D. Taylor, C. W. Alexander, F. D. Riley, and A. Souders*

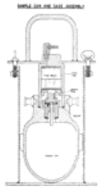
8:40 a.m. Preparation of Minor Actinide Oxides for Sphere-pac Transmutation Fuels
R. R. Brunson, G. D. Del Cul, A. S. Icenhour, L. K. Felker, D. F. Williams, and E. D. Collins*

9:05 a.m. The Retention of Actinides in Cladding Residues from Commercial Spent Fuel Reprocessing
G. F. Kessinger and M. C. Thompson*

9:30 a.m. Decontamination of Zircaloy Spent Fuel Cladding Hulls
Tracy S. Rudisill and Douglas C. Witt*

9:55 a.m. Break





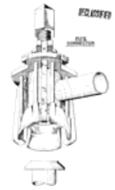
May 25, 2006

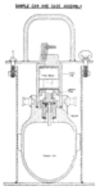
Technical Session VII
EMSL Auditorium

Tank Waste

Session Chair: Andy Felmy, PNNL

10:20 a.m.	Development of Aqueous Thermodynamic Models for HLW Tank Solutions: U(VI)/Pu(VI) Phosphates/Carbonates and the Inclusion of Oxalic Acid *Andrew R. Felmy*, Zheming Wang, Dhanpat Rai, Odeta Qafoku, and Yuanxian Xia*
10:45 a.m.	Uranium and Plutonium Solubility in Actual Savannah River Site Tank Waste *William D. King*, William R. Wilmarth, and David T. Hobbs*
11:10 a.m.	Actinide Gluconate Complexation and Hanford Tank Waste Remediation *Leigh R. Martin*, Ryan L.P. Witty, Aurora E. Clark, Gregory L. Helms and Kenneth L. Nash*
11:35 a.m.	Development of an Improved Titanate-Based Sorbent for Strontium and Actinide Removal from High Ionic Strength Waste Solutions *D. T. Hobbs*, M. D. Nyman, M. J. Barnes, M. E. Stallings, F. F. Fondeur, and S. D. Fink*
12:00 p.m.	Lunch Break
1:30 p.m.	Resorcinol-Formaldehyde Resin Testing for Cs Removal at WTP: Status of Bench and Pilot Testing *W.R. Wilmarth*, W. D. King, F. F. Fondeur, D. J. Adamson, M. D. Fowley, J. L. Steimke, T. J. Steeper, M. Williams, and C. E. Duffey*





May 25, 2006

Technical Session VIII
EMSL Auditorium

Solvent Extraction

Session Chair: Ken Nash, WSU

1:55 p.m. Supramolecular Approach to Third Phase Formation in Solvent Extraction
Renato Chiarizia

2:20 p.m. New Derivatives of CMPO Systems with Special Coordination Properties
Keith H. Pannell, Ramon Villazana, Francisco Cervantes-Lee, Mary Ann Stroud, and Scott Sportsman*

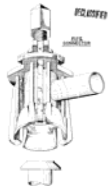
2:45 p.m. NOPOPO Ligands as Selective Actinide Ion Extractants
Robert T. Paine

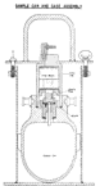
3:10 p.m. Break

3:35 p.m. Prospects for Improving the Performance of the TALSPEAK Process
Kenneth L. Nash, Kelly M. Cooper, and Mikael Nilsson*

4:00 p.m. Extraction and Separation of An(III) and Ln(III) Using the Tetradentate Ligand 6,6'-Bis-(5,6-Dipentyl-[1,2,4]Triazin-3-Yl)-[2,2']Bipyridinyl (C5-BTBP)
M. Nilsson, C. Ekberg, M.R.S. Foreman, J.-O. Liljenzin, and G. Skarnemark*

4:25 p.m. Separation of Actinides and Tc(VII) from HLLW by Using N,N,N',N'-Tetraalkyl-3-Oxa-Glutaramides: Solvent Extraction and Structural Studies
Linfeng Rao and Guoxin Tian*





30th Actinide Separations Conference and Seaborg Award Banquet

Stone Ridge Event Center
5960 Burden Blvd.
Pasco, WA 99301

Social Hour - 6:30 p.m.
Dinner - 7:00 p.m.

Presentation of the 2006 Glenn T. Seaborg Award to

Renato Chiarizia

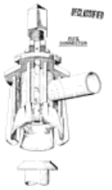
Introduction by Ken Nash

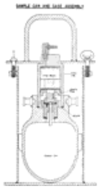
After Dinner Presentation – *"Kennewick Man and the First Americans"*

Dr. James C. Chatters
Forensic Anthropologist
AMEC Earth and Environmental, Inc.

Jim Chatters is a forensic anthropologist who formerly served Benton and Franklin Counties in Washington State, and an archaeologist with more than 35 years experience in the Pacific Northwest. Dr. Chatters studied at Washington State University and the University of Washington and currently is employed as an archaeologist and paleontologist for AMEC Earth and Environmental, Inc. in Kirkland, WA. He is author of the book, *Ancient Encounters: Kennewick Man and the First Americans.*

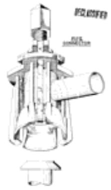
Kennewick Man, a 9400-year-old human skeleton discovered along the banks of the Columbia River in July 1996, has received worldwide attention because of its age, completeness, and the legal controversy over its disposition. Jim Chatters was the first scientist on the scene and has been intimately involved with the find for nearly 10 years. In this presentation he will take the audience on a journey of discovery, legal maneuvering between scientists and the US Government, and the study of the skeleton once the legal case came to an end. He will also compare Kennewick Man to other early American skeletons and discuss what these finds tell us about the origin of the first peoples in the Western Hemisphere.

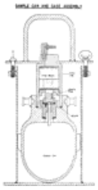




Opening Session
May 23, 2005

Presentation Summaries





Actinide Separations Research Supported by DOE Office of Basic Energy Sciences

Lester R. Morss and William S. Millman,* DOE - Office Basic Energy Sciences

The Office of Basic Energy Sciences (BES) has traditionally supported basic research in actinide chemistry as well as in separations science and will continue to do so. The intersection of these two fields – separations that make use of 5f electrons – is an important theme for advanced nuclear fuel cycles. Recognizing the significance of this topic, BES staff and the research community are planning for new basic research initiatives in actinide separations. This presentation will summarize current research being pursued under BES auspices and research needs identified by recent workshops.

Tracing the Steps of Illicit Civil Plutonium

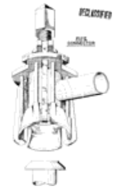
Leonard W. Gray, Bartley B. Ebbinghaus, Jor-Shan Choi, Patrick Epperson, Jim Lawson,*
Doug Manatt, Les Nakae, Darrell Pugh, and Paul Yap-chiongco
Lawrence Livermore National Laboratory

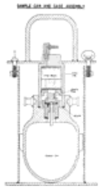
Concerns about nuclear terrorism rose to new levels when A. Q. Khan, the father of Pakistan's nuclear bomb, confessed to peddling nuclear weapons technology to Libya and other rogue states. His confession punctured any remaining illusions that 60 years of nonproliferation efforts had kept nuclear weapons technology out of the hands of countries hostile to the US. Moreover, he enhanced fears that terrorist groups bent on destroying the US may be closer than anyone had realized to acquiring nuclear weapons. Given the grim realities of the post-9/11 world, fear of nuclear terrorism has dominated response to Khan's revelation. Our infant program's response has been to ask the question: "If a clandestine package of plutonium were intercepted, could we determine its origin?"

Fingerprints and forensic analysis have played important roles in criminal law for well over a century. In the relatively new field of "nuclear forensics" similar methods can be applied to determining information about the production and history of special nuclear materials with high degrees of accuracy. Just as with human fingerprinting, nuclear material can be identified, examined, and profiled. The determination of radioisotopes, isotopic and mass ratios, material age, impurity content, chemical form and physical parameters may reveal a "nuclear fingerprint" of the material. General areas in which forensic signatures can be usefully found include: isotopic composition, trace impurities, material properties, and physical packaging.

But nuclear forensic science involves more than determining the physical and chemical characteristics of the nuclear material. The goal is to identify as many clues in intercepted nuclear and radiological samples as possible. These attribution indicators can provide not only a characterization of the nuclear material, but also provide environmental links that could help trace the path the material took from its point of origin or determine how recently it passed from legitimate to illicit use.

This work was performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

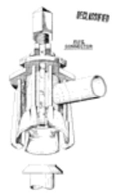


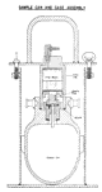


Technical Session I
May 23, 2005

"Medical Isotopes"

Presentation Summaries





Recovery and Purification of Ac-225 from LWBR Fuel Sources

D. H. Meikrantz, T. A. Todd, T. J. Tranter, J. P. Henscheid, and L. C. Lewis,* Idaho National Laboratory
E. P. Horwitz and D. A. McAlister, PG Research Foundation, Inc.

Two methods of recovery of Ac-225 from 70s era LWBR fuel sources will be presented. A batch precipitate, based upon the formation of thorium iodate, is periodically washed to recover the daughters, Ra-225 and Ac-225. The second method is a solvent extraction process that extracts both the uranium-233 and the thorium-232, 229 isotopes into neutral phosphorus based organic solvent that is continuously washed with nitric acid to recover the Ra and Ac isotopes. This method employs commercially available centrifugal contactors with flow rates of up to 600 liters per minute to efficiently recover Ra-225 and Ac-225 while limiting organic solvent radiolysis.

Both processes use extraction chromatography techniques to further isolate, purify, and recover the Ac-225. Actinium-225 is being studied in the medical field to provide bismuth-213 for the treatment of metastatic cancers. Phase II clinical trials are ongoing for acute myeloid leukemia using monoclonal antibodies as the targeting agent. Bismuth-213, with an 8 MeV alpha and a 46 minute half life, is an excellent tool in the selective destruction of cancer cells while causing little collateral cell damage. These two methods were developed to provide additional supplies of Ac-225 to the medical community, currently quite limited by lack of isotope.

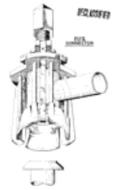
Recent Advances in the Extraction and Purification of ^{225}Ac

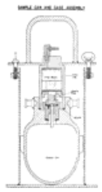
E. Philip Horwitz and Daniel R. McAlister,* PG Research Foundation, Inc.
David H. Meikrantz, Idaho National Laboratory

The need for improved methods for the extraction and recovery of actinium-225 ($t_{1/2}$ = 10d) has been driven by the recent interest in obtaining bismuth-213 ($t_{1/2}$ = 46m) for use in Radio-Immuno Therapy. Since significant quantities of ^{225}Ac are available only from rather sizeable quantities of ^{233}U/^{229}Th, great demands are placed on the separation chemistry. The problem is augmented by the need to isolate and purify the ^{225}Ac in a relatively short period of time.

Our studies have focused on the use of three extraction chromatographic resins which enable one to rapidly remove Th and U from ^{225}Ac, concentrate the ^{225}Ac from a large volume of HNO_3 at the same time separating ^{225}Ra (for storage and ingrowth of ^{225}Ac) and finally separating the ^{225}Ac from any lanthanides present. Our procedure involves no evaporation steps and can easily be repeated on a much smaller scale to achieve further decontamination.

The purified ^{225}Ac is then used in an automated selectivity inversion generated to generate ^{213}Bi as needed.

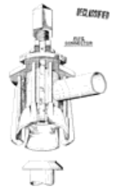


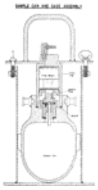


Technical Session II
May 23, 2005

"Complexation"

Presentation Summaries



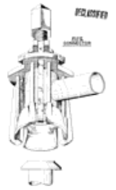


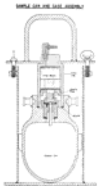
Understanding Actinide Chemistry: Combining Computational Modeling and Experiment

W. A. de Jong, J. Li, T. L. Windus, and H. M. Cho,* Pacific Northwest National Laboratory

Computational chemistry has reached the point where it can make significant contributions to actinide chemistry, to the understanding and interpretation of experimental data, the prediction of chemical and physical properties of heavy transition metal, lanthanide and actinide complexes. The results of a series of combined experimental and computational modeling projects will be presented. Sensitive experimental measurements using NMR and other spectroscopic techniques are combined with the interpretative power of *ab initio* theory to measure and understand the fundamental structural and bonding parameters in complexes containing uranyl, and to test the accuracy of the available computational methodologies. The uranyl complexes studied are relevant to increase the understanding of actinide speciation in waste tanks and in the subsurface.

This work was supported through the U.S. Department of Energy by the MSCF in EMSL at the Pacific Northwest National Laboratory. The MSCF and EMSL are funded by OBER in the U.S. Department of Energy. Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.





Application of Liquid Waveguide Capillary Cell Based Optical Absorbance Spectroscopy for Enhanced Actinide Speciation and Complexation

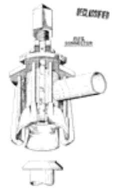
Sergei I. Sinkov and Gregg J. Lumetta,* Pacific Northwest National Laboratory

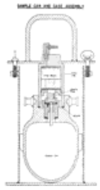
Optical Absorbance Spectroscopy (OAS) has been recognized as a convenient noninvasive technique for studying actinides' redox speciation and complexation in solution. However, its sensitivity is limited to the high submillimolar to low millimolar range of 5f-element concentration. This limitation makes it difficult to apply conventional OAS to study actinide complexation in situations when either the ligand itself or the complex being formed is not soluble enough in aqueous solution to probe formation of higher complexes or simply to allow reliable spectral measurement in solution with developing turbidity. Laser induced photoacoustic spectroscopy and thermal lens spectroscopy, proposed several decades ago for enhanced actinide detection and speciation, proved to be too sophisticated and expensive to implement and exploit on a regular basis in radiochemical laboratories.

In our lab, we are trying to improve sensitivity in OAS measurements of actinide solutions by employing the much more accessible Liquid Waveguide Capillary Cell (LWCC) technology. With LWCC, the optical pathlength of the sample being measured is increased from 1 cm to several hundred cm, while keeping the sample volume down to 1.2 mL. The advantage of using LWCC will be demonstrated on two complexation studies:

(i) Pu(IV) complexation with nitrilotriacetate (NTA) in nitric acid medium
(ii) Pu(IV) and Pu(VI) complex formation with phosphate in mixtures of phosphoric and nitric acids.

In both cases, done at 20 to 70 μM total Pu concentration, spectroscopic characterization of the complex species being formed was achieved and formation constants for 1:1 and 1:2 complex species were refined. Our findings on Pu(IV)-NTA complexation differ markedly from the data previously published on this system and show that the formerly measured value of the first binding constant appears to be significantly underestimated. Possibilities of further improving the LWCC based OAS measurements for actinide detection and speciation in a wider spectral range will be discussed.

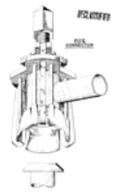


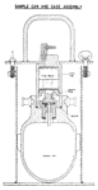


Comparative Stability of Uranyl Amide Complexes

Gary S. Groenewold and Garold L. Gresham,* Idaho National Laboratory
Michael J. Van Stipdonk, Wichita State University

Insight into fundamental separations behavior can be simplified by observing reactivity and vibrational spectroscopy in the gas phase, where complex composition can be controlled. The CMPO class of ligands are bifunctional, containing both phosphoryl and amide ligating groups; the nucleophilicity and solubility of these ligands can be changed by altering substituents on the functional groups. We have examined the relative binding of a series of amide model compounds to the nitratouranyl cation, which has shown that nucleophilicity relative to uranyl follows gas phase basicity patterns: methyl substitution on both the amide carbonyl and on the amide nitrogen increases nucleophilicity; substitution on the carbonyl is slightly more effective than substitution on nitrogen. Comparisons were based on competitive fragmentation reactions occurring for complexes containing two different amide ligands. The binding of the amide ligands relative to acetone were evaluated using infrared spectroscopy and showed that methylacetamide was a more aggressive ligand, shifting the uranyl frequency lower by 25 cm^{-1}. This finding indicates that the nitrogen functional group is either donating electron density directly to the metal or strengthens the carbonyl.



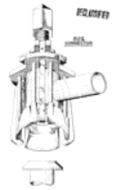


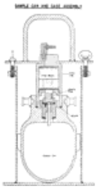
Coordination Chemistry of Technetium Under Solvent Extraction Conditions

Bruce McNamara, Herman Cho, Wibe A. de Jong, and Lanée Snow,* Pacific Northwest National Laboratory

In the Purex process, nuclear fuel is dissolved in nitric acid and the formation of tri-n-butyl phosphate (TBP) complexes of $[UO_2(NO_3)_2(TBP)_2]$ and $Pu(NO_3)_4(TBP)_2$ are considered responsible for the two phase extraction of uranium and plutonium. Technetium is thought to co-extract with uranium and plutonium into the organic phase but the nature of the technetium complexation is not well understood. Recent developments in the coordination chemistry of the pertechnetate anion have resulted in structures with pertechnetate directly coordinated to actinide cations, such as $[UO_2(TcO_4)DPPMO_2)_2]^+$, $UO_2(TcO_4)_2(Ph_3PO)_3$, $Th(TcO_4)_4(n\text{-}Bu_3PO)_3)$, and $(NpO_2)_2(TcO_4)_4.3H_2O$. These complexes have been prepared under laboratory conditions that are typically different than used in the extraction process. Under extraction conditions other coordinative modes can be reinforced because of lipophilic interactions that arise between the aqueous and organic phase components and because of competitive protonolysis of the pertechnetate anion itself. Other coordinative modes might include actinide mixed nitrato-pertechnetate coordination and/or hydrogen bonding of pertechnetic acid, $HTcO_4$, to the phosphoryl moiety in TBP. Yet another possibility in acidic media is extraction of the cationic species TcO_3^+.

We present solvent extraction data, NMR IR, Raman, UV-Vis spectroscopic data and relativistic Density Functional Theory simulations of the NMR data that indicate that protonation of $KTcO_4$ at acid concentrations as low as 0.5 to 1M produces a Tc(VII) species that is extractable using the anionic (pentamethylcyclopentadienyl)tris(diethylphosphito-P)cobalt(III) ligand (Et-Kläui, Na^+ form). The extraction data are consistent with the competitive protonolysis of the ligand, which begins to inhibit technetium extraction above 1M HNO_3. The idea was driven by reported work on the characterization of Et-Kläui –TcO_3^+ and ReO_3^+ complexes from nitric acid. Our ^{99}Tc NMR data are consistent with the loss of up to 50% of the pertechnetate form because of its protonolysis in HNO_3, $HClO_4$, H_2SO_4, and H_3PO_4 media below 5M. Observed and calculated chemical shifts together with calculated nuclear quadrupole coupling constants for several Tc(VII) candidates indicate that at best only low equilibrium concentrations of Tc_2O_7 and TcO_3^+ are formed at nitric acid concentrations below 1M. The extraction of Tc by the anionic Et-Kläui ligand from nitric acid (between 0.5 and 1M) suggests that either pertechnetic acid is extracted, or plausibly, dehydration of pertechnetate is in equilibrium with the acid formation and that equilibrium is driven by the extraction to the TcO_3^+ moiety. Similar chemistry has been discussed for the formation of the nitronium ion by dehydration of HNO_3 in sulfuric acid solutions.



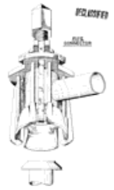


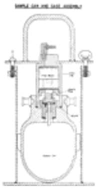
Technical Session III

May 23, 2005

"Plutonium Processing"

Presentation Summaries





Uranium Plutonide-Possible Formation During Aging of Plutonium Metal and Some Reactor Fuels

Roberta N. Mulford, Los Alamos National Laboratory

Accommodation of uranium within the plutonium lattice and the possibility of the formation of the compound uranium plutonide within the grain boundary is of some interest in predicting the behavior of plutonium metal at advanced ages. This compound must be considered in determining the behavior of metallic reactor fuels as diffusion proceeds at operating temperatures. Formation of the high density intermetallic compound UPu could affect the dimensions and mechanical integrity of Pu metal or plutonium-uranium alloys. Disposition of uranium in new castings is generally believed to be to U_6Fe at grain boundaries, but a few cases have been found where iron concentrations are low and provide a stoichiometric limitation to this pathway. Data obtained from plutonium samples is compared with predictions from measured and calculated phase diagrams from the literature, and some mechanisms for uranium accommodation are examined.

An Improved Method to Dissolve Plutonium Residues

Danièle Cardona-Barrau, Patrick Vedrenne, Laurent Pescayre, and Hervé Chollet,* CEA Valduc

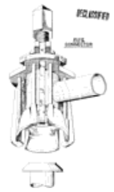
The activities of VALDUC Nuclear Center generate various types of plutonium residues, which do not meet the required purity specifications to be directly reused, or present too high plutonium content to be discarded.

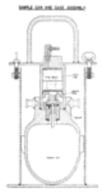
A nitric acid based process has been currently performed to recycle plutonium metal since the seventies. It consists in four main stages:

- Direct dissolution of plutonium metal in sulfamic acid.
- Conversion into a plutonium nitrate form.
- Solution purification.
- Conversion into plutonium dioxide and metal.

This process exhibits several disadvantages. It is not suitable either for alloyed plutonium metal residues, which are difficult to dissolve, or for metal residues containing chloride salts. It is not designed for many by-products bearing plutonium, such as magnesia crucibles. And most of all, it does not meet the current safety criteria which are required for any new installation setting-up.

The purpose of the current studies is to develop a new dissolution process, based on the comprehensive conversion of all plutonium residues to their oxide form, followed by a nitrofluorhydric dissolution. The goals are to warrant a full burning of metal based residues, even metal deposits on any kind of support, and a high dissolution yield of the oxide (>80%) with good kinetics.





Separation of Metallic Beryllium from Plutonium by Selective Ammonium Fluoride Dissolution

*Fausto G. Bajao, Walt Close, Karen Dodson, Andrea Goins, Oscar Krikorian, and Richard A. Torres**
Lawrence Livermore National Laboratory

Calcining metallic Pu/Be mixtures for long-term storage produces a material with a high neutron dose rate because of the Be (α, n) reaction. To avoid this problem, we are investigating the utility of selectively dissolving the Be with aqueous ammonium fluoride solution before the calcining operation. We will discuss the advantages and disadvantages this process might have compared to an alternative process that uses aqueous sodium hydroxide solution as the selective solvent. We will present our operational experiences with testing the method on small (~30 g) batches of material.

Electrochemical Deoxidation of Mixed CaO-$CaCl_2$ Residues

Séverine Ched'Homme, CEA Valduc

It is possible to prepare plutonium metal from its oxide by the Direct Oxide Reduction (DOR) Process. The DOR Process occurs at 850°C in molten $CaCl_2$ according to the following reaction:

$$PuO_2 + 2\ Ca \rightarrow Pu + 2\ CaO.$$

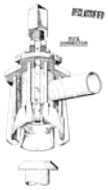
One problem with this process is that it produces a significant quantity of residual mixed CaO-$CaCl_2$ salt. To optimize this process and minimize the production of spent salt, oxygen removal has been considered. Two methods to remove oxygen have been studied:

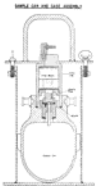
- Electrolysis of dissolved CaO to obtain Ca and O_2,
- Chlorination of the molten CaO-$CaCl_2$ with Cl_2.

An original study of the feasibility of electrolysis has been carried out in the frame of a PhD thesis. For electrolysis to be feasible, several issues such as chlorine gas production and anodic gas redissolution in the molten salt must be solved.

The selective oxidation of O^{2-} without production of chlorine gas would minimize corrosion. One way to avoid chlorine gas production is to prevent the chloride ions from reaching the anode by using a selective membrane. The prevention of anodically produced gas dissolution in the melt can be done with a compartment that physically separates the anode from the rest of the reaction media.

Results will be presented of some feasibility studies of electrochemical deoxidation of CaO-$CaCl_2$ melt at 850°C with yttrium-stabilized zirconia and porous magnesia anodic membranes.





Chloride-To-Nitrate Solution Conversion

Robert A. Pierce and Ann E. Visser,* Savannah River National Laboratory

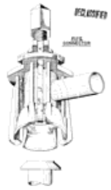
The chosen process for pit production involves pyrochemistry to recover and purify Pu metal, and a mixture of aqueous chloride processing and aqueous nitrate processing to recycle Pu. To simplify aqueous recycle, the Savannah River National Laboratory (SRNL) proposed and performed initial demonstration of a process for stripping chloride from solutions and converting those solutions to nitrate-based solutions using NO_2 gas.

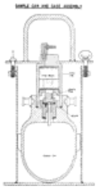
In this approach, chloride-bearing solids are dissolved in either HCl or HNO_3. The resulting solution is contacted with NO_2 gas which strips the chloride as NOCl and converts the solution to a nitrate solution. The NOCl can be scrubbed with either a wet or dry scrubber. Initial testing showed that solutions with as much as 5 M Cl^- could be stripped to less than 20 ppm Cl^- in less than 60 minutes at ambient temperature and pressure. Additional testing explored the effects of temperature and acid concentration. Experimental results using radioactive and non-radioactive solutions will be presented.

A Kinetic Model for Predicting Hydroxylamine Nitrate Chemical Stability in Plutonium Process Solutions

G. Scott Barney,* Self-Employed
Marc A. Vial, Duke COGEMA Stone & Webster, LLC

Accidents involving the rapid decomposition of hydroxylamine nitrate (HAN) – nitric acid solutions have been experienced in nuclear processing facilities in the United States. These reactions release heat and gases that can damage process equipment, disrupt processing, and spread chemical and radioactive contamination. The rapid decomposition of HAN is due to an autocatalytic reaction of HAN with HNO_3 that generates more HNO_2 than can be consumed by a HNO_2 scavenging reaction with HAN. The autocatalytic reaction is accelerated by high temperatures, high nitric acid concentrations, and the presence of dissolved metal catalysts such as iron and plutonium. The reaction mechanisms are complex and involve about twenty different forward reactions and several equilibria. A model was developed that uses rate laws, rate constants, and equilibrium constants measured previously for these reactions. Boundary conditions for HAN stability [temperatures and concentrations of HAN, HNO_3, Fe(III), and Pu(III)] that were predicted using the model were found to duplicate experimental results with reasonable accuracy. At usual respective process concentrations, dissolved Pu(III) is more effective than Fe(II) in decreasing the stability of HAN solutions. Both of these metal ion species promote HAN instability by reducing HNO_3 to HNO_2.

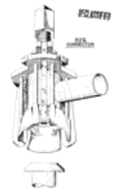


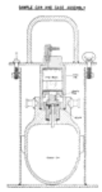


Development of a CO_2 Cleaning Technology for the Removal of Plutonium Contamination on Highly-Enriched Uranium Metal Surfaces

Michael S. Blau, Lawrence Livermore National Laboratory

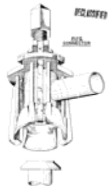
The purpose of this study was to determine if CO_2 cleaning technology could decontaminate highly-enriched uranium (HEU) metal to meet the Y-12 acceptance specification (trace transuranic contamination to less than 20 disintegration per minute (dpm) per 100 cm^2 of surface area). The decontamination level obtained during the cleaning experiments with a Cold Jet® laboratory scale decon unit reduced alpha counts to less than 2 dpm transuranics and less than 6 dpm uranium. Then after the HEU was allowed to oxidize in air for three months, the dpm changed to less than 15 dpm transuranics and less than 20 dpm uranium. Cold Jet® has fabricated a production-scale deconing system that is being installed at Lawrence Livermore National Laboratory (LLNL). Once the installation is complete, LLNL will demonstrate that the production scale system can decon plutonium contaminated HEU parts currently in the LLNL inventory. Once demonstrated at LLNL, the CO_2 cleaning technology will be transferred to other DOE sites.

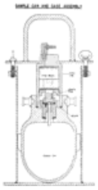




Poster Session
May 23, 2005

Presentation Summaries





Thermodynamic of Cs/Sr Isolation in the UNEX Process: Calorimetric Study

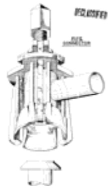
Peter Zalupski and Ken Nash*, Washington State University
Terry Todd, Scott Herbst, and Dean Peterman, Idaho National Laboratory

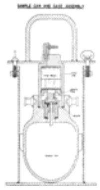
Separation of cesium and strontium from spent nuclear fuel is an essential component of advanced nuclear fuel cycles. The fission products ^{90}Sr/^{90}Y and ^{137}Cs/^{137m}Ba are primary heat and radiation sources during the first 300 years after defueling. Efficient removal of Cs and Sr at the initial stages of the reprocessing cycle could yield a significant reduction of radiation exposure (for personnel, equipment and reagents), allowing more engineering flexibility to successive stages of the SNF treatment facility. Simultaneous separation of cesium, strontium, and the actinides from acidic waste streams by Universal Extraction Process, UNEX, has been demonstrated through several tests with radioactive wastes. Its remarkable efficiency has been achieved without a fundamental understanding of the overall process. The primary objective of this project is to elucidate the chemical equilibria accounting for Cs and Sr partitioning in the UNEX process. In particular, the thermodynamic parameters of liquid-liquid distribution reactions will be investigated for Cs and Sr using calorimetry. The biphasic calorimetric titration experiments will be designed to establish the primary relationships between components of the complex extractant solution and system performance. The conceptual design of the investigated system and initial results will be presented. (Work supported under subcontract to the Idaho National Laboratory, Laboratory Director's Research and Development program)

Thermodynamic Studies of Actinyl Carbonate Interactions with Hydrogen Peroxide

Tom Shehee, Leigh R. Martin, and Kenneth L. Nash,* Washington State University

Hydrogen peroxide is recognized as an important product of the alpha radiolysis of water in nuclear fuel processing applications and is probably equally significant in repository performance assessment. Recent results in the literature indicate that its importance as a complexing agent may have been underestimated. In fact, it has been shown that in carbonate or bicarbonate media, the triscarbonato uranyl complex ($UO_2(CO_3)_3^{4-}$) reacts with peroxide to form an intensely orange colored complex with peroxide incorporated into the structure. Np(VI) and Pu(VI) analogs have also been reported. Though the uranyl complex has been relatively well characterized, the thermodynamics of complex formation has been overlooked. The results presented here describe the beginning of an investigation into the enthalpy of formation of this complex in various carbonate and bicarbonate media. A description of proposed spectroscopic and thermometric titrations are offered and supported by early results. (Work supported by the DOE AFCI/U-NERI program)





Removal of Radioactive Residues from $Al(NO_3)_3$ by Solvent Extraction

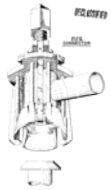
Ryan Harrington and Kenneth L. Nash,* Washington State University

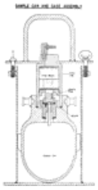
Because of the complexity of alkaline tank wastes, aqueous alkaline leaching can be expected to not achieve complete success in minimizing waste volumes during the cleanup of underground waste tanks. Previous laboratory investigations on Hanford tank sludge simulant samples indicated that an acidic scrub can enhance the dissolution of Al from various sludge matrices. If acidic leaching was deployed, the resulting acidic $Al(NO_3)_3$ leachate solution could contain measurable amounts of solubilized transuranic elements and so would demand treatment prior to disposal. In this study, a liquid-liquid extraction system for the decontamination of the $HNO_3/Al(NO_3)_3$ aqueous leachate by contact with 60% v/v tributyl phosphate (TBP)/*n*-dodecane organic solution has been examined. The partitioning of U and Eu between the TBP phase and solutions of varying $[HNO_3]$ and $[Al(NO_3)_3]$ containing small amounts of Cr or ascorbic acid have been investigated. The results indicate that more than 99% of both species could be removed from the aqueous phase using such a process. (Work supported by the DOE EMSP program)

Synthesis and Characterization of N, N'-Bis(2-Methylpyridyl)Piperazine Extractant for Trivalent Actinide Partitioning

Mark D. Ogden and K. L. Nash,* Washington State University

Owing to the chemical similarities of trivalent Ln and An, the mutual separation of the two groups is one of the most challenging tasks in separation science. The prior literature teaches us that donor atoms softer than oxygen, e.g. N, S, Cl, are most effective for accomplishing this separation. It also has been shown that more sterically hindered ligands in which donor atoms are favorably preoriented have an increased overall binding affinity. Work underway at WSU addresses the design, synthesis and characterization of a series of tetradentate amine ligands containing both "soft" and "hard" nitrogen donors with increased steric "focus" of their donor groups. In this presentation, we will discuss early results on the synthesis of various sterically hindered bis-2-methylpyridyl diamine ligands. We will also report on the preliminary investigation into the complexation of trivalent lanthanides by N,N'-bis(2-methylpyridyl)piperazine (BPMPIP). This work will be discussed in the context of nuclear fuel reprocessing and with the emphasis on future work to be performed, highlighting the different types of ligands that will be synthesized and investigated. (Work supported by the DOE AFCI/U-NERI program)





Thermodynamic Features of Lanthanide and Actinide Interactions with α-Hydroxyisobutyric Acid

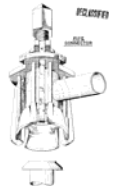
Maria Kriz and Kenneth L. Nash,* Washington State University

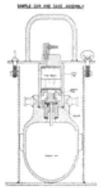
Alpha hydroxyisobutyric acid (HIBA) is used for the mutual separation of trivalent lanthanides and actinides. Since its introduction in 1956, HIBA has remained the most effective separating agent used for this application, though many related reagents have been examined. Further, the thermodynamic features of this system have been described in aqueous media. The aim of this investigation is to explore the solvation energetics of this system and its effect on the separation of the lanthanides series. We plan to examine the effect of alcohol substitution on both the separation efficiency and on the thermodynamic features of the metal complexes. It is suspected that increasing the methanol concentration will decrease the second-sphere solvation of the lanthanide complexes and thus affect the mutual separation of lanthanide ions. At this early stage, it is impossible to predict whether changing the solvent will improve the separation or cause it to deteriorate. It is also conceivable that other complexants will exhibit improved separation under such conditions; hence we plan to examine the effect of solvent substitution on lanthanide separation efficiency mediated by structurally-similar complexing agents. In the later stages of this study, we plan to extend our examination to consideration of trivalent actinide separations. In this presentation the overall experimental plan will be outlined emphasizing methods that will be employed in the study.

Kinetics of Lanthanide Complexation Reactions with Aminopolycarboxylates in Lactic Acid Media

Aymeric Martin and Kenneth L. Nash,* Washington State University

An important feature of the chemistry of the TALSPEAK process (for the separation of trivalent actinides from lanthanides) is the interaction of trivalent lanthanide and actinide cations with aminopolycarboxylic acid complexing agents in lactic acid buffer systems. To improve our understanding of the mechanistic details of these processes, we have begun an investigation of the kinetics of lanthanide complexation by EDTA in concentrated lactic acid solutions. The reactions occur in a time regime suitable for study by stopped-flow spectrophotometry. Progress of the reaction is monitored using the distinctive visible spectral changes attendant to lanthanide complexation by the colorimetric indicator ligand Arzenazo(III). Experiments have been conducted as a function of pH, lactic acid concentration, EDTA concentration and temperature. Under all conditions the kinetic traces are adequately adjusted using the rate law appropriate for a single exponential decay. The reaction proceeds as a first order approach to equilibrium over a wide range of conditions, allowing the simultaneous determination of complex formation and dissociation rate constants. Lactate anions are strongly involved in both the complex formation and dissociation reactions, suggesting the presence of mixed ligand complexes. Further studies are planned to examine the rate and mechanism of EDTA complexation with heavier lanthanide cations, and for lanthanide interactions with DTPA (diethylenetriamine-N,N,N',N",N"-pentaacetic acid). (Work supported by the DOE AFCI/U-NERI program)





Hydraulic and Mass Transfer Testing off Commercial 5-cm Annular Centrifugal Contactors at the INL

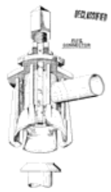
T. G. Garn, D. H. Meikrantz, N. R. Mann, J. D. Law, and T. A. Todd,* Idaho National Laboratory

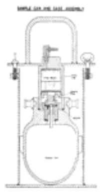
Commercially available, engineering/production scale, annular centrifugal contactors are currently being evaluated at the INL in support of Advanced Fuel Cycle Initiative (AFCI) goals. The evaluation to date has consisted of hydraulic testing, low mix/high mix comparison testing, and mass transfer testing using single-stage 5-cm centrifugal contactors. Hydraulic testing using normal paraffin hydrocarbon and water established optimum rotor speed ranges, total throughput, heavy-phase weir diameters, and o/a phase ratio tolerance. The optimized conditions were then successfully tested in extraction, scrub, and strip sections in a transuranic extraction (TRUEX) process flowsheet. Mass transfer testing provided single-stage extraction and strip section efficiencies of >95% at optimum rotor speeds and throughput. The hydraulic testing of the solvent/sodium carbonate wash section exposed an emulsion formation during the third solvent turnover using the high mix bottom plate. As a result, additional testing was performed to evaluate the applicability of the low mix sleeve for the wash section. The results from the low mix wash testing revealed that the low mix option adequately washed the solvent before reacidification and recycle. Additional mass transfer efficiency results indicated that the low mix option provides about one-third less mixing than the high mix option in forward extractions.

Modular CSSX Unit

Ryan McNew, Washington Savannah River Company

The Modular CSSX Unit (MCU) is under construction at the Savannah River Site. MCU will provide cesium removal capability from the dissolved salt solution in the SRS tank farms. MCU is downstream from the Actinide Removal Process (ARP) which removes entrained sludge and reduces strontium and actinides with Monosodium Titanate (MST) adsorption. This clarified salt solution is the feed to MCU. MCU is primarily made up centrifugal contactors that contact the clarified salt solution with a unique solvent which removes the cesium. The cesium is then stripped from the solvent and ultimately vitrified. After stripping the cesium, the salt solution is then suitable for on-site grouting and disposal. The combination of MCU and ARP provides the capability to continue processing waste until the Salt Waste Processing Facility is constructed.





Development of Custom Processing Flowsheets for Unique Actinide-Bearing Residues

G. F. Kessinger, A. E. Visser, and W. D. Rhodes,* Savannah River National Laboratory

After more than 50 years of production activities, numerous "unique" items that are not amenable to dissolution by the standard Savannah River Site processes have been produced. These items include uranium-bearing slag-flux materials that were recovered subsequent to uranium refinement, failed plutonium fluoride reduction residues, glovebox "sweepings" generated during facility deactivation, and "standards" used for instrument calibration. Generally, the only knowledge about these items is a description of the process that generated the material, the fissile content, and the gross mass of the items. Occasionally, only the fissile content and the mass are known.

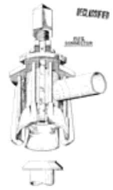
In general, the approach to the flowsheet development included the following steps: visual inspection, structural characterization (X-ray diffraction and/scanning electron microscopy), development of dissolution chemistry, and characterization of dissolver product solutions and solid residues. In this presentation, a few of the most unique items, such as uranium processing slag and failed plutonium fluoride reductions and the activities associated with the flowsheet development for these items, will be discussed.

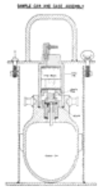
Separation of Ac-225/Bi-213 from Un-Irradiated Light Water Breeder Reactor Fuel

T. J. Tranter, T. A. Todd, D. H. Meikrantz, J. P. Henscheid, and L. C. Lewis,* Idaho National Laboratory

Bismuth-213 is one of the primary isotopes being used in clinical trials for alpha immunotherapy (API). This isotope is preferred by the medical community because of its decay properties and chemical characteristics. The decay chain of Bi-213 includes several high energy alpha emissions without producing significant gamma radiation. The isotope can also be efficiently linked to the delivery agent, i.e. monoclonal antibody. Actinum-225, which is a parent of Bi-213, is typically used to produce a cow from which the short-lived bismuth isotope is milked. The primary source of Ac-225 is from the decay of Th-229.

Fuel left over from the circa 1970 light water breeder reactor (LWBR) program contains valuable amounts of Th-229 resulting from the approximately 35 year decay of U-233. A separation method is proposed which separates the U-233 from the bulk of the thorium in the LWBR fuel. The thorium is precipitated and then this precipitate is used as a cow to produce the desired isotopes, Ac-225/Bi-213. This method was tested at bench-scale using actual LWBR pellets. Results of this testing, including product purity and recovery will be presented and discussed.





Characterization of *Trans*-Dioxotechnetium (V) Excited States and Spectroelectrochemical Detection of Pertechnetate

Samuel A. Bryan, Andrew S. Del Negro, Zheming Wang, and Timothy L. Hubler*
Pacific Northwest National Laboratory

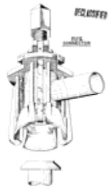
William R. Heineman and Carl J. Seliskar, University of Cincinnati

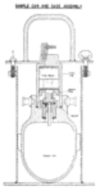
We report the first examples of Tc(V) excited-state luminescence. We have examined a series of *trans*-dioxo complexes of technetium(V) and compared their photophysical properties with the corresponding *trans*-dioxo rhenium(V) analogues. When excited with a 415 nm laser, the technetium complexes luminescence in the 700-800 nm range and have excited state lifetimes (τ) on the range of several microseconds at room temperature. The low-temperature luminescence spectra of the technetium complexes have also been investigated. Distinct vibrational band progressions are resolved in the low-temperature luminescence spectra. Excited state lifetimes at 5 K vary between tens of microseconds to several milliseconds for the dioxo-technetium complexes. Characterization of the new dioxo-technetium(V) excited state as well as application of the *trans*-$[\mathrm{TcO_2}]^+$ chromophore for use in a spectroelectrochemical sensor for pertechnetate will be discussed.

Actinide Sorption by an Extraction Chromatography Resin Containing an Alkyl-Substituted Kläui Ligand

Tatiana G. Levitskaia, Gregg J. Lumetta, and Serguei I. Sinkov,* Pacific Northwest National Laboratory

Lanthanide and actinide ions form stable complexes with ligands containing hard donor atoms such as the oxygens of carboxylate and phosphonate. Among other organophosphorus ligands, the interesting family of Kläui ligands consisting of cyclopentadienyltris(dialkylphosphito)cobalt(III) anions exhibits uniquely strong for affinities for the multivalent actinide ions. Kläui ligands act typically as bulky tripodal chelators and form 1:1 and 1:2 metal-to-ligand complexes with the actinide ions. To address a common need to separate actinide ions for the analytical purposes we have recently prepared extraction chromatography resins containing $\mathrm{Cp^*Co[P(O)(OR)_2]_3^-}$ ($\mathrm{Cp^*} = \eta^5\text{-}\mathrm{C_5Me_5}$; R = Et, 0.75 wt% or R = nPr, 1.0 wt%) on Amberlite® XAD-7 solid support. These resins were previously shown to strongly absorb $\mathrm{Am^{3+}}$ and $\mathrm{Pu^{4+}}$ ions. In this report, the speciation and transport behavior of tri-, tetra-, penta-, and hexa-valent actinides using chromatography resin containing the n-propyl Kläui ligand is described. Systematic distribution measurements as a function of the aqueous solution composition containing 0.1 – 8 M nitric acid and ligand loading are reported. These distribution results are correlated with the actinide redox speciation analysis using UV-vis spectrophotometry.





Spectrophotometric Studies on the Complexation of NpO_2^+ and PuO_2^{2+} with Dicarboxylic Acids

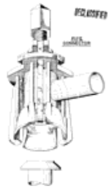
Guoxin Tian and Linfeng Rao,* Glenn T. Seaborg Center, Lawrence Berkeley National Laboratory

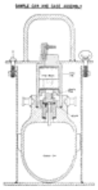
Complexation of NpO_2^+ and PuO_2^{2+} with oxalic acid (OX), 2,2'-oxydiacetic acid (ODA), 2,2'-iminodiacetic acid (IDA), 2,2'-thiodiacetic acid (TDA), and malonic acid (MA) has been studied using spectrophotometry in 1 M $NaClO_4$. Both the position and the intensity of the absorption band of NpO_2^+ at 980 nm and PuO_2^{2+} at 830 nm are affected by the formation of AnO_2^+/dicarboxylate complexes, providing useful information on the complexation strength, the coordination mode and the structure of the complexes. Both 1:1 and 1:2 complexes were observed with OXA, ODA, IDA, and MA, but only 1:1 complex was observed with TDA. The results confirm that, for the actinyl ions with f^2 electronic configuration, the *f-f* transitions should be totally forbidden if a center of inversion exists in the complexes, resulting in the "silence" of the absorption bands of NpO_2^+ at 980 nm and PuO_2^{2+} at 830 nm.

Plutonium/Americium Solubility StudiesUsing Simulated Savannah River Site Waste Solutions

Tracy S. Rudisill, David T. Hobbs, and Thomas B. Edwards*, Washington Savannah River Company

To address the accelerated disposition of the supernate and salt portions of Savannah River Site high level waste, solubility experiments were performed to develop a predictive capability for plutonium (Pu) and americium (Am) solubility. This study used a statistically designed experimental matrix to evaluate the effects of six major anionic components (hydroxide, aluminate, sulfate, carbonate, nitrate, and nitrite) and temperature (25 and 80 °C). Solubility data were collected at approximate one month intervals over a five month period for both elements. A first-order model of the Pu data indicated that the solubility is a function of hydroxide and carbonate concentrations. These factors were statistically significant with at least 90% confidence. The Pu solubility data obtained from this study were also combined with historical data from the literature to develop a modified response surface model. All of the salt concentrations and temperature terms were statistically significant at the 90% confidence level. Only trends in the data collected for Am solubility will be presented; a filtration study conducted with one sample set showed that small Am-containing particles were not effectively removed during sample preparation.





Disposition of Sources, Standards and Miscellaneous Nuclear Material at PFP

T. J. Venetz, Fluor Hanford

Efforts are underway to close and deinventory the Plutonium Finishing Plant. Stabilization and Packaging of surplus Plutonium Material in preparation for offsite shipment was completed in 2004. This poster presentation will describe efforts since then to disposition excess nuclear material, primarily in the form of unused sources and standards and excess nuclear material that was not in the scope of the long term packaging efforts. Disposition has included shipment offsite for beneficial re-use, redeployment on-site, and packaging for disposal as waste. These materials vary in material form and composition, some are unique one-of-a-kind materials, and many require individual disposition planning. This poster will describe the efforts to date and those planned to ensure completion of the project.

Tantalum Corrosion with Pu-Ti Alloys

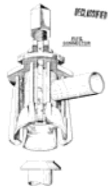
T. J. Paget and R. F. Watson,* AWE

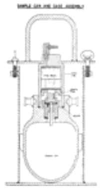
During the processing of Pu-Ti alloys a number of material compatibility issues have been observed. In particular, tantalum stirrers that have been used previously without problems, have shown significant pitting corrosion when processing Pu-Ti alloys. Observations suggest that the presence of titanium is required to initiate and propagate the reaction. It is suggested titanium dissolved in the plutonium is incorporated into tantalum grain boundaries. Plutonium then dissolves material at the grain boundaries causing whole grains to be removed.

S-Functionalized Cysteine Ligands for Complexation with $M(CO)_3^+$ (M=Re, ^{99m}Tc) for Diagnostic Applications

Brienne N. Bottenus, Glenn A. Fugate, and Paul Benny,* Washington State University

Technetium and rhenium can be converted into the $[M(OH_2)_3(CO)_3]^+$ species which is a useful labeling agent in the formation of diagnostic and therapeutic radiopharmaceuticals. Tridentate ligands can form linking agents to attach the organometallic species to promising targeting agents. The functionalization of cysteine by converting the free thiol to a thioether can improve the complexation of *fac*-$M(CO)_3^+$ (M= Re, ^{99m}Tc) and serve as a synthetic handle for coupling the ligand to biomolecules. Several model amino acid and peptide analogs were coupled with cysteine. The cysteine linked peptides were examined with rhenium and structurally characterized by standard chemical analyses to determine the specific coordination at the N, O, S donors of the S-modified cysteine section of the compound. Radioactive ^{99m}Tc complexes were prepared and compared to the retention times of the analogous rhenium compounds on HPLC showing >90% labeling efficiency.





In Situ Formation of Tridentate Ligands in Aqueous Media from 2, 4-pentanedione to Form Imine Complexes Around $M(CO)_3^+$ (M=Re, Tc) Centers

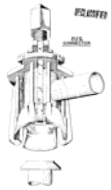
Glenn A. Fugate, Brienne N. Bottenus, and Paul Benny,* Washington State University

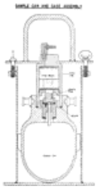
Technetium-99m and Rhenium-188 are useful isotopes for diagnosis and treatment using organometallic radiopharmaceuticals. The reduction of TcO_4^- or the oxidation of $Re_2(CO)_{10}$ can form the $[M(CO)_3(OH_2)_3]^+$ (M = Tc, Re) species at macroscopic or tracer level concentrations. The $[M(CO)_3(OH_2)_3]^+$ (M = Tc, Re) species can be attached to a variety of target specific compounds by the addition of a tridentate donor. Exploration of new methods for radiolabeling that enhance biological affinity and separation has led this investigation to prepare a multidentate compound by reacting 2 ligands on a metal center. A family of 2, 4-pentanedione (acac) complexes with the $[M(CO)_3(OH_2)_3]^+$ (M=Re, Tc-99m) species has been synthesized on the macroscopic and radiotracer level. Several "2 + 1" type donor systems complexes of the form $[M(CO)_3(acac)L]$ were made where M = Re or Tc-99m and L is a simple amine ligand such as pyridine. Several acac based tridentate ligands were synthesized using the metal center as a template.

Surface Charge of Layered U(VI):Silicate Solids

Samuel W. Chen, Sarah E. Pepper, and Sue B. Clark,* Washington State University
Laurence C. Hull, Idaho National Laboratory

The sorption of cations to clay minerals is an important process controlling the dissolved concentration, and thus mobility, of contaminants. Some U(VI)-silicates are structurally similar to clay minerals, in that the U(VI)-silicates form negatively charged sheet-like structures. These layered structures that are held together by interlayer cations and water. Common examples of these layered U(VI):silicates are uranophane, boltwoodite, and sklowdowskite. In this work, we are synthesizing and characterizing sodium boltwoodite, $(Na(H_3O)[UO_2)(SiO_4)])$, a 1:1 U(VI)-silicate with Na^+ and water in the interlayer. Little is known about its overall surface charging properties, which we are studying using electrophoretic mobility as a function of pH and ionic strength. The goal of this work is to develop a thermodynamic description of sodium boltwoodite's surface charging properties that can later be used to predict cation sorption to the solid.





Adsorption of Lanthanum to Goethite in the Presence of Oxalate

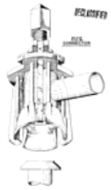
François Marsal, Sarah E. Pepper, and Sue B. Clark,* Washington State University

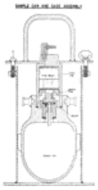
In an effort to understand and predict the environmental impact of radioactive waste, it is important to understand the behaviour of the actinides in the environment. Their sorption to mineral surfaces has been shown to be one of the most important controls on their mobility. The iron oxide goethite (FeOOH) has been shown to sorb many metals including the actinides and lanthanides. In this study, we have investigated the sorption of trivalent lanthanum (La^{3+}), as an analogue for the trivalent actinides, to goethite as a function of concentration and pH. The effect of oxalic acid, a common soil component, has also been investigated under similar experimental conditions. In an attempt to obtain a quantitative description of the adsorption reactions, the data has been interpreted using the diffuse double layer model.

Surface Charge in Montmorillonite

Sarah E. Pepper, Francois Marsal, and Sue B. Clark,* Washington State University
Laurence C. Hull, Idaho National Laboratory

In a waste disposal environment, sorption of cations to clay minerals may limit their dissolved (and hence, mobile) concentrations. Montmorillonites are a class of common aluminosilicate minerals that may be important surfaces to which the actinides may sorb, but little is known about the mechanisms of sorption, and the thermodynamic data to represent such interactions are often not available. In this study, montmorillonite has been characterized using electrophoretic mobility and potentiometric titrations to determine the point of zero charge. The sorption of trivalent lanthanides (as analogs to the trivalent actinides) has been investigated as a function of pH and ionic strength as has the reversibility of the reaction to check for hysteresis. This data has then been inputted into a geochemical model in an attempt to parameterize sorption. These results are intended to lead to a better understanding of the processes that control radionuclide transport in the environment.





Improved Milling and Grinding Process

John Stong*, Richard Salazar, Anthony Lupinetti, and Cynthia Kowalczyk, Los Alamos National Laboratory

In an effort to reduce time and dose in the milling and grinding process, a search was launched to find a more efficient method. The present method requires a two step process. The first step is to reduce moderately sized particles via a jaw crusher and the second step is to further reduce the size of the particles by using a pulverizer. At best, this process currently takes approximately two to four hours to complete.

After extensive brain storming, an electric residue processor was selected and a series of tests were scheduled and completed using graphite blocks, our hardest material to size reduce. The device reduced processing time from two to four hours down to fewer than ten minutes. This improvement not only means that personal dose will be significantly reduced, but it will also increase the efficiency in the milling and grinding process.

LA-UR-06-2267

MOX Fuel Fabrication: New Requirements Will Enhance Safety

Archie Nixon*, D. Garcia, J. Roybal, J. Valdez, Y. Martinez, and J. Brock, Los Alamos National Laboratory

A requirement that has been imposed on the MOX Fuel Fabrication process enhances safety by ensuring that the pressure relief valve (PRV) on the ion exchange column is changed annually. Along with ensuring that the resin does not dry out, and that the resin does not receive too much dose (<500 MRads), these new interim Technical Safety Requirements (iTSRs) add formality and paperwork to a routine plutonium processing operation.

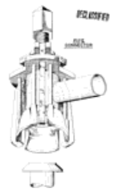
LA-UR-06-3161

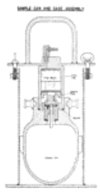
MOX Fuel Fabrication: Where We've Been, Where We Are, and Where We Hope to Be

Devin Gray* and Archie Nixon, Los Alamos National Laboratory

The MOX fuel fabrication effort has been a success story for the Los Alamos National Laboratory as a whole, and specifically a success for our group, Actinide Process Chemistry, NMT-2. More tasks remain, yet there are turbulent waters ahead. With the changes on the forefront, and plans for process optimization, improved process efficiency and waste minimization, much work lies ahead. These are some of the tasks to accomplish to continue on the past successes of others and carry on one of the vital missions of our plutonium facility.

LA-UR-06-3162





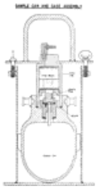
The LLNL Heavy Element Facility
Facility Management, Authorization Basis, and Readiness Assessment Lessons Learned in the Heavy Element Facility (B251) Transition from Category II Nuclear Facility to Radiological Facility

Leonard Gray, Brian Anderson, Mark Mitchell, and Erik Brown,* Lawrence Livermore National Laboratory

This paper presents Facility Management, Readiness Assessment, and Authorization Basis experience gained and lessons learned during the Heavy Element Facility Risk Reduction Program (RRP). The RRP was tasked with removing contaminated glove boxes, radioactive inventory, and contaminated ventilation systems from the Heavy Element Facility (B251) at Lawrence Livermore National Laboratory (LLNL). The RRP was successful in its goal in April 2005 with the successful downgrade of B251 from a Category II Nuclear Facility to a Radiological Facility. The expertise gained and the lessons learned during the planning and conduct of the RRP included development of unique approaches in work planning/work control ("*Expect the unexpected and confirm the expected*") and facility management. These approaches minimized worker dose and resulted in significant safety improvements and operational efficiencies. These lessons learned can help similar operational and management activities at other sites, including facilities restarting operations or new facility startup.

B251 was constructed at LLNL to provide research areas for conducting experiments in radiochemistry using transuranic elements. Activities at B251 once included the preparation of tracer sets associated with the underground testing of nuclear devices and basic research devoted to a better understanding of the chemical and nuclear behavior of the transuranic elements. Due to the age of the facility, even with preventative maintenance, facility safety and experimental systems were deteriorating. A variety of seismic standards were used in the facility design and construction, which encompassed eight building increments constructed over a period of 26 years. The cost to bring the facility into compliance with the current seismic and other requirements was prohibitive, and simply maintaining B251 as a Category II nuclear facility posed serious cost considerations under a changing regulatory environment. Considering the high cost of maintenance and seismic upgrades, the RRP was created to mitigate the risk of dispersal of radioactive material during an earthquake by removing the radioactive materials inventory and glove box contamination. LLNL adopted the goal of reducing the hazard categorization of the Facility from a Category II Nuclear Facility to a Radiological Facility.

To support the RRP, B251 transitioned from a standby to a fully operational Category II Nuclear Facility, compliant with current regulations. A work control process was developed, procedures were developed, Authorization Basis Documents were created, work plans were written, off-normal drills practiced, a large number of USQ reviews were conducted, and a "Type II" Readiness Assessment (RA) was conducted to restart operations. Subsequent RA,s focused on specific operations. Finally, a four-step process was followed to reach Radiological Status: (1) Inventory Reduction and D&D activities reduced the inventory and radiological contamination of the facility below the Category III threshold (DOE-STD-1027), (2) Radiological Safety Basis Document (SBD aka HAR) was approved by NNSA, (3) the inventory control system for a Radiological Facility was implemented, and (4) verification by NNSA of radiological status was completed.



Key to this success is the RRP philosophy in a schedule driven paradigm.

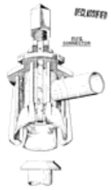
- *"Expect the unexpected and confirm the expected"*
- Recognize when you reach the point of diminishing returns,
- Develop robust processes that anticipate and can handle surprises,
- Plan, plan, and re-plan *"Measure twice, cut once"*

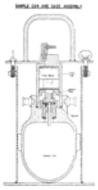
This work was performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under contract No. W-7405-ENG

Development of Capillary Electrophoretic Methods for Preconcentration and Separation of Trivalent Lanthanides and Actinides

Erin Finn, Colt Heathman, and Sue Clark,* Washington State University
Judah Friese, Pacific Northwest National Laboratory

Separation of the trivalent lanthanides from each other, and their separation from the trivalent actinides is challenging due to the similarities in their chemistries. Capillary electrophoretic (CE) techniques facilitate such separations due to their high efficiency and resolution, although a lack of sensitivity is often a limitation. On-capillary preconcentration can improve the limits of detection for UV-Vis in capillary electrophoresis. Isotachophoresis (ITP) is one preconcentration technique that is compatible with capillary electrophoresis; concentration factors on the order of 50-100 have been achieved using ITP. We are developing CE and ITP methods for lanthanide and actinide separations that are based on α-hydroxyisobutyric acid (HIBA) as the separating agent in aqueous and mixed aqueous-methanol solvents. Complexation of the lanthanides and actinides by HIBA are governed largely by hydration effects; the mixed aqueous-methanol system is intended to reduce the endothermic dehydration enthalpy that occurs in pure water systems. In this presentation, we will describe an ion exchange approach to elucidate hydration enthalpy and entropy contributions to trivalent lanthanide complexation and separation.



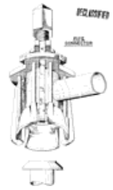


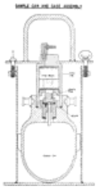
Update on Los Alamos National Laboratory Chemistry and Metallurgy Research Facility Replacement Project

T. R. Leckbee, L. Schulte, V. Hatler, B. T. Martinez, W. Smyth, and Z. Svitra*
Los Alamos National Laboratory

The overall purpose of the Chemistry and Metallurgy Research Replacement Project (CMRR) is to replace the analytical chemistry, materials characterization, and actinide research and development laboratories in the aging CMR facility and to integrate these functions efficiently with the existing functions at TA-55. The proposed CMRR will include the necessary new facilities to achieve this replacement, located at TA-55. The new facility will increase the reliability of the various research and development (R&D) programs and enhance the safety of these operations for the employees, the public, and the environment. The CMRR will be built to satisfy present Department of Energy (DOE) safety standards for a nonreactor nuclear facility. Its modern laboratories will accommodate the plutonium analytical chemistry and materials characterization activities now carried out in the existing CMR Facility. This poster will show an update of the detailed preliminary layout of the Nuclear Facility (NF) & Radiological Laboratory (RL) & to Support Analytical Chemistry, Materials Characterization and Actinide R&D.

LA-UR-06-2621

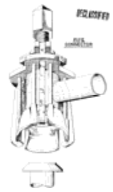


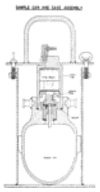


Technical Session IV
May 24, 2005

"Facilities"

Presentation Summaries





Chemistry and Metallurgy Research Replacement (CMRR) Project Update

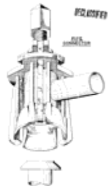
L. D. Schulte, V. A. Hatler, T. O. Nelson, S. D. Dinehart,*
T. R. Leckbee, B. T. Martinez, W. D. Smyth, and Z. Svitra
Los Alamos National Laboratory

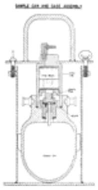
The Chemistry and Metallurgy Research Replacement (CMRR) Project provides a key component of NNSA's mission supporting a wide range of scientific and technological capabilities including nuclear materials handling, materials processing, fabrication, stockpile management, manufacturing technologies, nonproliferation programs, special nuclear material storage (vault), and waste management activities.

The CMRR Project is essential for LANL to ensure mission essential program continuity in support of NNSA's stockpile stewardship objectives beyond the lifetime of the existing Chemistry and Metallurgy Research (CMR) building. The CMR Basis of Interim Operation (BIO) is scheduled to expire at the end of 2010. Almost all of LANL's stockpile stewardship mission support functions require analytical chemistry, materials characterization, and actinide research and development support. Many of these capabilities currently exist within the CMR Building and are not available elsewhere in the DOE complex. Without these capabilities, the reliability/aging of the existing stockpile components cannot be measured (Surveillance), the existing stockpile cannot be certified as reliable (Certification), and new pits cannot be qualified (Pit Manufacturing).

The CMRR Project consists of three primary elements that define the scope and drive the acquisition strategy: Phase A, the Radiological Laboratory/Utility/Office Building has awarded Design/Build contract and is in design; Phase B, Special Facilities Equipment, which includes instrumentation and gloveboxes, is in Preliminary Design; and Phase C, the CMRR Security Category I, Hazard Category 2 Nuclear Facility, which includes a special nuclear material vault, is in Preliminary Design.

LAUR-06-2622



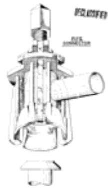


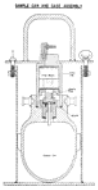
Update of Fuel Cycle Development Activities at the Radiochemical Engineering Development Center

L. K. Felker, P. D. Bailey, D. E. Benker, E. D. Collins, R. J. Vedder, and E. A. Walker*
Oak Ridge National Laboratory

The Oak Ridge National Laboratory (ORNL) is participating in several areas of the Advanced Fuel Cycle Initiative Program. Two of these areas are being studied at the Radiochemical Engineering Development Center (REDC) because the facilities needed to handle the radioactive materials of interest are readily available. One of these areas is the demonstration of various parts of the UREX+ process in the Solvent Extraction Test Facility in the hot cell processing area. The focus of recent testing has been on the group separation of the lanthanide and actinide elements using the reverse TALSPEAK process and a planned kinetic study of the direct TALSPEAK process for this group separation. Feed solutions generated from the chemical processing of highly irradiated targets have been and will be used for these demonstrations.

The second area is the continued development and demonstration of the modified direct denitration (MDD) process for various fuel processing product and waste streams. Nitric acid product streams can readily be converted to oxide products for further use in fuel fabrication or storage and disposal forms. Conversions of uranium/plutonium, uranium/plutonium/neptunium, and uranium/plutonium/neptunium/americium have been demonstrated with consistent oxide product yields. Results of these tests and the TALSPEAK demonstrations will be presented.

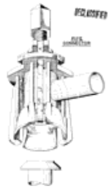


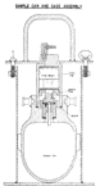


Technical Session V
May 24, 2005

"Actinide Storage"

Presentation Summaries





Failure Analysis of Breached Container 38621

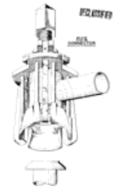
David Kolman, Paul Blumberg, Vince Garcia, and Kirk Veirs,* Los Alamos National Laboratory

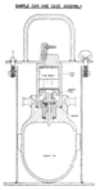
A slip top container, Item 38621, was breached during the annual inventory on December 19, 2005, resulting in worker contamination. It is of interest to understand the mechanism of the containment loss to prevent any future releases. Following the breach, item 38621 was triple-bagged and radiographed. A radiograph of item 38621 revealed that the item was composed of a plastic bottle inside of a bag-out bag inside of a taped, slip-lid can. The radiograph suggested that plutonium oxide was present underneath the tape and along the top rim of the can body. Item 38621 housed approximately 1000 g of non-weapons grade plutonium dioxide. A plan for performing the failure analysis was reviewed and approved by a committee of Laboratory and DOE reviewers. This presentation will review the findings and discuss conclusions from the performed failure analysis.

Preparation of Material for the Surveillance and Monitoring Large Scale Corrosion Studies and Initial Results

Obie W. Gillispie, Elizabeth E. Kelly, Annabelle S. Lopez, Joshua E. Narlesky, Dennis D. Padilla,*
Leonardo A. Trujillo, D. Kirk Veirs, Edward L. Wilson, and Laura A. Worl
Los Alamos National Laboratory

The Surveillance and Monitoring Program at LANL is responsible for conducting studies to predict the long-term behavior of plutonium bearing materials packaged in 3013 containers. Corrosion and gas generation are of primary interest in these studies. Earlier studies have indications that a hygroscopic salt found in plutonium process residues is potentially corrosive to the 3013 container. Recently a "master blend" was prepared by a statistical mix and stabilization of anode heels and pyrochemical residues from the LANL electrorefining process. This generated approximately sixteen kilograms of homogeneous material for these studies, where prompt gamma and calorimetry measurements were used to determine the composition and homogeneity of the batch. Material will be placed in both small and large scale 3013 surveillance containers where corrosion and gas generation will be monitored.





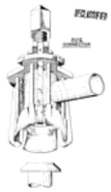
Prompt Gamma-Ray Analysis of Plutonium Oxide Inventories at the Plutonium Finishing Plant

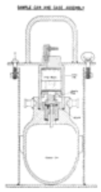
J. M. Tingey, S. A. Jones, and C. H. Delegard,* Pacific Northwest National Laboratory
D. M. Fazzari, Fluor Hanford

Prompt gamma-ray analysis was implemented at the Plutonium Finishing Plant (PFP) on the Hanford Site to screen impure plutonium oxide inventory items for the presence of sodium and potassium chloride salts. Approximately 65% by mass of the PFP plutonium oxide inventory required screening. Destructive analysis was performed on eighteen samples from a cross section of the PFP inventory items, and the results from these destructive and the prompt gamma-ray analyses were compared. The nondestructive prompt gamma spectral measurements performed at PFP were found to provide a semi-quantitative analysis of the Cl^- and, to a lesser extent, Na^+ concentrations in the bulk material. The analytical data show that F^- also could have been quantified by prompt gamma analysis.

Sodium and potassium chloride salt impurities present in electrorefining salts have been implicated in processing and moisture measurement difficulties associated with high temperature (950 ºC) thermal stabilization of plutonium oxide. These difficulties arise from the evaporation of the chloride salts resulting in plugged off-gas filters, localized corrosion, and high loss-on-ignition values that can be falsely attributed to water. Thermal analysis of these electrorefining salts show significant mass loss from the evaporation of the sodium and potassium chloride salt impurities beginning at approximately 850 ºC.

Non-radioactive mock-ups using surrogate materials for the stabilization of the plutonium oxides inventory items at PFP resulted in a 25 fold reduction in the amount of chloride salt vaporized during stabilization at 750 ºC compared to the normal stabilization temperature (950 ºC). The presence of high energy prompt gamma peaks representing the natural ^{35}Cl, ^{23}Na, and ^{39}K isotopes and sodium-to-chlorine peak area ratios in the range measured for plutonium oxide materials known to contain electrorefining salts provided the necessary evidence to identify the plutonium oxide materials that qualified for this lower temperature processing.





Accurate Calculation of NDA Gamma Spectroscopy Correction Factors

Thurman D. Cooper, Fluor Hanford Company

Plutonium masses within packages, equipment, and structures must be accurately determined for the safe and responsible operations of DOE facilities. The first analytical technique for estimating plutonium masses is typically NDA Gamma Spectroscopy. The gamma spectrometer measures gamma rays entering the detector, but has no direct knowledge of the gamma rays that were emitted but for some reason did not reach the detector. To account for all gamma rays, the operator typically inserts correction factors into the calculation to account for these non-detected gamma rays. These correction factors typically are calculated assuming slab absorber geometries and far-field conditions. More complex geometries and near field conditions have historically been considered too difficult to calculate.

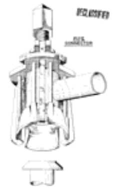
A rigorous mathematical model is described for accurately calculating NDA Correction Factors for Slabs, Cubes, Cylinders, and Spheres. Results are presented for all of these geometries for a wide range of reduced distances.

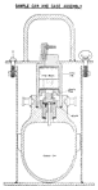
The calculated correction factors vary significantly for the various geometries and between the near and far fields.

Neptunium Oxide Moisture Concerns at SRS

Jeff Jordan and Paul Palmer,* Washington Savannah River Company

The HB-Line facility at SRS is currently producing Neptunium oxide powder. The current process recovers Np nitrate solution, concentrates and purifies it, and then calcines it to an oxide powder. The oxide product is packaged in 9975 shipping containers for shipment to INL. Based on shipping requirements, there is a maximum moisture content allowed for each can. During initial development and production, the process was expected to be robust with respect to moisture. Later sampling indicated a possibility of high moisture content for some cans.
The presentation will address the specific concerns with moisture as well as the additional process controls that were implemented to address the problem. Some of the basic lessons learned from the Np oxide moisture issue are applicable to other process startups.





Evaluation of Expanded Neptunium Oxide Production

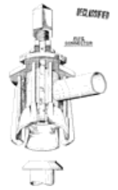
Steve Hensel, Robert Watkins, and Ron Livingston,* Washington Savannah River Company

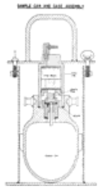
Savannah River Site (SRS) anticipates completion of the current neptunium oxide (NpO_2) production campaign in early summer 2006. This campaign has produced in excess of 200 kg of NpO_2 for future Pu-238 production. The product is packaged and transferred using the 9975 shipping container.

In addition to the current campaign, SRS has approximately 50 kg of neptunium present in several impure solutions that require disposition to meet site objectives. The preferred option for stabilization of these impure neptunium solutions is to expand the current NpO_2 production campaign to utilize existing infrastructure and associated facility resources.

The current NpO_2 flowsheet uses anion exchange combined with a partition wash to concentrate and purify the neptunium feed solution. The anion exchange product is subsequently precipitated using oxalic acid and converted to NpO_2 at elevated temperature.

The impacts of alternate feed streams are being evaluated to determine if process adjustments are needed to meet existing impurity limits established for NpO_2 transportation.



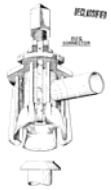


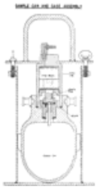
Technical Session VI

May 25, 2005

"Fuel"

Presentation Summaries





Remote Hot-Cell Fabrication of Actinide-Aluminum-Cermet Targets at the REDC for Heavy Element Production

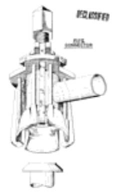
R. D. Taylor, C. W. Alexander, F. D. Riley, and A. Souders,* Oak Ridge National Laboratory

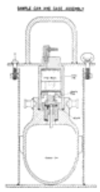
The Radiochemical Engineering Development Center (REDC) at the Oak Ridge National Laboratory (ORNL) has been irradiating Pu, Am, and Cm reactor targets for approximately forty years, producing heavy isotopes from ^{249}Bk through ^{257}Fm, the heaviest isotope produced in quantity by neutron irradiation. Remote hot-cell fabrication of actinide-aluminum-cermet targets for irradiation in the High Flux Isotope Reactor (HFIR) at ORNL has been an integral part of the Transuranium Element Program during much of that period. Current methods and equipment for remote target fabrication will be reviewed, with emphasis on recent target fabrication campaign experiences. Target fabrication technology development and applicability to other actinide R&D inititatives will also be discussed.

Preparation of Minor Actinide Oxides for Sphere-pac Transmutation Fuels

R. R. Brunson, G. D. Del Cul, A. S. Icenhour, L. K. Felker,*
C. H. Mattus, D. F. Williams, and E. D. Collins
Oak Ridge National Laboratory

Sphere-pac technology was developed in the 1960-1990 period for thermal and fast spectrum reactors of nearly all types. Transmutation fuels sphere-pac technology has the potential to be a lower-cost alternative for the production of transmutation fuels. This technology offerings great flexibility in tailoring fuel elements to match the exact requirements of any particular reactor core at any given time in the cycle. The sphere-pac fuel consists of a blend of small spheres, often in two or three different size fractions, contained in a fuel rod. For optimum binary packing, the diameters of the two sphere fractions need to differ by at least a factor of 7. A sphere pack transmutation fuel containing about 70 vol % uranium oxide (LEU) as coarse spheres and 30 vol % americium oxide as fine spheres is being developed. Steps to develop the equipment and techniques to fabricate the fine spheres (~80-mm particles) of ^{241}Am have been studied. Two weak acid resins, Serdolit CHE and Bio-Rex 70, were evaluated using surrogate ytterbium to optimize resin loading and calcination parameters for the production of oxide microspheres in the desired particle size range. The preparation of americium oxide microspheres has been initiated to obtain products for blending and preparation of test irradiation targets. An overview of the process for preparing the minor actinide microspheres and the characterization of the products will be presented.





The Retention of Actinides in Cladding Residues from Commercial Spent Fuel Reprocessing

G. F. Kessinger and M. C. Thompson,* Savannah River National Laboratory

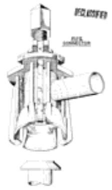
The primary goal of this study was to evaluate the efficacy of the nitric acid chop-leach spent fuel dissolution process for removal of actinides and fission products from Zircaloy cladding during dissolution. The desired results would be a cladding residue that meets LLW disposal criteria. Analysis of the cladding residues after dissolution shows that actinides are present in the cladding at concentrations in the range 5000 – 40,000 ηCi/g (50 to 400 times greater than the acceptable TRU limit in LLW).

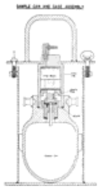
It appears that the nitric acid used for dissolution (initial concentration 4 M, with 10 M added as the dissolution proceeded to keep the $[H^+]$ above 2 M) is inadequate for complete dissolution of the UO_2 fuel meat. Scanning electron micrographs of the as-sampled cladding surface showed particles of material high in U on the surface of the cut samples, suggesting the fuel meat was not completely dissolved. If cladding residues are to meet LLW disposal limits, it appears that a more robust chemical treatment that can completely digest the fuel meat will be required. Preliminary results suggest that a secondary treatment of cladding residues with a mixed HNO_3-HF media should result a product that meets LLW disposal criteria.

Decontamination of Zircaloy Spent Fuel Cladding Hulls

Tracy S. Rudisill and Douglas C. Witt,* Savannah River National Laboratory

The Advanced Fuel Cycle Initiative (AFCI) funded by the Department of Energy's Office of Nuclear Energy, Science and Technology is developing advanced fuel treatment technologies to address the disposal of commercial reactor fuel by reducing the quantity and toxicity of waste requiring geologic disposal. Current light water reactor fuel reprocessing technologies require the shearing of spent fuel bundles into short lengths for subsequent dissolution of the fuel. Left untreated, the cladding hulls, which account for approximately 25% of the spent fuel mass, must be dispositioned as a high level waste. The cladding hulls are highly contaminated with both actinide and fission product elements. If most of the contamination is removed, the hulls could potentially meet low level waste (LLW) disposal criteria resulting in significant disposal cost savings. To investigate the potential for disposing of spent fuel hulls as a LLW, a literature survey was performed to identify the decontamination requirements, evaluate approaches for hull decontamination, and recommend a program to evaluate the leading decontamination processes compatible with proposed AFCI reprocessing flowsheets. This presentation will summarize the results of the literature review and the objectives of the subsequent experimental program which is evaluating hull decontamination processes.



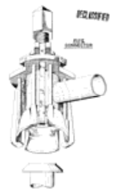


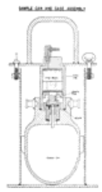
Technical Session VII

May 25, 2005

"Tank Waste"

Presentation Summaries





Development of Aqueous Thermodynamic Models for HLW Tank Solutions: U(VI)/Pu(VI) Phosphates/Carbonates and the Inclusion of Oxalic Acid

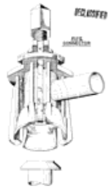
Andrew R. Felmy, Zheming Wang, Dhanpat Rai, Odeta Qafoku, and Yuanxian Xia*
Pacific Northwest National Laboratory

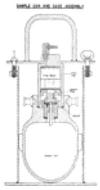
Over the past decade we have been developing aqueous thermodynamic models valid to high electrolyte concentration for application to the HLW tanks at Hanford. This presentation will briefly summarize some of the progress in this area as well as highlight new thermodynamic data for Na-U(VI)/Pu(VI) phosphates and U(VI)-carbonate aqueous complexes, as well as a completely new model for oxalate species in the chemical system $Na\text{-}Ba\text{-}Ca\text{-}Mn\text{-}Sr\text{-}Cl\text{-}NO_3\text{-}PO_4\text{-}SO_4\text{-}H_2O$ at 25°C. The work on U(VI)/Pu(VI) phosphates will highlight not only the importance of these phases in tank chemistry but the importance of considering nanoparticle formation in developing accurate thermodynamic models. This oxalate model is our first step in developing accurate thermodynamic models for predicting the impact of oxalate species on tank processing strategies and in predicting the dissolution of tank wastes by additions of oxalic acid.

Uranium and Plutonium Solubility in Actual Savannah River Site Tank Waste

William D. King, William R. Wilmarth, and David T. Hobbs*, Savannah River National Laboratory

Due to safety concerns associated with actinide precipitation and accumulation in waste storage tanks and transfer lines, uranium and plutonium solubility tests have been conducted on various Savannah River Site radioactive waste solutions. Samples utilized for testing included liquids from various sources, such as evaporator drop tanks, evaporator feed solutions, dissolved saltcake, aged waste from dormant tanks, and recently generated waste. The compositions of the samples varied considerably, although all samples were caustic, sodium salt solutions ($[Na^+]$ range: 0.5 to 12 M). Mixing of these solutions during waste processing operations has the potential to promote precipitation, since actinide solubility varies with liquid composition. Solubility tests were conducted by two methods: 1) the addition of small volumes of acidic solutions of uranyl nitrate and plutonium oxide, and 2) the addition of pre-formed uranium and plutonium solids. Uranium and plutonium concentrations in the liquid phase were measured periodically and selected solid samples were characterized. Results were compared to predictions generated from statistically-based solubility models developed from data on simulated waste solutions.





Actinide-Gluconate Complexation and Hanford Tank Waste Remediation

Leigh R. Martin, Ryan L.P. Witty, Aurora E. Clark, Gregory L. Helms, and Kenneth L. Nash*
Washington State University

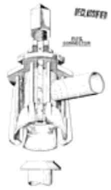
The gluconate anion is known to exist in the Hanford tank wastes from strontium recovery campaigns. This organic complexant is problematic as it has the unusual ability of preventing precipitation of metal hydroxides under basic conditions. This could be problematic for waste tank remediation processes in which actinides are expected to remain in the sludge phase as metal hydroxides. There is little cohesive literature on the interactions of gluconate with the actinides to help describe the processes involved in such interactions. The work presented here is the result of a detailed investigation using multiple techniques including UV-vis spectrophotometry, ATR-IR and NMR spectroscopies, calorimetry and theoretical calculations to characterize the coordination chemistry of the gluconate anion with UO_2^{2+} across the pH range 3-13.

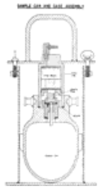
Development of an Improved Titanate-Based Sorbent for Strontium and Actinide Removal from High Ionic Strength Waste Solutions

D. T. Hobbs, M. J. Barnes, M. E. Stallings, F. F. Fondeur, and S. D. Fink*
Savannah River National Laboratory
M. D. Nyman, Sandia National Laboratory

Monosodium titanate (MST), a hydrous metal oxide sorbent, is the baseline material for the removal of ^{90}Sr and alpha-emitting radionuclides (principally ^{238}Pu, ^{239}Pu, ^{240}Pu and ^{237}Np) from alkaline waste solutions generated during the processing of irradiated nuclear materials at the Savannah River Site. This material will be used in two pretreatment facilities, the Actinide Removal Process (ARP) and the Salt Waste Processing Facility (SWPF). The ARP facility is scheduled to begin operations in FY07. The SWPF is in the final design stage and scheduled for radioactive operations in FY11. The plutonium removal efficiency of MST is a dominant factor limiting the operational capacity in the pretreatment facilities. We have developed a new titanium-based sorbent similar in composition to MST. This material exhibits significantly improved performance compared to MST for the removal of strontium and actinides from strongly alkaline and high ionic strength solutions. We will present results evaluating the performance of these materials with both simulated and actual SRS waste solutions.

We acknowledge financial support of this work by the Department of Energy through grants from the Office of Cleanup Technologies in the Office of Environmental Management and the Environmental Molecular Science Program in the Office of Science.



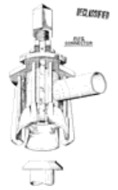


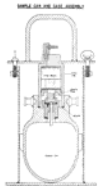
Resorcinol-Formaldehyde Resin Testing for Cs Removal at WTP: Status of Bench and Pilot Testing

W. R. Wilmarth, W. D. King, F. F. Fondeur, D. J. Adamson, M. D. Fowley,*
J. L. Steimke, T. J. Steeper, M. Williams, and C. E. Duffey
Savannah River National Laboratory

Although construction for the Pretreatment Building is on hold due to design issues, research continues to evaluate an alternative ion exchange resin for the removal of cesium from highly alkaline wastes for use in the Waste Treatment Plant. The baseline technology is to employ SuperLig® 644, an IBC Advanced Technologies product, which has been shown to perform adequately. The project, however, has been examining other resins such as a spherical resorcinol-formaldehyde resin manufactured by Sintef, a Norwegian firm. This product offers some unique properties for column application.

Our research has been examining the physiochemical properties and radiation stability of the resin over the last couple of years. The resin appears fairly stable and maintains a high specificity for cesium upon exposure to the highly alkaline waste and under high radiation dosage. The most recent results from the investigation into the low temperature nitration of this organic resin will be reviewed. In addition, SRNL has been involved in a ½ scale pilot testing of the resin. A total of sixteen cycles were completed and examined a number of process parameters of interest. Column behavior including permeability, pressure drop, and integrity were examined. The results of these tests will also be reviewed.

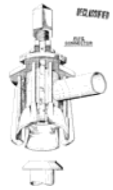


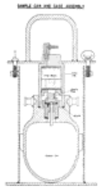


Technical Session VIII
May 25, 2005

"Solvent Extraction"

Presentation Summaries





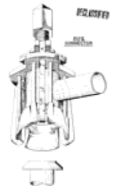
Supramolecular Approach to Third Phase Formation in Solvent Extraction

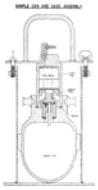
Renato Chiarizia, Argonne National Laboratory

The organic phase species identified through conventional coordination chemistry in the solvent extraction of metal species cease to exist at high extractant concentrations and high loading of the organic phase. Under these conditions, which are more representative of process applications, self-assembly of extractants and their metal complexes takes place in the organic phase, often leading to the generally unwanted phenomena of third phase formation.

In the Chemistry Division of Argonne National Laboratory studies are underway with the aim to determine the mechanism and energetics of third phase formation when tri-*n*-butyl phosphate (TBP) is the extractant. The results obtained in the extraction of various cations of nuclear interest will be summarized and discussed from a colloid chemistry standpoint. A general mechanism for third phase formation based on interaction between small reverse micelles will be presented.

This work was funded by the U. S. Department of Energy, Office of Basic Energy Science, Division of Chemical Sciences, Biosciences and Geosciences under Contract No. W-31-109-ENG-38.



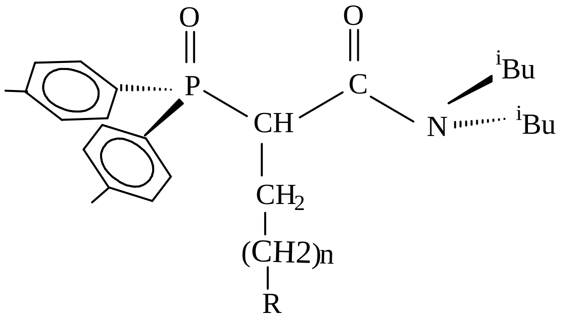


New Derivatives of CMPO Systems with Special Coordination Properties

Keith H. Pannell, Ramon Villazana, and Francisco Cervantes-Lee,* University of Texas, El Paso
Mary Ann Stroud and Scott Sportsman, Los Alamos National Laboratory

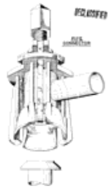
The utility of CMPO ligands for actinide extraction is well-established. We wish to report the formation of new CMPO extractants in which the methylene bridge has been used to form derivatives with special functionality. Thus, treatment of CMPO with NaH yields the corresponding sodium salt by extraction of a methylene proton, that *via* a series of synthetic steps, produces derivatives with thiol, **1a**, cyano**, 1b** or carboxylate, **1c**, terminating chains**.**

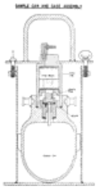
Systems of the type **1a** bind to gold *via* the thiol group and actinides *via* the CMPO moiety thus suggesting utility in membrane separation technologies. Similarly, the formation of **1c** suggests extra facility for actinide extraction from carboxylate rich solutions due to the extra activity of the CMPO-carboxylate unit.



R = SH (**1a**); CN (**1b**); COOH (**1c**)

Full experimental details, with spectroscopic and single crystal X-ray analysis of the new extractants and their metal complexes will be provided.





NOPOPO Ligands as Selective Actinide Ion Extractants

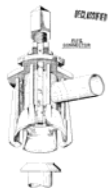
Robert T. Paine, University of New Mexico

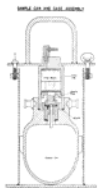
A new family of robust chelating ligands, 2,6-bis(phosphinomethyl)pyridine N,P,P-trioxides (**NOPOPO**) have been discovered in our group under DOE-BES sponsorship, and these ligands show potential for trivalent f-element ion partitioning. A summary of the development of practical syntheses, the characterization of selected aspects of the lanthanide and plutonium ion coordination chemistry and initial characterization of extraction performance of these ligands will be presented. In addition, we will outline a proposed collaborative work plan for the further development and characterization of the extraction properties of **NOPOPO** ligands within the context of UREX+ process development. Finally, in the traditional spirit of the workshop format of the ASC, we will seek input from the separations community represented at the conference on a collaborative research program recently funded under the DOE-AFCI Spent Fuels Separations Technology Program.

Prospects for Improving the Performance of the TALSPEAK Process

Kenneth L. Nash, Kelly M. Cooper, and Mikael Nilsson,* Washington State University

One of the most challenging separations to perform in the processing of spent nuclear fuels is the partitioning of trivalent actinides from trivalent lanthanides. In one capacity or another, ligand donor atoms softer than oxygen (N, S, Cl^-) have proven essential to the development of viable aqueous separation processes. A historically proven technique that has received much attention and proven to work satisfactorily, at least under some conditions, is the TALSPEAK process (Trivalent Actinide Lanthanide Separations by Phosphorous-reagent Extraction from Aqueous Complexes). Stripped to its essential elements, TALSPEAK chemistry combines a separation platform, most commonly an acidic organophosphorus extractant, with an aqueous medium containing a moderate concentration of a complexing carboxylic acid buffer and an aminopolycarboxylate selectivity enhancing reagent. As originally introduced by Weaver and Kappelmann (1968), the process uses bis(2-ethylhexyl)phosphoric acid (HDEHP) as the extractant, lactate as the buffer and diethylenetriamine-N,N,N',N",N"-pentaacetic acid (DTPA) as the reagent accounting for actinide-lanthanide selectivity. A wide variety of possible alternative reagents could potentially function as well. The performance of some have been examined, others have not. In this presentation, the particular features of TALSPEAK and TALSPEAK-like separations will be discussed, emphasizing known challenges and approaches that could improve the viability of the extraction systems.

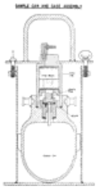




Extraction and Separation of An(III) and Ln(III) Using the Tetradentate Ligand 6,6’-Bis-(5,6-Dipentyl-[1,2,4]Triazin-3-Yl)-[2,2’]Bipyridinyl (C5-BTBP)

M. Nilsson[1,2], C. Ekberg[2], M.R.S. Foreman[3], J.-O. Liljenzin[2], and G. Skarnemark[2]*
[1]Department of Chemistry, Washington State University,
[2]Department of Chemical and Biological Engineering,Chalmers University of Technology
[3]Department of Chemistry, University of Reading

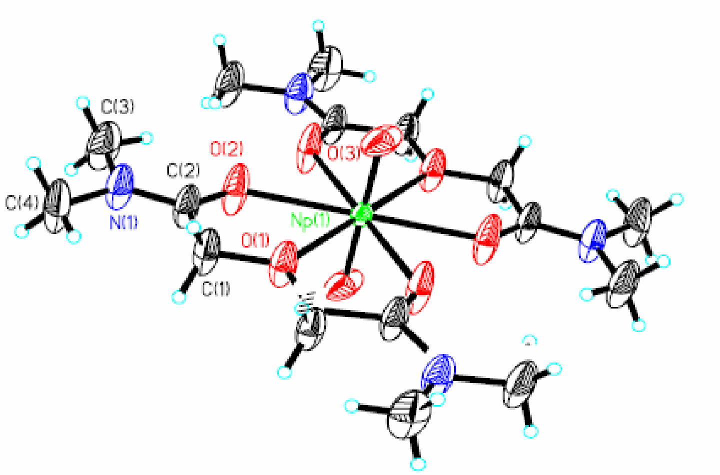
Research on the separation of trivalent actinides and lanthanides in spent nuclear fuel is currently given much attention throughout the world. In the European Union one project focusing on this subject is the ongoing EUROPART-project involving more than 20 European laboratories. In EUROPART, the separation of trivalent actinides and lanthanides is realized through solvent extraction by heterocyclic soft nitrogen bearing ligands. Tridentate nitrogen donor ligands, such as 2,6-bis(1,2,4-triazine-3-yl)pyridines, BTP, were introduced in the late 90s by Kolarik. More recently, tetradentate ligands (the 6,6’-bis(1,2,4-triazin-3-yl)-[2,2’]bipyridinyl or BTBP) have been developed. These novel extracting agents must be tested for extraction and stability to assess their suitability for implementation in a process. The work presented here is a summary of some screening investigation of one of these ligands, a BTBP with pentyl groups attached to the outer rings, C5-BTBP. The ligand has been tested for extraction in different organic and aqueous media. The kinetics and temperature dependence of the extraction and the stability of the ligand were briefly investigated. The C5-BTBP demonstrated good extraction and separation properties for the trivalent actinides and lanthanides. Some issues regarding the solubility of the ligand in the organic phase and its radiolytic stability may also prove to be a problem. The BTBP class ligand is, however, a step in the right direction towards finding an extracting reagent capable of producing high separation and fulfilling the CHON principle.



Separation of Actinides and Tc(VII) from HLLW by Using N,N,N',N'-Tetraalkyl-3-Oxa-Glutaramides: Solvent Extraction and Structural Studies

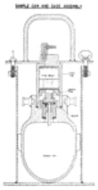
Linfeng Rao and Guoxin Tian,* Lawrence Berkeley National Laboratory

The extraction behavior of U(VI), Np(V), Pu(IV), Am(III), and TcO_4^- with N, N, N', N'-tetraisobutyl-3-oxa-glutaramide (TiBOGA) were investigated. An organic phase of 0.2 mol/L TiBOGA in 40/60% (V/V) 1-octanol/kerosene showed good extractability for actinides (III, IV, V VI) and TcO_4^- from aqueous solutions of HNO_3 (0.1 to 4 mol/L). At 25°C, the distribution ratio of the actinide ions (D_{Am}) generally increased as the concentration of HNO_3 in the aqueous phase was increased from 0.1 to 4 mol/L, while the D_{Tc} at first increased, then decreased, with a maximum of 3.0 at 2 mol/L HNO_3. The slope analysis of the dependence of D_M (M = An or Tc) on the concentrations of reagents suggests that the formula of extracted complexes were $UO_2L_2(NO_3)_2$, $NpO_2L_2(NO_3)$, $PuL(NO_3)_4$, $AmL_3(NO_3)_3$, and $HL_2(TcO_4)$ where L = TiBOGA. The enthalpy and entropy of the corresponding extraction reactions, Δ_rH and Δ_rS, were calculated from the dependence of D on temperature in the range of 15 – 55°C. A test run with 0.2 mol/L TiBOGA in 40/60% 1-octanol/kerosene was performed to separate actinides and TcO_4^- from a simulated acidic high-level liquid waste (HLLW), using tracer amounts of ^{238}U(VI), ^{237}Np(V), ^{239}Pu(VI), ^{241}Am(III) and $^{99}TcO_4^-$. The distribution ratios of U(VI), Np(V), Pu(VI), Am(III) and TcO_4^- were 12.4, 3.9, 87, > 1000 and 1.5, respectively, confirming that TiBOGA is a promising extractant for the separation of all actinides and TcO_4^- from acidic HLLW.

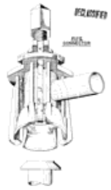


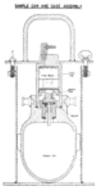
Structures of the actinide complexes with N, N, N', N'-tetramethyl-3-oxa-glutaramide (TMOGA) were determined at the Beamline for Small-Crystal Crystallography at the Advance Light Source.

Acknowledgment. Part of the experimental work was performed at the Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing, China.



Notes:





Notes: