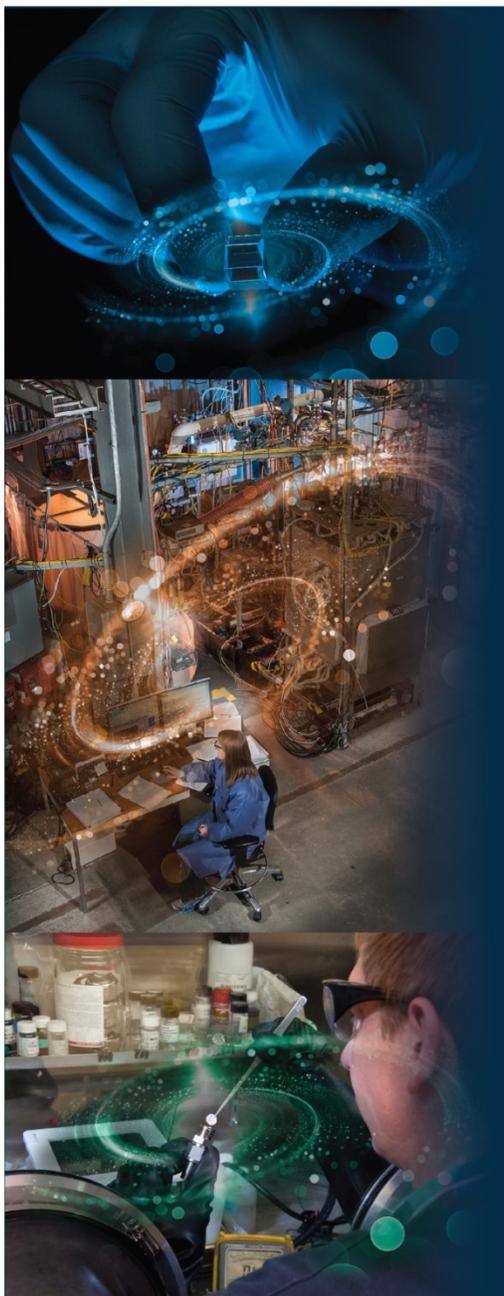




OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS



2014

Savannah River National Laboratory

Laboratory Directed Research and Development Program

Annual Report

*"Imagination will"
take you everywhere*

-Einstein



<http://srl.doe.gov/>

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STI No.: SRNL-STI-2015-00165

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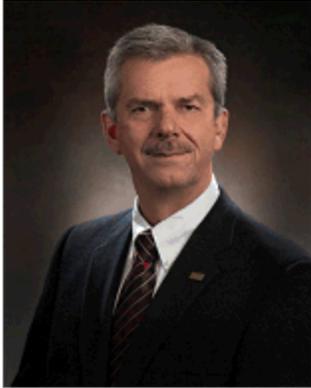
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Note: CE-clean energy; EM-environmental management; ND-nuclear deterrent; NP-non-proliferation



An innovative and effective Laboratory Directed Research and Development (LDRD) program is the backbone of the work of a National Laboratory, ensuring the nation's current and future needs in security, energy and policy matters. Technology today is evolving exponentially seeded by advances in computing speed, communication bandwidth, miniaturization and increased connectivity. We are now seeing a much broader level of convergence between information and traditional domains, such as energy and transportation. To quote Einstein, "Logic will take you from A to B, but imagination will take you everywhere." Thus, we are challenged to harness these advances and use them to create innovations to resolve our DOE mission requiring unique skill sets, imagination and creativity that are outside the bounds of traditional research practices. I am excited about the opportunities that the Savannah River National Laboratory (SRNL) LDRD program is creating for the laboratory and the nation. The program continues to demonstrate advancements in scientific underpinnings that reveal the quality of SRNL's research.

This report demonstrates the execution of our LDRD program within the objectives and guidelines outlined by the Department of Energy (DOE) through the DOE Order 413.2B. The projects described within the report reflect and facilitate SRNL's strategic vision and provide great value to the DOE. The diversity exhibited in the research and development projects underscores the DOE Office of Environmental Management (DOE-EM) mission and enhances that mission by developing the technical capabilities and human capital necessary to support future DOE-EM national needs. I'd like to highlight specifically our new initiative entitled "Reinventing Nuclear Chemical Engineering" that emphasizes our core values in efficiency and safety by applying the principles of smart manufacturing and process intensification towards resolving the nation's legacy waste cleanup program. As a multiprogram national laboratory, SRNL is applying those core values to achieve tangible results for the nation in Environmental Stewardship, as well as National Security, Clean Energy and Nuclear Materials Management.

On behalf of the SRNL Senior Management team, I would like to congratulate those members of the SRNL staff, and their collaborators, for their accomplishments and the quality of their work. Their efforts create a product that continues to be a critical mechanism to demonstrate why SRNL's competencies are important to the nation.

Dr. Terry A. Michalske
Laboratory Director
Savannah River National Laboratory

Overview of 2014 Laboratory Directed Research and Development Program

Laboratory Directed Research and Development is a congressionally authorized program that provides the ‘innovation inspiration’ from which many of the Laboratory’s multi-discipline advancements are made in both science and engineering technology. The program is the backbone for insuring that scientific, technical and engineering capabilities can meet current and future needs. It is an important tool in reducing the probability of technological surprise by allowing laboratory technical staff room to innovate and keep abreast of scientific breakthroughs. Drawing from the synergism among the EM and NNSA missions, and work from other federal agencies ensures that LDRD is the key element in maintaining the vitality of SRNL’s technical programs.

The LDRD program aims to position the Laboratory for new business in clean energy, national security, nuclear materials management and environmental stewardship by leveraging the unique capabilities of the Laboratory to yield foundational scientific research in core business areas, while aligning with SRS strategic initiatives and maintaining a vision for ultimate DOE applications.

The FY14 LDRD Program focus areas were as follows:

Nuclear Materials Management & Environmental Stewardship – Unique concepts that lead to new approaches and options for critical EM risk reduction challenges in processing high activity liquid waste and nuclear materials, remediating contaminated soil, groundwater and facilities, as well as validating long-term remediation strategies are needed.

Clean Energy – Advance research in development, demonstration, and deployment of clean energy technologies; enhance associated development and commercialization of intellectual property. Innovative technologies to assure the future utilization of clean, reliable energy that dramatically improve the energy efficiency of industrial, manufacturing, transportation, and/or building technologies and strengthen SRNL’s Core Capabilities are required.

Non-Proliferation & Nuclear Deterrent - Unique concepts that address national security mission area needs that are currently underserved by the DOE Lab system. Game-changing innovations and tools that advance the national security agenda for the United States Government, including monitoring, nonproliferation, and deterrence are needed.

Supplemental Call: Reinventing Nuclear Chemical Engineering – Unique concepts and/or control systems that address multiple unit operations applied to nuclear processing in available facilities in a manner which significantly decreases operating costs while maintaining or enhancing processing efficiency

Tangible accomplishments resulting from persistent technical efforts in FY14 include:

Scientific Productivity

Research efforts supported by the LDRD program led to securing intellectual property and peer reviewed publications. Six invention disclosures were submitted, along with two patent applications related to research supported through the LDRD program in FY14. Additionally, two projects published results in peer reviewed journals.

Post-Doctoral and Student Involvement

- Five post-doctoral researchers were members of 4 LDRD supported research teams in FY14, three performed research at SRNL.
- Four LDRD projects supported graduate student involvement in FY14. Two projects supported undergraduate participation.

Long-term, In-situ Monitoring for Subsurface Contaminant Stability

Project Team: C.E.Turick, C.E. Milliken, and H. Colon-Mercado

Subcontractors: S. Greenway, Greenway Energy LLC
E. Atekwana, and G. Abdel Aal, Oklahoma State University

Project Start Date: October 1, 2012
Project End Date: September 30, 2014

We have developed and tested inexpensive methods to monitor the subsurface in real time, with permanent probes providing electrochemical data consistent with biogeochemical changes without the need to take physical samples. This allows for greater monitoring frequency and improved precision for unambiguously detecting subsurface changes over time. These techniques will be used as a means to monitor progress in bioremediation activities or as a sentinel technology to detect sudden environmental perturbations and can be used to direct conventional sampling. Our versatile electrode configuration allows for detection of changes in: bacterial numbers associated with growth; cellular

status; carbon source conversion; fluid conductivity; mineral reduction; and rates of change. In addition we are able to determine if microbially mediated sulfate reduction or iron reduction is occurring as well as fermentation that is coupled or uncoupled to methanogenesis. Nondestructive monitoring of bacterial biofilms on surfaces is also a capability of this new technology.

FY2014 Objectives

We developed techniques to monitor biogeochemical changes related to microbial activity and contaminant behavior in the subsurface without need for water samples or laboratory tests. Our in-situ approach uses electrochemical techniques to monitor progress in bioremediation activities and/or as a sentinel technology for environmental perturbations, especially related to monitored natural attenuation and can be run in conjunction with conventional tests as needed for confirmation of results.

- A sentinel technology that warns of contamination events from spills and leaks;
- Sensors that detect remediation/bioremediation activity including contaminant behavior, mineral transformations and microbial activity;
- Electrochemical techniques that can delineate sulfate reduction, iron reduction, and fermentation coupled or uncoupled to methanogenesis;
- Nondestructive interrogation of surfaces for biofilms and corrosion.

Introduction

The need for environmental sensors capable of rapid and accurate measurement of contaminants and specific groundwater parameters was the focus of this work. We used electrochemical impedance spectroscopy as a data rich method that provides information on key physical, chemical and biological parameters relevant to DOE-EM. In addition, the electrode arrays and instrumentation also served to analyze the chemistry of the bulk groundwater as needed. The outcome of this project is directly relevant to technical needs related to long term monitoring, including providing inexpensive and sufficient monitoring events related to contaminant content and fate as well as evaluating an array of groundwater parameters linked to biogeochemical behavior of contaminants. The latter information is necessary for detection of changes that could affect contaminant behavior.

Monitoring the subsurface for active or passive long-term management strategies is essential but time consuming and labor intensive. For example, evidence of microbial activity and subsequent geochemical alterations include: increases in cell numbers; carbon source conversion; changes in mineralogy; and soluble metal content in the subsurface. With conventional strategies, disadvantages include labor intensive and expensive sampling and analytical techniques that force a minimalistic approach to data gathering and potentially data misinterpretation.

Electrochemical techniques, such as impedance spectroscopy offer enormous potential to provide valuable information about changes to subsurface parameters and contaminant behavior, in-situ. The installation of subsurface probes to monitor electrochemical parameters as often as needed to provide valuable and abundant information regarding biogeochemical conditions required for monitored natural attenuation and long term subsurface waste containment.

Approach

The cost effective technology designed as part of this project incorporates electrochemical techniques, including impedance spectrometry and is expected to lead to a new paradigm in data collection and utilization. Electrochemical sensors and techniques offer significant advantages by providing the capability to acquire abundant real-time data directly related to pertinent geochemical and biogeochemical changes to the subsurface, thereby minimizing the cost compared to conventional sampling. These techniques are designed to monitor progress in active or passive activities and also as a sentinel technology to serve as an “early warning system” for environmental perturbations, especially related to monitored natural attenuation or waste containment.

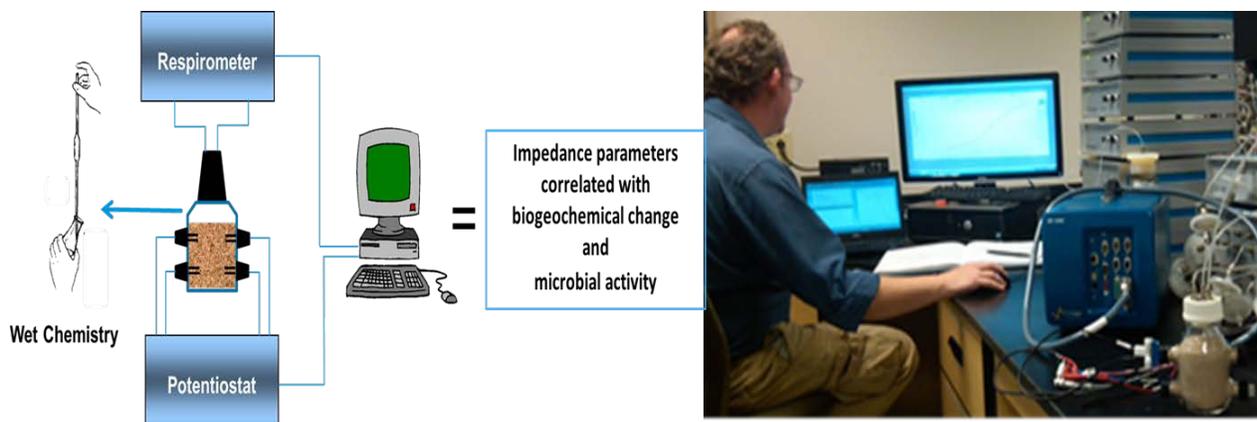


Figure 1. Correlation of microbial activity to impedance parameters. Schematic of experimental set up and laboratory arrangement.

Inexpensive patterned electrode arrays imbedded into subsurface probes provide electrochemical data pertaining to the subsurface without the need to remove samples. This allows for a greater monitoring frequency needed for increased precision. This approach will also be useful in directing sampling activities to specific sites of interest, based on electrochemical monitoring and is designed to be run in conjunction with conventional tests as needed for confirmation of results (Fig.1). This approach incorporates electrochemical techniques that evaluate impedance parameters related to biogeochemical changes in sediments. The change in properties of an electrical signal at a specific

frequency passing through environmental media furnishes impedance data. This inherent complexity provides a data-rich analytical platform capable of delivering specific information regarding numerous multifaceted parameters. We used this approach to determine: changes in fluid composition (conductivity, reaction and diffusion rates); mineral composition and possible changes (oxidation or reduction); bacterial density, metabolic activity and growth status; and contaminant availability. Our electrode design also uses cyclic voltammetry and linear sweep voltammetry which expands the capability of the sensors to easily and more fully interrogate the subsurface for such features as contaminant concentrations and electron shuttles, with some potential to detect unknown or unexpected contaminants. These factors relate to subsurface monitoring and can potentially be determined remotely, numerous times a day, if desired.

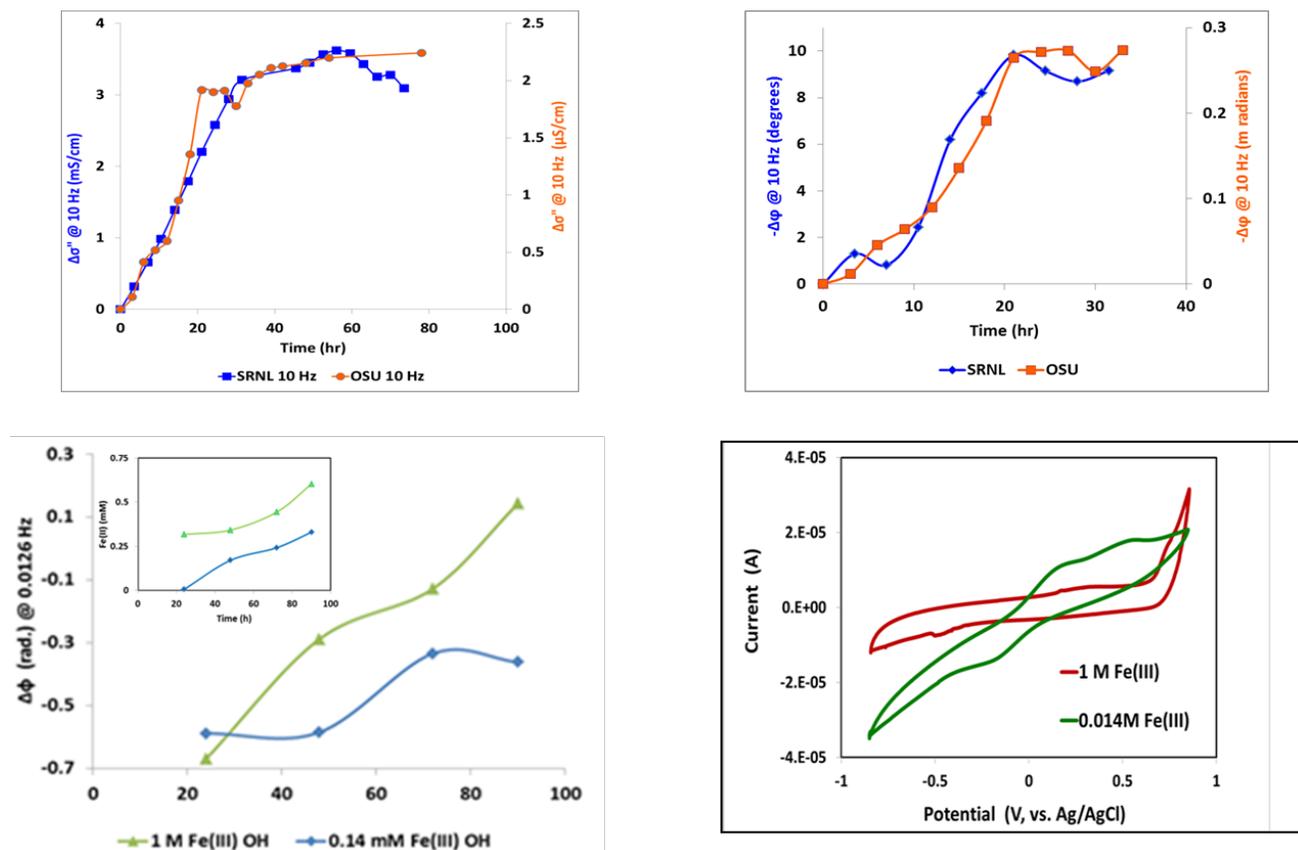


Figure 2. Changes in complex conductivity (top left) and phase shift (top right), both at 10 Hz, followed bacterial growth and correlated well with the two techniques evaluated. Electrochemical impedance spectroscopy had a significantly higher degree of resolution. Fe(III) oxide reduction was tracked with phase shift at 0.0126 Hz (bottom left) and followed wet chemistry analyses (insert). The versatile electrode configuration also allowed for voltammetric analyses (bottom right) demonstrating that electron shuttles produced at the lower Fe(III) concentrations can be detected with cyclic voltammetry.

Results/Discussion

Impedance studies focused on the following: phase shift (ϕ), indicative to geochemical change at low frequencies (0.01 -1.0 Hz) and bacterial density at mid-level frequencies (10-1000 Hz); conductive energy storage/polarization via complex conductivity (σ'') related to cell activity; relative permittivity

(ϵ'/ϵ_0) (capacitance) measures cell membrane charge at 0.01 Hz and indicates cell viability; as well as parameters useful in determining changes in fluid properties due to microbial growth, such as total impedance, Nyquist plots (in-phase vs. out-of-phase impedance), and changes in fluid conductivity. Our results correlated well with microbial activity and geochemical changes associated with it (Fig. 2). In addition, we have also shown that these techniques are applicable to the vadose and capillary fringe zones along with the saturated zone. We also evaluated electrochemical and biological changes during active Fe(III) (Fig. 2) and SO_4 reduction and methanogenesis. These reactions are very common in the subsurface and play significant roles in contaminant fate. Combining our impedance studies with other electrochemical techniques such as cyclic voltammetry, stripping voltammetry and chronoamperometry is providing a greater dimension to our approach and allows us to gain a better understanding of subsurface activities through these versatile techniques (Fig. 2).

We also compared two impedance techniques, spectral induced polarization developed by our university collaborators and electrochemical impedance spectrometry. Spectral induced polarization has been demonstrated to provide useful field information regarding microbial activity and geochemical change associated with bioremediation. Electrochemical impedance spectrometry is a useful technique to study microbial activity and electrochemical changes associated with microbial growth. This design also allows us to exploit the versatility of our electrode configuration to incorporate other electrochemical techniques as needed (Fig. 2).

Our approach of incorporating electrochemical techniques, especially impedance spectroscopy has enormous potential to provide valuable information about changes in subsurface microbial activity and contaminant behavior in-situ. The installation of subsurface probes to monitor electrochemical parameters is expected to provide valuable and abundant information regarding biogeochemical conditions required for bioremediation, monitored natural attenuation and long term subsurface waste containment.

FY2014 Accomplishments

- Comparison of two techniques, electrochemical impedance spectrometry and spectral induced polarization. The two techniques correlated well when both were used to track microbial growth over time. Electrochemical impedance spectroscopy had almost 3 logs greater resolution.
- Both techniques will provide utility in the saturated zone, capillary, fringe and the vadose zone (down to 20% moisture).
- Electrode configuration was designed to accommodate several electrochemical techniques that supplement overall technical capabilities.
- Nondestructive evaluation of surface biofilms was achieved with electrode design configured for electrochemical impedance spectroscopy.
- Biogeochemical activities were delineated and include: sulfate reduction, Fe(III) oxide reduction, fermentation coupled and uncoupled to methanogenesis.
- Production of electron shuttles by Fe(III) oxide reducing bacteria.
- Complex conductivity was linked for the first time to electron transport activities of the bacterial membrane.

Future Directions

We are currently pursuing funding or establishing collaborations as follows:

Proposed work with Department of Defense (DoD) being perused;

- SERDP proposal submitted for subsurface monitoring
- Related DTRA proposal submitted with positive review - funding pending FY 15 budgets (\$1M)

Preliminary interest from;

- Oil industry - (detect oil souring)
- Drilling industry - (hydrofracking activities)
- Bioremediation industry – monitoring microbial activities
- Belgian Nuclear Research Centre - (monitoring stored waste)
- DOE – EERE – WTE
- DoD
 - ESTCP
 - U.S. Army

Biogeophysics;

- Correlating field data with different techniques with OSU
- High resolution impedance to link microbial physiology with OSU

Biofilms/Biocorrosion/Structural deterioration

- SRNL – Materials Science & Technology

Publications/Presentations

- Three manuscripts will be submitted for publication based on patent application filing. The tentative titles are as follows:
 - Interrogation of Biofilms on Aluminum 1100 Alloy using Electrochemical Impedance Spectrometry.
 - Electrochemical Impedance Spectrometry for Monitoring Microbial and Biogeochemical Activity.
 - Electrochemical analysis for Monitoring Balanced and Unbalanced Methane Fermentation
- Second International Conference on Biosensors & Bioelectronics, “Monitoring Biogeochemical Changes in the Subsurface”. Chicago, Ill. June/17-June 19, 2013.
- American Society for Microbiology, “On-line Electrochemical Monitoring of Methanogenesis and Fermentation”. South Carolina Branch. Columbia, SC, November 15, 2015
- Fourth International Conference on Biosensing Technology, “Microorganisms as Subsurface Biosensors”. Lisbon, May 10-May 13, 2015
- Gordon Conf. – Applied and Environmental Microbiology, Non-destructive, real time monitoring of Biogeochemical activity”, South Hadley, MA 6/12-17, 2015

Patent Apps/ Patents Awarded

A comprehensive Invention disclosure was filed and is being reviewed for patentability.

Spectroscopic Techniques for the Characterization of Particulates from Proliferation Activities

Project Team: E. Villa-Aleman, Glenn Fugate

Project Start Date: October 1, 2012
Project End Date: September 30, 2014

Chemical composition of particulates related to nuclear proliferation activities is of extreme importance to the nonproliferation efforts at the Department of Energy (DOE) and the International Atomic Energy Agency (IAEA). Molecular characterization of Uranium-bearing particulates dispersed in an environmental sample is a

formidable task. Chemical identification can be conducted with infrared, Raman and luminescence spectroscopy. Unfortunately, the application of these spectroscopic techniques is limited by their detection sensitivity. Coherent spectroscopic techniques such as Stimulated Raman Scattering (SRS) and Coherent Anti-Stokes Raman Scattering (CARS) have emerged as highly sensitive techniques (several orders of magnitude) to detect and image particulates on a substrate. It is proposed to develop these micro-spectroscopic techniques to enable characterization of particulates in environmental samples. In this project, CARS and SRS experimental setups will be assembled in the laboratory using Ti-Sapphire lasers to conduct femtosecond and picosecond spectroscopy.

FY2014 Objectives

- This project addresses DOE's NNSA (NA-22) MPD objective to develop methods for detection of materials related to nuclear proliferation activities.
- Develop new coherent spectroscopic platforms for the analysis of particulates related to proliferation activities such as CARS and SRS.
- Demonstrate the use of deep ultraviolet Raman spectroscopy
- Prepare samples with boron and irradiate in a reactor to produce fission tracks for further analysis with CARS and SRS setups.

Introduction

NNSA funds research to develop technologies for the identification of foreign nuclear weapons programs. Uranium (U) enrichment, fission track analysis for the identification of U-235 and Pu and cold hydrodynamic tests (CHT) are in the top of the list for proliferation detection. DOE is in great need for new technologies and methodologies for the detection of U and Pu-bearing particulates of interest. It is proposed to develop unique coherent laser spectroscopic techniques to identify particulates related to weaponization activities in environmental samples. The proposed techniques will enable detection and imaging in a fraction of a time to current Raman and luminescence spectroscopic techniques used in the laboratory. Once the successful demonstration of the technology has been shown, proposals will be submitted to the Defense Nuclear Nonproliferation Research and Development (DNNRD) Office of Proliferation Detection within NNSA, DoD, and IAEA as a means to identify particulates of interest from environmental samples.

Coherent anti-Stokes Raman spectroscopy (CARS), stimulated Raman spectroscopy (SRS) and deep ultraviolet Raman spectroscopy (DUV-RS) can provide enhanced detection sensitivities for molecular detection and characterization. SRS has been shown to enhance detection sensitivity by several orders

of magnitude (up to six) while CARS has been shown to increase detection by at least two orders of magnitude. DUV-RS eliminates the fluorescent background in environmental samples providing a high signal to noise ration.

This work will develop technologies that could be used in the detection of molecular species such as uranyl fluoride, plutonium oxide and materials from cold weapons tests.

Approach

Review the scientific literature to identify different experimental setups for CARS and SRS, their advantages and disadvantages. Select optical design and procure optical and mechanical components for the experimental setup to be assembled in one optical table. Develop SRS and CARS setups in the same table. Lasers from previous projects and other lasers purchased in this program will be combined in the development of CARS and SRS setups. The CARS setup will require a femtosecond laser, photonic crystal fiber (PCF) and a large number of filters, mirrors, mounts, time delay lines, etc. The SRS setup, a significantly complex system, will require a femtosecond and a picosecond laser, and highly specialized electronics to synchronize both lasers in time and space. The picosecond laser will be modulated at high frequencies (10 MHz). Both laser beams will be directed to the sample of interest for analysis.

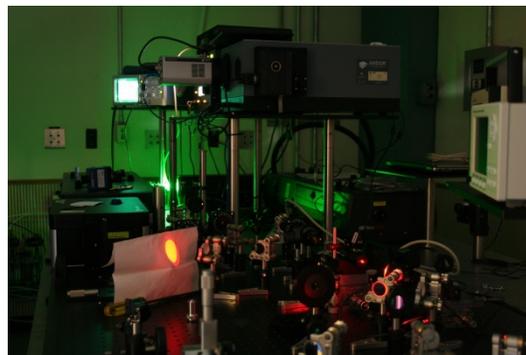


Figure 1. CARS setup and yellow/red light produced by a photonic crystal fiber.

The deep ultraviolet Raman scattering setup (DUV-RS) setup is based on an argon ion laser with an intracavity doubling crystal. Ultraviolet light (UV) at 244 and 257 nm will be used in conjunction with a microscope equipped with UV optics to measure Raman spectra without fluorescence. In the three setups, significant laser beam alignment is conducted to match beams temporally and spatially in the target.

Results/Discussion

The development of these spectroscopic techniques (CARS, SRS and DUV-RS) is a significant challenge. Each technique presents unique experimental challenges in the design and construction of the experimental setups. After receipt of the laser and the new modulator, alignment of the picosecond laser was accomplished. Synchronization between the femtosecond and picosecond lasers was demonstrated which is important for the SRS technique. The CARS and SRS setups require both laser systems and multiple laser line beams were created to handle both experiments.

In the case of the DUV-RS, the frequency doubled line at (244 nm) produced with the 488 nm fundamental of the argon ion laser was aligned into a Raman microscope equipped with a detector, mirrors, objective and gratings that could work in the ultraviolet region. Although the proper line band pass and edge filters have not been received DUV-RS was demonstrated for a variety of compounds. This is the first DUV-RS microscope available at SRNL.

FY2014 Accomplishments

Significant development of spectroscopic characterization techniques was accomplished during this LDRD. These techniques will have a profound direction in the research of advanced topics at SRNL and capabilities for material characterization understanding.

- Titanium:Sapphire lasers operating at 76 MHz became operational for the first time at SRNL.
- The operation of the Ti:Sapphire laser in the femtosecond mode was demonstrated for the first time at SRNL. Femtosecond lasers opened the doors for ultrafast spectroscopy research at SRNL.
- The operation of the Ti:Sapphire laser in the picosecond mode was also demonstrated for the first time at SRNL.
- The synchronization of two ultrafast lasers (femtosecond and picosecond) was accomplished for the first time at SRNL with a synchro-lock unit.
- A second and third harmonic generator unit was used for the first time to produce ultraviolet light from a femtosecond and a picosecond laser.
- Deep-ultraviolet microscopy was accomplished with an argon ion laser for the first time at SRNL.
- An experimental setup for coherent anti-Stokes Raman spectroscopy was assembled and operated for the first time at SRNL.
- An experimental spectroscopy setup for stimulated Raman scattering was assembled for the first time at SRNL.
- Demonstrated the operation of Raman spectroscopy in the terahertz region (5 to 200 cm^{-1}) and used it to study lattice modes of crystals from uranyl compounds.
- Produced fission tracks from boron particles embedded in plastics.

Future Directions

- Environmental samples with uranium oxide particles will be analyzed with the SRS, CARS and DUV-RS spectroscopic techniques.
- SRS and CARS will be coupled with a microscope for high speed analysis of materials.
- SRS, CARS, DUV-RS will be used in the analysis of plutonium compounds. These techniques will be used in a Pu particle study funded by DOE NNSA NA-22 for three years.
- CARS and SRS techniques will be applied in the analysis of ablated material from the new LDRD proposal entitled "Characterization of High Explosives Detonations Via Laser-Induced Plasmas"
- Femtosecond and picosecond lasers will be used in the LDRD entitled "Laser-Induced Ionization Efficiency Enhancement of a Filament for TIMS".

FY 2014 Publications/Presentations

1. List all reports written from this work during the year and all presentations about this work that were made during FY 2014.

References

1. NA.

Acronyms

DOE:	Department of Energy
IAEA:	International Atomic Energy Agency
NNSA:	National Nuclear Security Administration
CARS:	Coherent Anti-Stokes Raman Scattering

SRS: Stimulated Raman Scattering
U: Uranium
CHT: Cold Hydrodynamic Test
DNN R&D: Defense Nuclear Nonproliferation Research and Development
DoD: Department of Defense
PCF: Photonic Crystal Fiber
DUV-RS: Deep Ultraviolet Raman Scattering

Patent Apps/ Patents Awarded

None

Total Number of Post-Doctoral Researchers

None

Ternary Carbide Clad Coatings, and High-Conductivity Fuel System, for Accident Tolerant Light Water Reactor Fuel

Project Team:

B. L. Garcia-Diaz (PI), L. Olson, C. Verst, A. Duncan, R. Kesterson, and B. Sindelar

Subcontractor:

B. Hauch, K. Sridharan (Co-PI), Univ. Of Wisconsin-Madison

Project Start Date: October 1, 2012

Project End Date: September 30, 2014

Some of the MAX phases have a unique set of properties such as excellent heat conduction, oxidation resistance, and high temperature strength that make them attractive candidates for nuclear applications. One such application is in providing corrosion protection to the nuclear fuel during a Loss-of-Coolant Accident (LOCA) similar to the one that occurred at Fukushima through cladding coatings. Characterizations of the oxidation resistance, thermal diffusivity, wear, and tensile strength of MAX phase coatings and materials have been evaluated. Results demonstrate that the MAX phases give good thermal performance when

combined with existing in-core materials as coatings. Irradiation of MAX materials can develop passive layers on components, but basic thermal conduction properties are retained for many relevant MAX compositions. Cold sprayed MAX phase coatings showed good adhesion to cladding surfaces and superior resistance to oxidation to protect the cladding at LOCA test conditions.

FY2014 Objectives

- Optimize MAX cold-spray coatings on Zry-4 substrates
- Measure the thermal transport properties of MAX coated cladding materials
- Characterize coating adhesion using scratch testing
- Test oxidation performance of coated cladding samples
- Perform post-testing analysis of the MAX coated claddings

Introduction

Zirconium alloy claddings such as Zircaloy-4 (Zry-4) have a high neutron transparency and resist oxidation at standard commercial reactor operating conditions. However, the Zry-4 claddings oxidize much more rapidly under nuclear reactor Loss-of-Coolant Accident conditions that can reach up to 1200°C and release hydrogen as well as lose mechanical strength. There is a significant interest within the DOE complex to increase the accident tolerance of nuclear fuel claddings to improve overall reactor safety.

One method to improve the oxidation resistance of nuclear fuel claddings is to coat them with oxidation resistant materials. Coatings for nuclear fuel also need to have good thermal transfer properties that will not significantly reduce conduction of heat through the cladding at normal operating conditions. MAX phase materials are a unique class of materials that are both oxidation resistant at high temperatures similar to ceramics, but also have high heat conduction at normal operating conditions.

MAX phase materials have a unique microstructure that gives them their properties and are traditionally synthesized using high temperature annealing steps that cannot be directly performed on cladding

materials without significant alteration of their microstructure. Cold-spraying is a technique that can synthesize coatings of MAX materials by propelling MAX powder at the Zry-4 substrates at high velocity.

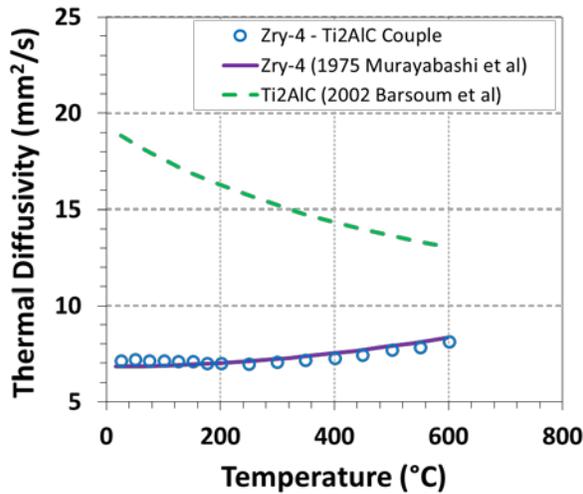


Figure 1. Thermal diffusivity of MAX-coated Zry-4 compared to the Zry-4 substrate and pure Ti₂AlC

material. Scratch testing was performed to characterize the mechanical adhesion of coatings on the samples. Oxidation testing in the range of 1000-1200°C was performed with an atmosphere of argon saturated with steam. The weight gains of the samples were measured and the oxidized samples were characterized using SEM/EDS analysis.

Results/Discussion

The thermal diffusivity for the MAX-coated Zr-4 was measured and compared with literature data for the thermal diffusivity of bare Zry-4 cladding and pure Ti₂AlC. The results (Figure 1) showed that the coated cladding had nearly identical thermal diffusivity to the bare Zry-4. This is as positive as the result can get since the thermal diffusivity of the coated material cannot be higher than the substrate material. This result demonstrates that MAX coatings should provide equivalent performance to uncoated cladding under normal operating conditions.

Figure 2 compares the weight gain in uncoated and Ti₂AlC coated Zry-4 samples. The oxidation of the uncoated cladding was shown to follow the kinetics for Zry-4 oxidation similar to the Leistikow-Schanz model from literature. The Ti₂AlC coated samples were coated on one side that equals 39% of the area. The maximum decrease in cladding oxidation should be 39% since the oxidation of the cladding occurs on a per unit area basis at relatively short times. The weight gain was reduced by 75-80% of the maximum possible reduction. This demonstrates that MAX coatings provide a marked protection against cladding oxidation.

SRNL is working with the University of Wisconsin-Madison to synthesize MAX coatings by cold-spraying them onto Zry-4 cladding samples. The synthesis of a MAX-coated fuel tube could provide a very near-term solution as an “Accident Tolerant Fuel” (ATF), attractive to the nuclear industry by keeping the cladding microstructure unchanged, while coating it with a material that affords oxidation protection for normal operation and accident conditions.

Approach

Ti₂AlC was chosen as a representative MAX phase material due to its commercial availability and high oxidation resistance at elevated temperature. The thermal transport properties of MAX-coated Zry-4 samples were measured using laser flash analysis (LFA) that measures the thermal diffusivity of the

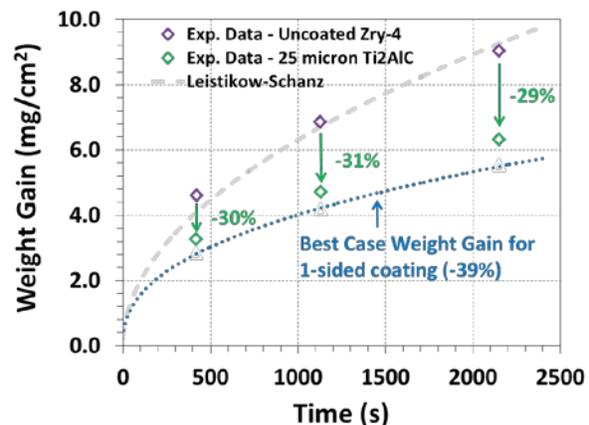


Figure 2. Comparison of weight gain during oxidation at 1005°C for uncoated and Ti₂AlC coated Zry-4 samples (SRNL data)

Figure 3 shows an SEM image of the Ti_2AlC -coated sample after oxidation testing. The SEM does not show oxidation of the Zry-4 substrate beneath the coating. This indicates that the coating is protecting the substrate from oxidation. The EDS image shows diffusion of a 1:1 TiAl alloy about 20 microns into the Zry-4 substrate. The coating also shows some enrichment of Al and depletion of Ti at the surface of the MAX coating. The formation of a Al_2O_3 rich surface layer should assist in blocking oxidation of the Zry-4 substrate.

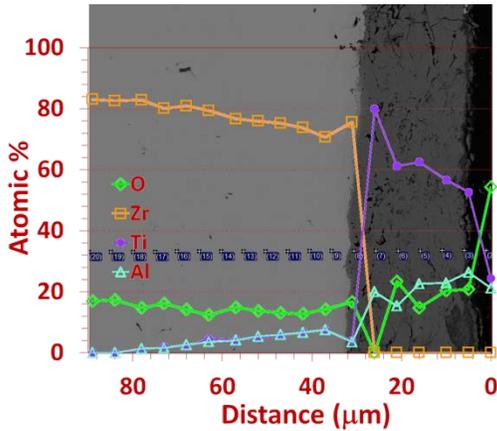


Figure 3. SEM/EDS analysis of the Ti_2AlC -coated sample after oxidation testing

- Ti_2AlC coated Zry-4 was able to withstand a 50 N scratch with only a 20 micron penetration

FY2014 Accomplishments

- Demonstrated thermal diffusivity for Ti_2AlC coated Zry-4 was within 5% of the thermal diffusivity for the Zry-4 substrate.
- Ti_2AlC coated on a single side of Zry-4 achieved 75-80% of the possible decrease in weight gain compared to uncoated Zry-4 samples.

Future Directions

- Develop method of directly coating MAX phase materials on the Zry-4 substrate
- Compare Ti_2AlC with different MAX materials for preventing oxidation of nuclear fuel
- Work with AREVA on DOE NE ATF program project to improve MAX coatings for nuclear fuel.

FY 2014 Publications/Presentations

1. B. L. Garcia-Diaz, E. N. Hoffman, R. L. Sindelar, D. J. Tallman, M. W. Barsoum, "MAX Phases for Nuclear Applications," Presented at CIMTEC 2014, Montecatini Terme, Italy, June 2014.

References

N/A

Acronyms

Zry-4 – Zircaloy-4

LFA – Laser Flash Analysis

SEM – Scanning Electron Microscopy

EDS – Electron Dispersive X-ray Spectroscopy

Patent Apps/ Patents Awarded

None

Total Number of Post-Doctoral Researchers

None

Structural integrity of dual-purpose canisters for used nuclear fuel under extended storage and transportation

Project Team:

P. S. Korinko (PI), A.J. Duncan, R.L. Kesterson, and R.L. Sindelar, P.S. Lam, T. M. Adams

Project Start Date: October 1, 2012

Project End Date: September 30, 2014

Two aspects of the structural integrity of dual-purpose (extended storage and transportation) canisters for used nuclear fuel are being studied. First, fracture assessment methodologies are applied to the canisters under both extended storage and transportation conditions. Fracture mechanics based flaw stability acceptance criteria will be defined to assure pits and cracks caused by marine and industry deposited salt will not cause canister failure. The second aspect is directly applicable

to the fuel being stored and transported inside the canister. Two tests of the ductility of hydrided fuel cladding are being compared and evaluated to ensure they demonstrate sufficient ductility exists for normal and off-normal loads during transportation and storage of used nuclear fuel.

FY2014 Objectives

- Develop a Framework for Assessing the Likely Failure Modes of a Multipurpose Fuel Canister
- Compare proposed approaches to codified methodologies
- Develop a method to form uniform and rim type hydrides in ZIRLO
- Develop a method to generate radial hydrides
- Determine the Ductile to Brittle Transition using both Ring Compression Tests and Three Point Bend Tests

Introduction

Nuclear energy systems continue to be a significant and growing component of the worldwide energy portfolio. However, the final disposition of used nuclear fuel (UNF) represents a continued challenge to the long-term viability of nuclear energy. The used fuel are initially stored in storage pools and then transferred to dry cask storage after sufficient time to allow cooling via radioactive decay. The present regulatory basis for dry cask storage is 60 years but longer storage times will likely become necessary as the U.S. Department of Energy (DOE) and the U. S. Nuclear Regulatory Commission (NRC) evaluate repository and reprocessing components under the modified open cycle strategy. In addition, even as the UNF storage times are projected to extend far beyond 60 years, the trend in the commercial power production industry is to push fuel to higher burn-up (>45GWD/t), partially because of the shortage of the storage pool capacity. This creates a UNF storage challenge as higher burn-up increases cladding degradation, fission product concentrations, and other phenomena that will affect fuel performance during UNF storage.

It is proposed to develop a fracture mechanics-based flaw disposition protocol to establish the acceptance criteria for continued service of these canisters in the dry storage system. The first step in

protocol development would be the determination of instability crack lengths for flaw postulates at critical canister locations under loading conditions. Instability crack lengths would be estimated based on the fracture toughness of the materials of construction. The service loads may include accident conditions in combination of the residual stress since the canisters may not be stress relieved after welding. The evaluation of flaw stability for the purpose of developing flaw acceptance criteria is outlined in this paper. Subcritical flaw growth, which could occur with SCC, would be also considered in the establishment of intervals under an in-service inspection program. This would include, for example, a more frequent examination of reported flaws. This consideration is outside the scope of this paper.

In addition to the concerns regarding the cask, the integrity of high burn up fuel clad is of interest; and a primary point of concern for long term spent fuel dry storage planning is that when the cladding experiences the thermal-mechanical conditions of the storage container drying process and subsequent transport that the risk for clad failure during normal and accident conditions is understood and minimized. The generation of radial reoriented hydrides in the clad during cooling with clad hoop stresses will change some cladding properties and thus data on the factors influencing the reorientations and the subsequent property impacts is of value in modeling and design.

Approach

To address the concerns for the multi-use canister, two general approaches were used, the J-integral and failure assessment diagram (FAD).

Fracture toughness (J_{Ic} or K_{Ic}) is a method of determining a materials resistance to ductile crack growth in the presence of a flaw (e.g., crack or weld defect) and is measured using methods recommended by ASTM [1]

$$J = C(\Delta a)^m$$

Where C and m are curve fitting parameters, Δa is the incremental crack growth, and J is the fracture energy. In addition, consideration has to be given to the Tearing Modulus (T) which incorporates the slope of fracture toughness curve (dJ/da), yield strength (σ_o) and tensile modulus (E).

$$T = (E/(\sigma_o)^2) * (dJ/da)$$

Crack growth is stable as long as $T < T_R$, where T_R is the tearing modulus of the material. The intersection of the applied load as determined by analysis due to external loading and the material property measurement determined by testing dictates the stable crack growth limit. This approach was developed for Electric Power Research Institute (EPRI) by General Electric in the 1980s [2, 3].

The failure assessment diagram (FAD) is a crack growth resistance curve in terms of L_r (abscissa) and K_r (ordinate), where the stress ratio L_r is traditionally defined as the ratio of the applied load (P) to a reference load (P_o); and K_r and J_r are the ratios of elastic force to the resisting force:

$$L_r = P/P_o$$

$$K_r = K(a, P)/K_R(\Delta a)$$

$$J_r = J^e(a, P) / J_R(\Delta a)$$

where K is the stress intensity factor at the tip of a crack due to the applied load, and K_R is related to J_R as $K_R^2(\Delta a) = E' J_R(\Delta a)$ and is the fracture toughness of the material (e.g., K_{IC} or J_{IC}).

These parameters can be modified for the loading conditions, i.e., plane stress and plane strain, such that a non-dimension parameter K and J can be related.

$$K_r^2(a, P, \Delta a) = J_r(a, P, \Delta a)$$

Then, when the assessment point is below this curve, the crack is considered stable. The original FAD was developed in 1986 by Milne et al. [4] and is considered a codified approach, although it has a sound technical basis. These two methods will be evaluated to determine the most suitable approach for assessing flaw acceptance criteria.

The effects of accidents on clad were also investigated. Hydrogen enters the zirconium-based clad through the reaction of cooling water forming ZrO_2 and putting hydrogen into solution in the clad. If or when the hydrogen content exceeds the solubility limit, then hydrides will precipitate. The quantity, location, and orientation of the hydrides depend on the fuel burn-up, the temperature gradient and the temperature. Upon use of the fuel to its desired burnup, the used nuclear fuel (UNF) is removed from the reactor and placed in the spent fuel pool. After it has cooled sufficiently in the spent fuel pool, the UNF will be packaged into the MPC, described above and in order to minimize corrosion issues, and then dried.

UNF will be dried by heating under vacuum to a temperature not to exceed 400°C per ISG 11, Rev. 3. The fuel rods will be internally pressurized due to initial fill gas and fission products. The internal pressure can cause a hoop stress of 90 MPa [5] and high burn up rod could have a pressure of 2250 psi, which would result in an effective hoop stress of 128 MPa at 400°C during drying. In very high burn up rods, the effective stress could be as high as 160 MPa. To characterize the effects, samples were filled with gas pressures to generate stresses of 90, 130, and 170 MPa to have 40 MPa increments.

Samples were charged with hydrogen, aged with internal pressure, and then sectioned into the test articles. The test articles were either 8 mm long or 100 mm long segments of ZIRLO clad that had been charged with 99.95% purity hydrogen. Samples were tested to determine the quasi-ductile to brittle-transition-temperature (DBTT) using either a ring compression test (RCT) or three point bend test (TPBT). The test temperature ranged from room temperature to 200°C.

Results/Discussion

The stress analysis for the MPC and casks are generally not available in the open literature, the stresses needed for the analysis were extracted from a probabilistic risk assessment report, NUREG-1864 [1], which references some stress analysis results reported in HI-2002444 [5].

The material properties of Type 304 Stainless Steel, a common cask material, were used to bound the typical cask materials. These data were extracted from [6]. Since the vessels are all welded, the effect of

welding on the shell to baseplate (BP) residual stresses were also considered. No reduction in materials properties were included in the assessment since research [7] was shown that there is no reduction associated with the welds.

Thermal stresses, accident related drop event stresses, and weld residual stresses were considered. The hoop and axial thermal stresses can be used to develop flaw criteria for the MPC axial and circumferential welds and the highest stresses due to bending can be used for acceptance criteria at the junction between the MPC shell and BP. The stresses from a drop need to be calculated using finite element models with the resultant deformation being compared to data in [6]. The weld residual stresses were estimated based on [6]. Note that weld stresses depend on the welding parameters and the joint geometry.

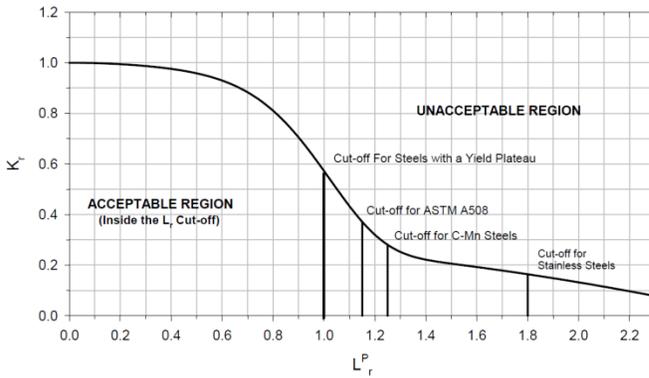


Figure 1. Typical Failure Assessment Diagram from API 579 (6).

acceptable from unacceptable is the critical flaw size.

The actual flaw may be an assumed size or based on the limits of detectability for the state of the art nondestructive evaluation (NDE) tools that are available. The coordinates of the assessment point are re-evaluated as the postulated flaw grows incrementally.

While the MPC effort relies heavily on literature and codes, the determination of the quasi-DBTT is primarily an exercise in experimentation. Samples internally hydrided exhibited one of three general morphologies, uniform hydride, inner diameter (ID) rim and outer diameter (OD) rim. A specimen with ID rim and one with OD rim are shown in Figure 2. Note that there are also circumferential hydrides present that are somewhat uniformly distributed throughout the tube wall.

Samples that had been hydrided at 100 and 200 weight parts per million (wppm) were subsequently treated with a radial hydride

Based on [7], a Level 3 assessment was indicated to provide the best estimate for the structural integrity of the MPC with a crack-like flaw. A typical FAD is presented in Figure. 1 and a material specific FAD can be constructed based on the tensile properties of interest for the MPC. The flaw size that lies on the curve dividing

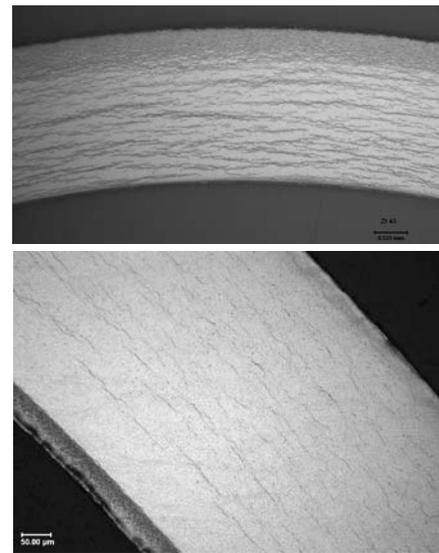


Figure 2. ZIRLO Samples with OD and ID Rim Structures.

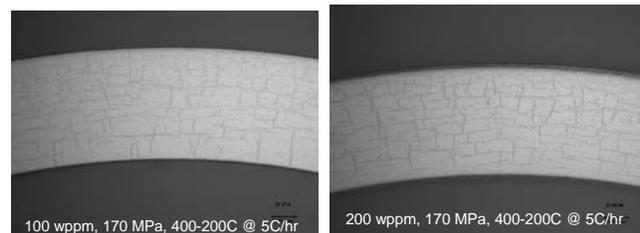


Figure 3. Effects of RHGT on uniformly precipitated hydrides.

growth treatment (RHGT) at 170 MPa. The effects of this RHGT due to heating with internal pressures to 400°C and cooling at 5°C/hour are shown in Figure 3. These samples were initially charged with hydrogen under conditions which produced uniform hydrides. The effect of the treatment is dramatic with the samples exhibiting numerous radial hydrides. Samples that were exposed at 90 MPa did not exhibit the radial hydride formation.

The quasi-DBTT was determined using RCT and TPBT. The RCT data for samples charged with 400 ppm Hydrogen and subjected to RHGT at 130 and 170 MPa is shown in Figure 4. These data show that increased stress increase the DBTT, an undesirable effect. A series of tests were conducted for samples charged with 100 to 800 wppm H and treated at 90, 130, and 170 MPa. While the stress seems to have a direct correlation with DBTT, the effect of hydrogen appears to be inversely related to the DBTT as shown in Figure 5 where lower hydrogen content samples exhibit higher DBTT.

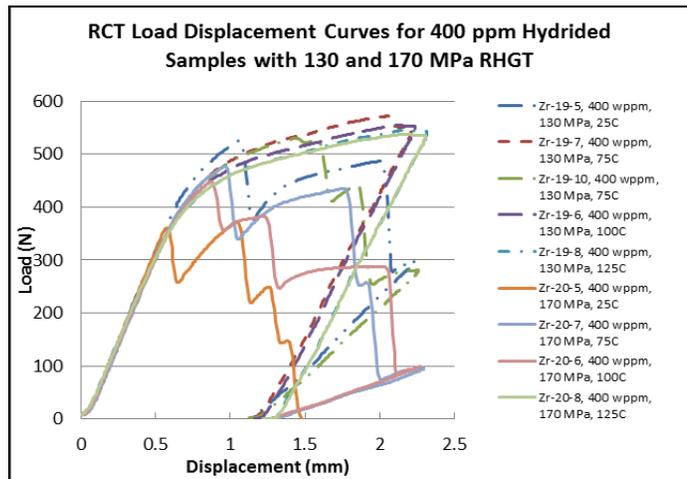


Figure 4. RCT data for samples charged with 400 wppm H and subjected to RHGT at 130 and 170 MPa.

The results from the TPBT were not as clear and brittle failure occurred after significantly higher total displacements than predicted. Also the effective DBTT was lower when measured by TPBT. The relative strains for TPBT is significantly higher than the one to five percent observed for the brittle behavior observed in the RCT.

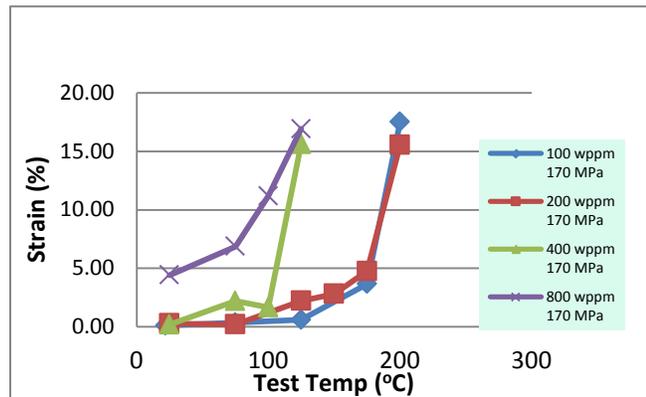


Figure 5. DBTT test results for ZIRLO charged with 100 to 800 wppm H and subjected to a 170 MPa RHGT.

FY2014 Accomplishments

- We developed a framework for instability flaw size estimation and flaw acceptance criteria for the multi-purpose canister in dry cask storage systems
- We adopted and applied the FAD approach in API 579 Part 9 with Level 3 Assessment to account for weld residual stress in the loading flaws in the shell body of the multi-purpose canister
- With the hydrogen charging and radial hydride treatment protocol that was developed in year 1, we investigated the DBTT for the simulated high burnup cladding, and found that the DBTT for RCT depends directly on the hoop stress used in the radial hydride treatment protocol, and inversely on the hydrogen content

- We determined that the DBTT from TPBT depends directly with the hydrogen content and is less sensitive at lower hydrogen contents than the RCT
- We established national laboratory lead oversight on behalf of DOE NE for the integrated research project led by the University of South Carolina for "Experimental Determination and Modeling of Spent Nuclear Fuel Drying by Vacuum and Gas Circulation for Dry Cask Storage"

Future Directions

- Continue to consult with DOE NE, NRC and EPRI to obtain funding to show the effects of testing method on DBTT
- Assist with and obtain funding for resolving the unanswered questions regarding long term dry storage of UNF.

FY 2014 Publications/Presentations

1. Comparison of Ductile to Brittle Transition Testing Method for Used Nuclear Fuel or ZIRLO Hydrogen Charging, Reorienting, and Testing, Paul Korinko, Robert Sindelar, Ron Kesterson, Thad Adams, Presented at the Second ASTM Zirconium Alloy Cladding Workshop, June 8-12, 2014, Jackson, WY.
2. Hydrogen Charging, Reorienting, and Testing of ZIRLO, P.S. Korinko, R. L. Sindelar, R. L. Kesterson, T. M. Adams, Presented at 34th Tritium Focus Group Meeting, Idaho Falls, ID, Sept. 23-25, 2014.
3. Hydrogen Embrittlement Testing of a Zirconium Based Alloy, P.S. Korinko, R. L. Sindelar, R. L. Kesterson, T. M. Adams, Presented at and Published in the Materials Science & Technology 2014, Environmentally Assisted Cracking: Nuclear: Symposium, Pittsburgh, PA, Oct. 12-16, 2014.
4. Hydrogen Embrittlement Testing of a Zirconium Based Alloy, P.S. Korinko, R. L. Sindelar, R. L. Kesterson, T. M. Adams, to be presented at and published in the TMS 2015, Conference Proceedings, Orlando, FL, March 15-20, 2015 also submitted to TMS in The Metallurgical and Materials Transactions E (MMT-E)
5. Comparison of Ring Compression Testing to Three Point Bend Testing for Unirradiated ZIRLO Cladding, PVP2015-45984, P.S. Korinko, R.L. Sindelar, R.L. Kesterson, To be presented at and published in ASME 2015 Pressure Vessel and Piping Conference, July 19-23, 2015, Boston, MA.
6. A Framework to Develop a Flaw Acceptance Criteria for Structural Integrity Assessment of Multipurpose Canisters for Extended Storage of Used Nuclear Fuel, P.S. Lam, R. L. Sindelar, A.J. Duncan, T. M. Adams, Presented at and Published in Proceeding of the ASME 2014 Pressure Vessel and Piping Conference, July 20-24, 2014, Anaheim, CA.

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4. Milne, I, Ainsworth, R.A., Dowling, A.R., and Stewart, A.T., 1986, "Assessment of the Integrity of Structures Containing Defects," Central Electricity Generating Board Report R/H/R6-Rev. 3, May 1986; Also in International Journal of Pressure Vessel & Piping, Vol. 32, pp. 3-104, 1988.
5. Kesterson ,R.L Sindelar, R.L., Vinson, "Used Nuclear Fuel Characteristics at End of Life" FCRD-UFD-2013-000130 March 29, 2013
6. Bjorkman, G., Chuang, T.-J., Einziger, R., Malik, S, Malliakos, A., Mitchell, J, Navarro, C., Ryder, R., Shaukat, S., Ulses, A., and Zigh, G., 2007, "A Pilot Probabilistic Risk Assessment of a Dry Cask Storage System at a Nuclear Power Plant", NUREG-1864, U.S. Nuclear Regulatory Commission Washington, DC.
7. API 579-1/ASME FFS-1, 2007, *Fitness-For-Service* (API 579 Second Edition), American Petroleum Institute, Washington, DC.

Acronyms

BP – Baseplate

DBTT – Ductile to Brittle Transition Temperature

FAD – Failure Assessment Diagram

ID – Inner Diameter

MPa – Megapascals

MPC – Multi-Purpose Canister

OD – Outer Diameter

RCT – Ring Compression Test

RHGT – Radial Hydride Growth Treatment

TPBT – Three Point Bend Test

UNF – Used Nuclear Fuel

wppm – Weight parts per million

Patent Apps/ Patents Awarded

None

Total Number of Post-Doctoral Researchers

None

Electro-Dynamic Particle Sorter

Project Team: J. L. Venzie (Primary),
M. J. Siegfried, M. S. Wellons, G. A.
Fugate

No subcontractors used.

Project Start Date: October 1, 2013
Project End Date: September 30, 2015

The Electro-Dynamic Particle Sorter project is focused on improving current electrostatic particle collection technology. By leveraging selected characteristic features, particles of interest can be manipulated during the collection process into a physical configuration conducive to subsequent microscopy and micro-scale laboratory analyses. In order to achieve this goal, a fundamental research and development effort is required to build an accurate model/understanding of how the desired particles behave in electric fields at

atmospheric pressure and what physical and chemical characteristics dominate or could be made to dominate their trajectories. Aspects of this work are related to ion mobility mass spectrometry and traditional aerosol science, but critical knowledge is lacking and must be developed as part of this effort.

FY2014 Objectives

- Procure specialized modeling software packages for ion trajectory simulations.
- Procure laboratory measurement, control and automation hardware for the aerosol test chamber.
- Calculate physical constants for particles of interest from laboratory data.
- Model existing SRNL collector technology to validate simulations.
- Build and test mechanically screened particle collector.

Introduction

SRNL has successfully leveraged electrostatic precipitator (ESP) based aerosol collection technology and made it available to selected national security customers. The current state of ESP technology is fundamentally an indiscriminate design, i.e. used to collect a broad range of sizes and types of particles. To date, this feature has been a benefit for SRNL's current customers. However, in order to expand into new markets, SRNL needs to use the knowledge gained through the application of the current technology to guide fundamental research into particle manipulation. The ability to collect samples in such a way that the particles of interest can be easily and quickly found for individual analysis increases the efficiency of numerous techniques such as scanning electron microscopy, secondary ion mass spectrometry, x-ray diffraction, Raman microscopy, etc. These and other similar per-particle analytical techniques are being used to obtain ever more information from the source of the collected particles, and finding the informative particles amongst background material is challenging for all of them.

This project will not only allow SRNL to make a significant contribution to collection technology within the DOE mission space, it will also reinforce and grow SRNL's reputation as the DOE center of expertise in aerosol sampling. In addition to maintaining our current customer relationships, the basic research being performed in this LDRD is enabling SRNL to expand its reputation into the larger open aerosol science community and will provide a vehicle to transition existing particle knowledge and expertise into the broader community as appropriate. The potential applications for dynamic particle sorting are broad and the ability to perform this type of advanced aerosol collection is of interest not

only the nonproliferation community, but the biology, industrial hygiene and pharmaceutical fields as well.

Approach

The Electro-Dynamic Particle Sorter project focuses on building the knowledge and infrastructure to perform advanced aerosol collection research and development. This overarching objective is being executed via three main areas. The first research area is developing the capability to simulate particle trajectories in ESP type collectors. Several commercially available software packages are being used in conjunction to simulate the effects of air flow, static and dynamic electric fields, and magnetic fields on particle populations. The second key area is the upgrading of an existing aerosol chamber to an automated collector test bed. Computer controlled power supplies, particle generators, data acquisition, and modular test components make it possible to quickly build and test new designs. These two areas focus on basic research and long term returns, the third area looks at simpler possibilities using commercially available equipment adapted for this purpose.



Figure 1. ImpACE showing the cylindrical particle impactor coupled to an ESP collector body.

Results/Discussion

In order to accurately simulate the trajectory of particles in a collection device several physical values that describe the particle population are needed. These include the mobility in air, the number and polarity of the electrical charges on the particles, and the particles' mass. Each of these physical features has a distribution of values that interact to create a complex population of particles that must be recreated in the simulations in order to develop useful collector designs. Using accepted empirical equations [ref] and laboratory data a series of calculations were performed using randomized variables to build a test particle population to use in the collector simulations. A specific example is shown in Figure X which illustrates how the probability distribution function (PDF) for the number of charges on a given particle changes based on the dielectric constant (ϵ) of the particle material.

Several initial simulations were performed modeling a well-established SRNL collector design. Some unexpected instabilities in the calculated air flow was eventually traced back to the mathematics used by that hydrodynamic software. Another hydrodynamic software package was identified and ordered that will resolve this issue and add several additional advanced features that will be useful in the future.

In addition to the modeling part of this project, a commercially available aerosol impactor was modified to behave as a large particle screen and coupled to an ESP collector. This device, termed the ImpACE, rejects the particles too large to be of interest (pollen, dirt, etc.) and collects the small size fraction. Even this relatively simplistic approach, reduces the number of nuisance particles collected. A

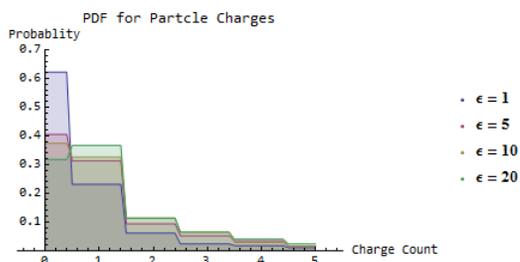


Figure 2. Probability of particle charge for materials with four dielectric constant values.

test collection was performed on sea salt particles in sea air and the particles measured by SEM. The results are currently being reviewed and analyzed.

FY2014 Accomplishments

- Procured and received required computational hardware required to run the particle trajectory simulations.
- Procured and received electrostatics modeling software (SIMION) that calculates particle trajectory in the presence of air flow vectors and electric and magnetic fields.
- Procured hydrodynamics software that is compatible with existing NTS engineering workflow and tools (Autodesk Simulation CFD). This software calculates the air flow vectors inside the aerosol collector which are subsequently imported into the SIMION software.
- The PI attended the 39th Aerosol and Particle Measurement Short Course at the University of Minnesota.
- Developed and field tested the ImpACE a multi-mode aerosol collector designed to improve the quality of the collected sample for microscopy based analytical techniques. The collected samples have been measured by SEM and the data is currently being reviewed.
- Procured and received process automation hardware and software (National Instruments) which will be used to upgrade an existing aerosol test chamber in year two. This upgrade will allow for more dynamic experiments to be performed while characterizing new collector designs.
- Procured and received R&D ion optics components (Kimball Physics) to be used to quickly build and test experimental designs in year two.
- Mathematically derived the physical constants for the particles of interest that will be used as inputs during subsequent computational simulations. These values were developed based on data and operating conditions collected from the current electrostatic precipitator design.

Future Directions

The second year of this project will build upon the accomplishments made to date. Specific tasks include:

- Incorporate Autodesk Simulation CFD into the simulation workflow.
- Simulate current collector design to validate the simulation.
- Build LabView controlled electrostatic precipitator for laboratory R&D.
- Perform one business development sample collection and analysis.
- Prepare patent application.
- Prepare and submit manuscript to peer reviewed journal.

FY 2014 Publications/Presentations

In order to protect the intellectual property rights of this work, publications and presentations have been postponed until the second year when a patent application is planned.

References

1. List any references used in the report.

Acronyms

ACE Aerosol Contaminant Extractor – an electrostatic precipitator developed at SRNL.

CFD	Computational Fluid Dynamics – modeling of fluid (or air) flow.
DOE	U.S. Department of Energy
eDPS	Electro-Dynamic Particle Sorter – title of this LDRD project.
ESP	Electrostatic Precipitator – particle collector technology using electric fields.
ImpACE	Impactor-Aerosol Contaminant Extractor
LDRD	Laboratory Directed Research and Development
NTS	Nonproliferation Technology Section – SRNL organization executing this LDRD.
PDF	Probability Distribution Function – probability that a variable will be less than or equal to a given value.
SEM	Scanning Electron Microscope
SRNL	Savannah River National Laboratory

Patent Apps/ Patents Awarded

Pending second year scope.

Total Number of Post-Doctoral Researchers

None

Novel Ceramic Membranes for Efficient Utilization of Natural Gas

Project Team: E.B. Fox (Primary), J. Amoroso, H. Colon-Mercado, K. Brinkman

Subcontractor:
F. Chen (USC)

Project Start Date: January 15, 2014
Project End Date: September 30, 2015

The exploitation of large shale gas reserves in the U.S. has enabled the drastic decrease in NG prices. This provides a cheap, clean source of gas for chemical processing and H₂ technologies provided that improved separations can be developed. Two membrane systems (oxygen and hydrogen) will be processed and tested in conjunction with catalytic cracking of the gas feed. This project focuses on the development of an improved reactor design which can target product specific feeds.

FY2014 Objectives

- Install and qualify the permeation system
- Characterize ceramic membrane materials for hydrogen separation.
- Procure, install and qualify the AutoChem II Chemisorption unit for catalyst testing
- Install natural gas reactor
- Synthesize BCFNO powders by two methods
 - Characterize physical and chemical properties.

Introduction

Large reserves of natural gas have enabled the expansion of US chemical industries and national energy independence. Natural gas is the primary source of hydrogen and synthesis gas used for chemical, transportation, and industrial needs. To utilize this hydrogen/carbon monoxide product in specialty chemical production, it is important to carefully control the H₂/CO ratio in the feed. This project is developing an improved reactor design for natural gas cracking and purification. Two membrane

systems (oxygen and hydrogen) will be processed and tested in conjunction with catalytic cracking of the gas feed. This project focuses on the development of an improved reactor design which can target product specific feeds.

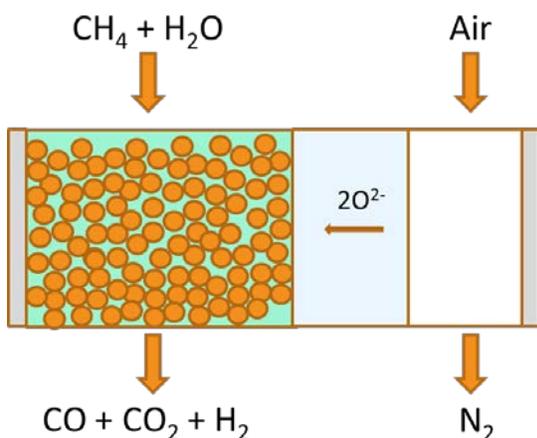


Figure 1. Schematic of an Oxygen Membrane Reformer

One proposed method is the Oxygen Membrane Reactor (OMR) [1-3], in which an oxygen selective membrane is used to transport oxygen from air to the feedstock for reaction. The benefits of an OMR include *in-situ* purification of oxygen from feed air to high purity oxygen for the reaction with a decrease in costs for the air separation unit. This work will detail the synthesis, characterization, and performance of BaCo_{0.7}Fe_{0.2}Nb_{0.1}O_{3-δ} (BCFNO) oxygen permeation membranes, which will be coupled in an oxygen membrane reactor system.

Hydrogen separation membranes based on high temperature proton conductors are pursued in this project because of their potential to greatly reduce the energy and capital cost of large-scale hydrogen production from steam methane reforming. A key to their successful applications is the development of a membrane with high performance and chemical stability. Ni-BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-δ} hydrogen separation membrane has shown high performance stability in dry H₂ and CO₂. However, the membrane needs to be used in the stream after steam methane reforming. The coexistence of concentrated H₂O and CO₂ in the stream poses a harsh challenge to the chemical stability of the membrane. This study will explore the stability of the membrane in processing conditions. Ni-BaZr_{0.8}Y_{0.2}O_{3-δ} is expected to meet both requirements for performance and chemical stability, however, BaZr_{0.8}Y_{0.2}O_{3-δ} is very refractory, making its densification very difficult.

Approach

BCFNO was synthesized by two different methods: solid state reaction and solution precipitation. The solution precipitation samples were prepared via urea gelation method. An appropriate molar amount of Ba(NO₃)₂, Co(NO₃)₂, Fe(NO₃)₃ and NbCl₅ were dissolved in 300 mL of DI H₂O. The solution was heated to 75°C to aid in dissolving the salts. Once the salts were dissolved, 45g of urea in 100mL of DI H₂O were added to the solution. The solution was heated to a gentle boil until precipitation occurred. Once precipitation occurred, the solution was allowed to continue to age for until three hours. Additional DI H₂O was added as needed. The solution was then cooled, filtered, and washed with additional DI H₂O. The precipitate was dried overnight in a vacuum oven at 120°C.

For the solid state reaction, in each batch stoichiometric amounts of reagent-grade Fe₂O₃, CoO, Nb₂O₅, and BaCO₃, powders (99.5 % purity) were added to make 30 g of final material. They were combined in a 250 ml plastic bottle with zirconia milling media, filled 2/3 full with deionized water, and agitated in a tumbler mixer for 1 hour. Subsequently, the slurry was poured into a pan along with additional rinse water used to collect any batch material remaining on the milling media and bottles. The pan was transferred to an oven where the slurry was dried overnight at 90°C. The dried material was bagged and used as feed stock for synthesis experiments.

Prior to sintering, pellets were pressed at ~5000 psi. Pressed pellets were then heated in a furnace over the course of ~2 days. Samples were initially heated to 650°C at 5 K/min. Subsequently, the heating rate was reduced to 0.3 K/min and 2 hour dwell periods were incorporated at 850°C, 900°C, 950°C, and 1100°C. Following the dwell period at 1100°C, the samples were allowed to furnace cool before further testing.

The time dependence of the performance of Ni-BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-δ} hydrogen permeation membrane was monitored in different concentrations of H₂O and CO₂. Ni-BaZr_{0.8}Y_{0.2}O_{3-δ} was prepared by

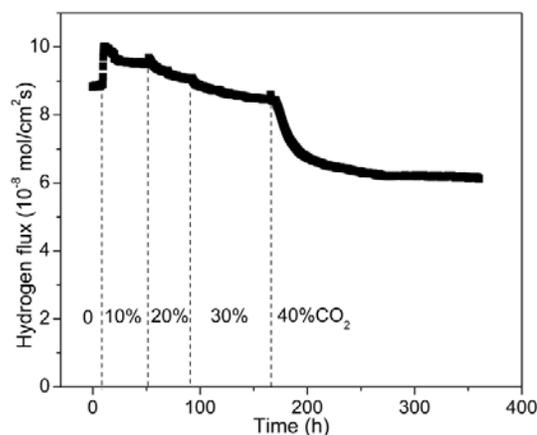


Figure 2. Time dependence of hydrogen permeation flux of a 0.56-mm-thick Ni-BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-δ} membrane in 40% H₂, 3% H₂O, X% CO₂, and (57-X)% He. X changes from 0, 10, 20, 30, to 40 with time as indicated in the figure [1].

various methods, including gel combustion, solid state reactive sintering, and solid state reaction.

Results/Discussion

The synthesized powders were analyzed by TGA under N₂ and air to determine oxygen uptake in the ceramic powder. The analysis was run on a Netzsch 209 FI thermogravimetric analyzer at a ramp rate of 10°C/minute in Al₂O₃ crucibles. The TGA analysis showed that the solid state reaction samples had minimal weight loss until approximately 862°C, under both N₂ and air. The solution precipitation samples had four distinct transition regions of weight loss. The first occurred below 185°C, the second at 188°C, the third at 260°C, and the beginning at 800°C. In-situ XRD is on-going to determine the phase transformations that occur in these regions.

Testing was initiated on the H₂ membranes. In wet 40% H₂ and 30% CO₂, the hydrogen permeation flux of Ni-BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-δ} membrane only decreased 11.4% at 900 °C, as shown in Figure 2 [4]. In comparison, the hydrogen permeation fluxes of Ni-BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-δ} and Ni-BaCe_{0.8}Y_{0.2}O_{3-δ} membrane decreased 42.3%, and 100% at the same condition, respectively [5].

Table 1. TGA mass loss, by synthesis method and carrier gas.

Method	% mass loss (N ₂)	% mass loss (air)	% change	Estimated molar absorption of O ₂ (mol/g)
Solid state	13.00	12.4	0.6	1.4e-4
Solution precipitation	27.99	26.9	1.09	6.8e-4

FY2014 Accomplishments

- Synthesized BCNFO powders by various methods, however were unable to obtain active perovskite crystal structure previously described in the literature.
- Procured and installed a Micromeritics AutoChem II to characterize chemisorption properties of catalysts used to natural gas reforming.
- Began design, installation and assembly of catalyst test stand for natural gas reforming.
- Installed permeation test system.
- Completed subcontract with the University of South Carolina to complete testing on hydrogen permeation membranes.
- Elucidated the interaction among H₂O, CO₂ and Ni-BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-δ} membrane.
- Fabricated dense Ni-BaZr_{0.8}Y_{0.2}O_{3-δ} with excellent permeation flux using highly refractory BaZr_{0.8}Y_{0.2}O_{3-δ}.

Future Directions

- Test oxygen membranes under various partial pressure differentials
- Use in-situ XRD to define phase transformations in ceramic powders
- Optimize chemical composition of oxygen membranes
- Develop new generation of Ni-BaZr_{0.8}Y_{0.2}O_{3-δ} (Ni-BZY) membrane with improved chemical and performance stability
- Fabricate asymmetric Ni-BZY membrane using methods such as tape casting

- Develop new generation of Ni–BaZr_{0.8}Y_{0.2}O_{3-δ} membrane with improved chemical and performance stability.
- Characterize hydrogen flux of ceramic membranes under different temperature, thickness, hydrogen content and moisture content.
- Demonstrate the long-term performance stability of Ni–BaZr_{0.8}Y_{0.2}O_{3-δ} in concentrated H₂O and CO₂.

FY 2014 Publications/Presentations

- Shumin Fang, Kyle S. Brinkman, Fanglin Chen, Hydrogen permeability and chemical stability of Ni–BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-δ} membrane in concentrated H₂O and CO₂, Journal of Membrane Science, 2014, 467, 85-92.
- Shumin Fang, Kyle Brinkman, Fanglin Chen, 225th ECS meeting, Orlando, Florida, USA. Fabrication of Ni–BaZr_{0.8}Y_{0.2}O_{3-δ} composite membrane for hydrogen separation.

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5. C. Zuo, S.E. Dorris, U. Balachandran, M. Liu, Effect of Zr-doping on the chemical stability and hydrogen permeation of the Ni-BaCe_{0.8}Y_{0.2}O_{3-δ}-alpha mixed protonic-electronic conductor, Chemistry of Materials, 2006, 18, 4647-4650.

Acronyms

- BCFNO – BaCo_{0.7}Fe_{0.2}Nb_{0.1}O_{3-δ}
- OMR – Oxygen Membrane Reformer

Patent Apps/ Patents Awarded

None

Total Number of Post-Doctoral Researchers

One at the University of South Carolina

Direct LiT Electrolysis in a Metallic Lithium Fusion Blanket

Project Team: B. L. Garcia-Diaz (Primary), H. R. Colón-Mercado, M. C. Elvington, J. A. Teprovich and D. W. Babineau

Project Start Date: October 1, 2013
Project End Date: September 30, 2015

We are developing a process for the extraction of tritium from molten lithium and lithium lead breeding blankets based on the direct electrolysis of lithium tritide (LiT). Tritium concentration in the form of LiT in the blankets/targets of fission/fusion reactors must be controlled, as high concentrations can lead to loss of tritium fuel and potential contamination due to permeation losses to the

surroundings. The work will identify, develop and test the processes capable of sustaining stable LiT electrolysis at high temperatures. The electrochemical cell has been designed and the process is being tested. Material synthesis and characterization is underway and will be tested in the new cell design.

FY2014 Objectives

- Milestone 1 - 12/30/13 – Complete design of an electrochemical cell and initial material synthesis
- Milestone 2 - 3/31/14 – Complete construction of an electrochemical cell and initial material testing
- Milestone 3 - 6/30/14 – Conductivity tests in high temperature cell and material optimizations
- Milestone 4 - 9/30/14 – Analytical demonstration of LiH decomposition in metallic Li electrode

Introduction

Liquid tritium breeder materials, such as lithium and Pb-Li eutectic, are attractive as their breeding potential is very high and separate neutron multipliers are not necessarily required. Because of it being a liquid, the tritium recovery system can be designed outside the neutron environment and the blanket tritium extraction system will not suffer from radiation damage. In the designs where the breeding material is also used as a coolant, the nuclear heating is directly deposited inside the breeding material simplifying blankets designs. However, there are a number of engineering design difficulties such as magnetohydrodynamic pressure drops, corrosiveness of liquid metal, and efficient tritium recovery and containment from the liquid metal breeder.[1,2]

In most applications, the tritium inventory in the blanket has to be kept low (~1 appm) for a reliable and safe operation. The extraction of tritium can be problematic since the tritium in the blanket exists bound to lithium in the form of LiT. Extraction from liquid Li is considered more challenging due to the high solubility of LiT in the melt. On the other hand, the solubility of LiT in Pb-Li eutectic is several orders of magnitude lower, making extraction somewhat less challenging. Nevertheless the state of the art extraction approaches are essentially similar. Among the considered extraction technologies are molten salt extraction followed by electrolysis (Maroni Process), “gettering”, permeation followed by molten liquid extraction, fractional distillation, cold trapping and a combination of all. However, all of the proposed extraction technologies require a series of complicated mechanical steps (expensive mechanical parts with limited lifetimes) in order to carry out the separation and prevent the buildup of impurities in the extraction process [1]. This work simplifies and eliminates many of the problems associated with the current extraction technologies.

Approach

In the typical Maroni process, molten Li is mixed with a molten salt in order to extract the LiT. Afterwards, the LiT is electrolyzed and the hydrogen extracted. Our approach simplifies the process, by eliminating many of the mechanical steps. Figure 1 shows the Maroni and the SRNL approach.

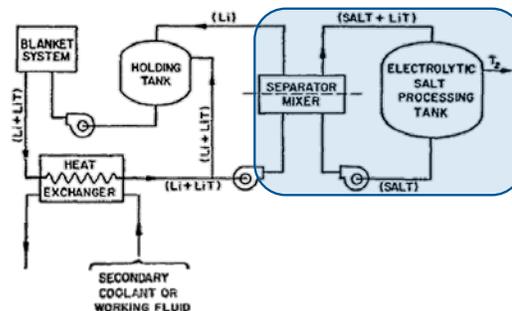


Figure 1. Simplified Maroni process [3] depicting the SRNL process approach.

Results/Discussion

Chemicals were purchased and received. Two main versions of the electrochemical cell were designed, made and preliminarily tested. Material characterization was started and runs with the new electrochemical cell began. Materials are being screened physically and electrochemically for stability and performance. Figure 2 shows the simplified schematic and cell that will be used to test the proposed process. The system involves a heated electrochemical cell inside an inert glovebox, where electrochemical and mass spectroscopy measurements will be used to characterize the system.

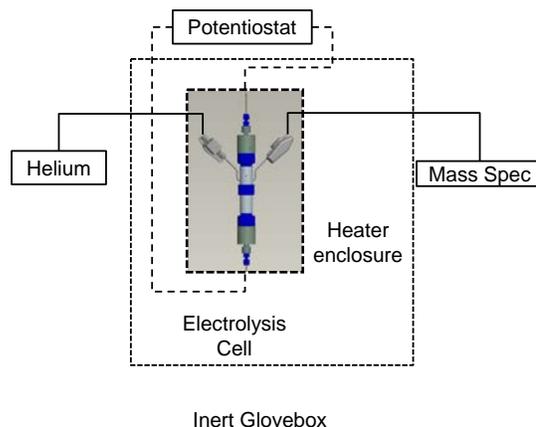


Figure 2. Simplified test set up to test the proposed process.

FY2014 Accomplishments

- 2 versions have been built for the electrochemical cell in order to fix issues with high temperature LiT electrolysis
- Issues with dissolving LiT in Li were resolved and mixtures have been prepared in order to test with our process

Future Directions

- Begin material testing and process testing to proof process concept.
- Incorporate mass spectrometer measurements that will support electrochemical findings

FY 2014 Publications/Presentations

NONE

References

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Acronyms

LiT lithium tritide

Patent Apps/ Patents Awarded

Disclosure filed and waiting for business development to submit patent.

Total Number of Post-Doctoral Researchers

2 postdoctoral students a quarter of their time.

Far Field Modeling Methods for Characterizing Surface Detonations

Project Team: A. J. Garrett (Primary),
E. Villa-Aleman, S. R. Chiswell, S. E.
Aleman, L. L. Hamm

Subcontractor: None.

Project Start Date: October 1, 2013
Project End Date: September 30, 2015

Abstract: The Far Field Modeling Methods for Characterizing Surface Detonations Project in FY-14 characterized particle size distributions from samples taken during high explosives (HE) tests conducted by DOE's National Nuclear Security Agency (NNSA). These samples were taken at a the detonation site and several kilometers downwind. Analysis of the particle samples showed that the sub-micron particles are lognormally distributed and uranium content correlates with particle size.

Theoretical and full-physics atmospheric transport and deposition simulations indicate that minimal depletion of plume particles would have occurred at the downwind sampling site. These calculations were verified by the particle analysis. In FY-15, SRNL will develop more quantitative methods to determine particle composition and will attempt to produce more accurate initial hot cloud specifications through use of a detonation model in addition to empirically derived functions.

FY2014 Objectives

- This project addresses DOE's NNSA (NA-22) MPD objective to develop methods for detection of nuclear proliferation:
- Exploit High Explosives (HE) test data collected as a part of a DOE NA-22 funded project.
- SRNL is using the unique particle data sets to determine if HE tests relating to nuclear weapons can be distinguished from other more conventional HE detonations.
- Extract particle size and composition data from airborne (rocket) and ground-based systems that collected particulate data within the blast cloud.
- Extract particle size and composition data from ground-based systems that were located several kilometers downwind from HE test site.
- Complete specifications for initial "hot cloud", which will be used to initiate atmospheric transport and deposition simulations.

Introduction

Signature assessment activities for high explosives fall within the Non-Proliferation Strategic Focus Area for SRNL who has participated in prior Nevada Test Site testing campaigns¹. High explosive devices produce debris clouds whose initial fireball temperatures and different particulate chemical/physical constituents are potential observables from implosion/explosion device detonations. These observables imply that there are near and far field opportunities to make remote and in-situ measurements that can be used to characterize the detonation event.

To understand the nature of an explosive test, NNSA is seeking potential signatures for interpreting the intent of such testing from a nonproliferation perspective. Recent DOE focus on assessing likely signatures has been on ground testing of implosive/explosive devices and near-field source characterization activities. Little interest to date has focused on far-field opportunities. Given the broad range of possible explosive device designs there is a reasonable expectation that far-field ground

deposition of debris will provide signatures that can help resolve the type and yield of a tested device. This work will address the far-field hypothesis and will assess potential signatures that could be exploited in future DOE testing or evaluation efforts.

This project focuses on developing/executing a computational strategy for estimating the far-field deposition of particulate matter due to atmospheric dispersion, transport, and ultimate deposition. The key outcome from this work will be the identification of potential particle properties that can be measured downwind using ground collection equipment that can provide statistically relevant insight into the type and yield of a suspect surface detonated device.

Approach

Extract statistics on composition and sizes of particles collected by SRNL during HE tests. Determine if depletion of cloud as a function of particle size and composition can be quantified by comparing particle data taken in cloud immediately after detonation to particle data taken several kilometers downwind. Use cloud size, temperature and composition measurements from DOE HE tests plus other HE tests to specify conditions in initial hot cloud. Refine initial hot debris cloud specifications by simulating detonation with Lagrangian hydrodynamic code. Perform atmospheric transport and deposition simulations. Use initial hot detonation cloud specifications to simulate particle transport and deposition with full-physics 3-D atmospheric code (Weather Research and Forecasting model²). Determine how far downwind particles specific to a weapons-related HE test can be detected.

Results/Discussion

Particle samples collected at the detonation site and several km downwind were analyzed with 3 different codes. One code was developed by SRNL and the other two were acquired from the open literature³ and Sandia National Laboratory. All 3 codes produced similar particle size distributions, i.e., particle size distributions were generally lognormal. Since the numbers of particles in different samples were different, the particles counts were normalized to 1000 for comparison of detonation site size distributions to downwind size distributions. These comparisons indicate that there was little depletion of the larger particles over the distance from the detonation site to the downwind collection site (Figure 1).

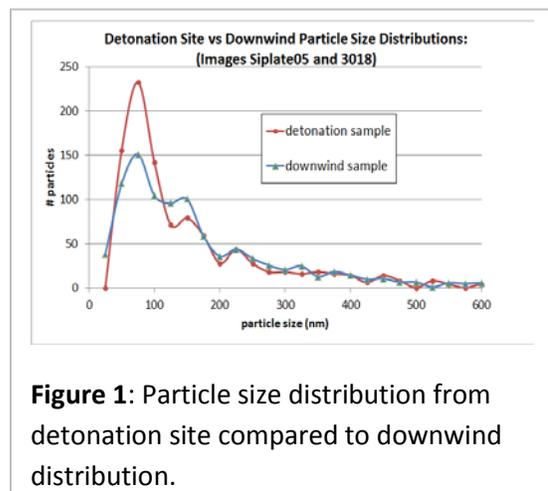


Figure 1: Particle size distribution from detonation site compared to downwind distribution.

Atmospheric transport and deposition simulations reproduced the observed behavior, i.e., the larger particles were not significantly depleted from the plume at the downwind sampling site. This behavior was also predicted by simple gravitational settling velocity calculations, which indicated that significant depletion of sub-micron particles would not occur until the plume had been transported 30 km or more downwind.

A computational framework based on smooth particle hydrodynamics (SPH) to simulate a high explosive (HE) detonation and dispersion process has been completed. The current Lagrangian SPH framework is being assessed to incorporate the multiphase flow of detonation gases and solid particulates through an Eulerian surrounding atmosphere.

FY2014 Accomplishments

- Particle size distributions were computed from collection media exposed at detonation site and several km downwind. Sub-micron particle uranium content correlated with particle size (Figure 2). Sub-micron particles are of primary interest because they will be transported long distances downwind.
- Atmospheric transport and deposition simulations of detonation cloud predicted that there would be minimal depletion of high uranium content particles between detonation site and downwind collection site. This prediction was verified by measured particle size distributions. This implies that signature of HE detonations performed as part of nuclear weapons program can be detected by analysis of samples taken at long downwind distances.

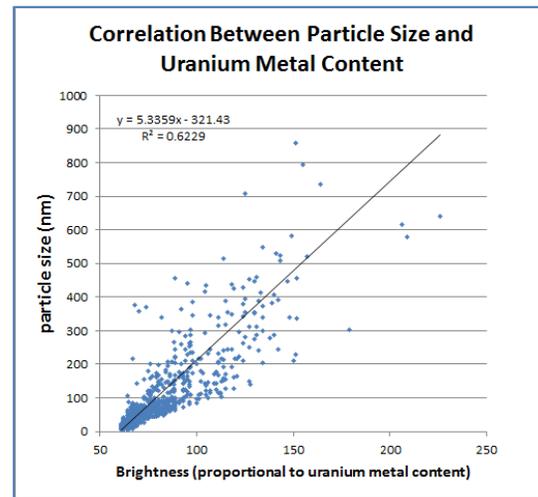


Figure 2. Representative sample that shows particle brightness is proportional to uranium.

Future Directions

- Develop a methodology that allows particle samples taken with different sensors to be converted into air concentrations by determining the volume of air that particles on collection media were extracted from.
- Evaluate fidelity of Lagrangian hydrodynamic code simulations of initial hot debris cloud relative to empirically derived functions that relate magnitude of detonation to cloud parameters such as temperature, initial volume and equilibrium elevation.
- The elemental composition of particulates will be quantified with a scanning electron microscope (SEM) with the energy dispersive X-ray analysis (EDX) in the mapping mode. The different approach will replace the less accurate brightness – uranium content method used in FY-14

FY 2014 Publications/Presentations

1. Mid-year Review of Far Field Modeling Methods for Characterizing Surface Detonations. Savannah River National Laboratory, May 6, 2014.

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Acronyms

NNSA: National Nuclear Security Agency

HE: High Explosives

SPH: Smooth Particle Hydrodynamics

SEM: Scanning Electron Microscope

EDX: Energy Dispersive X-ray

Patent Apps/ Patents Awarded

None

Total Number of Post-Doctoral Researchers

None

Next Generation Betavoltaic Cells – Increasing Power Density

Project Team: G.C. Staack and J.B. Gaillard (Primary), J.A. Teprovich, H.R. Colon-Mercado, B. Peters, J.T. Coughlin, G.H. Fisher, Jr.

Subcontractor:

Project Start Date: October 1, 2013
Project End Date: September 30, 2014

Betavoltaic batteries offer distinct advantages over traditional chemical batteries in that they can be manufactured to provide a predictable service life of years or even decades as well as provide reliable power output under extreme temperatures where chemical batteries fail. Both attributes can be invaluable in applications where frequent battery replacement is hazardous or cost prohibitive.

Betavoltaic batteries derive their energy from creating electron-hole pairs in a p-n junction semiconductor when exposed to a beta-particle. Although many beta emitting isotopes exist, tritium is considered ideal for several reasons: it is a “pure” beta emitter and does not require heavy shielding, the beta is not energetic enough to damage the semiconductor, it has a moderately long half-life and is readily available. The widespread application of tritium powered betavoltaics is limited by their low power output due to low beta particle flux. This research is targeted at improving the beta flux to the energy conversion device through the use of low Z tritium trapping materials.

FY2014 Objectives

- Establish partnership with betavoltaic manufacturing company
- Select and perform initial evaluations of materials for testing with tritium
- Design tritium loading cell that will allow either power measurement or 2 or 4-probe resistivity measurements
- Purchase equipment to measure low power output or resistivity
- Initiate discussions with the Savannah River Site Tritium Enterprise to tritium load the selected materials

Introduction

Betavoltaic batteries convert the kinetic energy from beta decay of a radioactive material into electrical energy. This is typically done by placing the radiation source in close contact with an energy conversion device capable of converting the beta particle energy to electron-hole pairs in a p-n junction. The e-h pairs are converted to useable electricity when they recombine by placing a load across the junction. In this regard, betavoltaics are the nuclear analog to photovoltaics. An illustration of a betavoltaic cell is given in Figure 1.

Conversion of beta decay energy from a radioactive source was initially proposed in the early 1950s. Testing performed by Rappaport using $^{90}\text{Sr} \rightarrow ^{90}\text{Y} \rightarrow ^{90}\text{Zr}$ proved the concept and provided the theory behind betavoltaic device operation. Unfortunately, the high energy beta emitted by ^{90}Y decay (2.28 MeV) damaged the semiconductor, resulting in a maximum power output decrease of 90% over one week. More recent efforts have focused on coupling high bandgap semiconducting materials with lower energy beta emitting materials. The use of high bandgap materials increases energy conversion

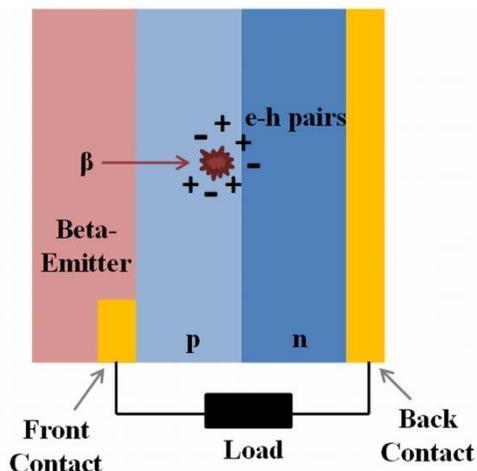


Figure 1. Simple semiconductor based betavoltaic cell.

efficiency while less energetic beta emitters minimize long term damage to the energy collection device [1].

The goal of this research is to increase the power output of long-lived betavoltaic batteries by evaluating the performance of tritium trapping materials that will increase the tritium beta flux delivered to the energy collection device. This will in turn increase their attractiveness for a wide variety of DOE and non-government applications, effectively expanding their marketability. Various potential tritium trapping materials were examined for their potential to decrease the self-absorption of the beta energy, thereby increasing beta flux delivered to the collection device. Promising materials and/or morphologies were selected for testing. Because of the minute amounts

of gas absorbed by the films in question, PVT measurements are not a reliable way of determining whether a material has absorbed hydrogen under a given set of conditions. To confirm loading with protium, a test cell was developed to measure four-probe resistivity of the film during hydrogen loading. This was critical to demonstrate that the loading technique was sound before testing is initiated with tritium.

Approach

Several factors must be considered when selecting an appropriate beta source: half-life, specific activity, cost/availability, decay modes, daughter products, and beta energy. Typical energy collection devices are damaged by beta energies in excess of about 250 keV, depending on the materials used. Sources with short half-lives, low specific activities, high cost or limited availability, incompatible daughter products, or high beta energy must be ruled out. Tritium meets most of the criteria above, but with a relatively low activity in gaseous form. When stored on titanium, activities on the order of 4.5E6 Ci/cc can be achieved. The principal drawback of using a hydride to store tritium is that it behaves as a blocking layer the beta must pass through before reaching the collector. Beyond a given thickness, depending on the material, the beta will be absorbed before it has an opportunity to interact with the semiconductor.

Isotope	T _{1/2} (years)	E _{max} (keV)	Activity (Ci/cc)
³ H	12.3	18.6	4.53E+06
⁶³ Ni	101	66.9	6.30
⁹⁰ Sr	28.8	546	52.2
¹⁴⁷ Pm	2.6	224	128.8

The approach taken to increase beta flux delivered to the collector is to utilize low Z tritium trapping materials. This will permit a greater fraction of beta to reach the collector at any given material thickness. Preliminary calculations show that beta flux may be increased by more than 5x over that provided by titanium tritide. In addition to implementing a palladium cap to facilitate hydrogenation, multiple materials and morphologies are being examined.

Results/Discussion

Results of the literature search and calculations were used to identify two low Z tritium trapping materials that held promise for increasing the beta flux delivered to the semiconductor. A comparison of the beta flux in comparison to titanium is given in Figure 2. Hydrogenation of one of these materials demonstrated the inadequacy of the existing hydrogenation apparatus with a significant thermal mass.

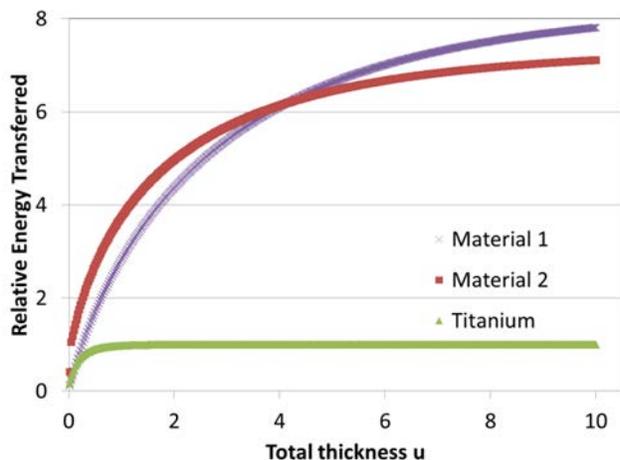


Figure 2. Potential increases in energy transferred to the semiconductor using alternate tritium trapping materials.

material.

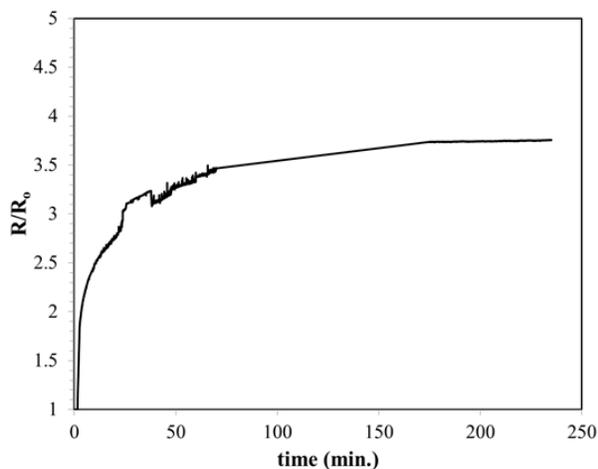


Figure 3. Normalized resistivity measurement taken in real time during hydrogenation of tritium trapping material.

A desire for better temperature control was coupled with feedback from personnel in the Savannah River Site Tritium Enterprise to develop a new apparatus that would be lighter while meeting their stringent design requirements. In addition, highly sensitive test equipment was procured to perform power output measurements of the tritium loaded devices that are anticipated.

Figure 3 below left shows an increase in the normalized resistance for the tritium trapping material as it is hydrogenated with protium. Partial hydrogenation was further confirmed via XRD analysis of the before and after films, Figure 4. The appearance of a peak at 27.95 in the hydrogenated film (red) represents the hydrogenated phase of the tritium trapping

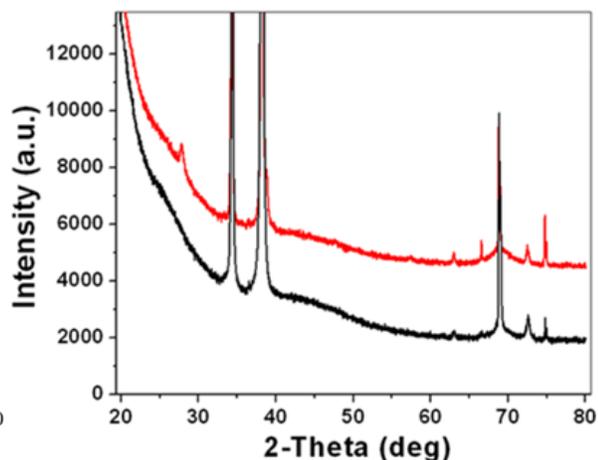


Figure 4. XRD before (black) and after (red) hydrogenation of trapping material.

While these results were positive and lead to the successful completion of milestones set for FY14, correcting for and controlling temperature fluctuations as well as controlling hydrogenation pressure proved challenging. The new cell designed in FY14 provides a leak tight pressure boundary enclosing a chamber that can be charged with gas as needed to load the sample. The cell has a port for gas inlet/exit and necessary control and instrumentation. A thermocouple is located near the sample to monitor internal chamber temperature. The cell is considerably smaller and less expensive than the Parr Reactor used for initial testing. The new design will result in quicker chamber temperature response during heat up, thereby permitting better temperature control. Electrical penetrations allow for either 2 or 4-probe resistivity monitoring of the sample during the hydrogenation process. Alternatively,

power measurements will be possible with this cell design when tritium testing begins. This new cell design incorporates CeramTec electrical penetrations through the pressure boundary and is currently being leak and pressure tested prior to installation in the Savannah River Site Tritium Enterprise. The new design is shown below in Figure 5.

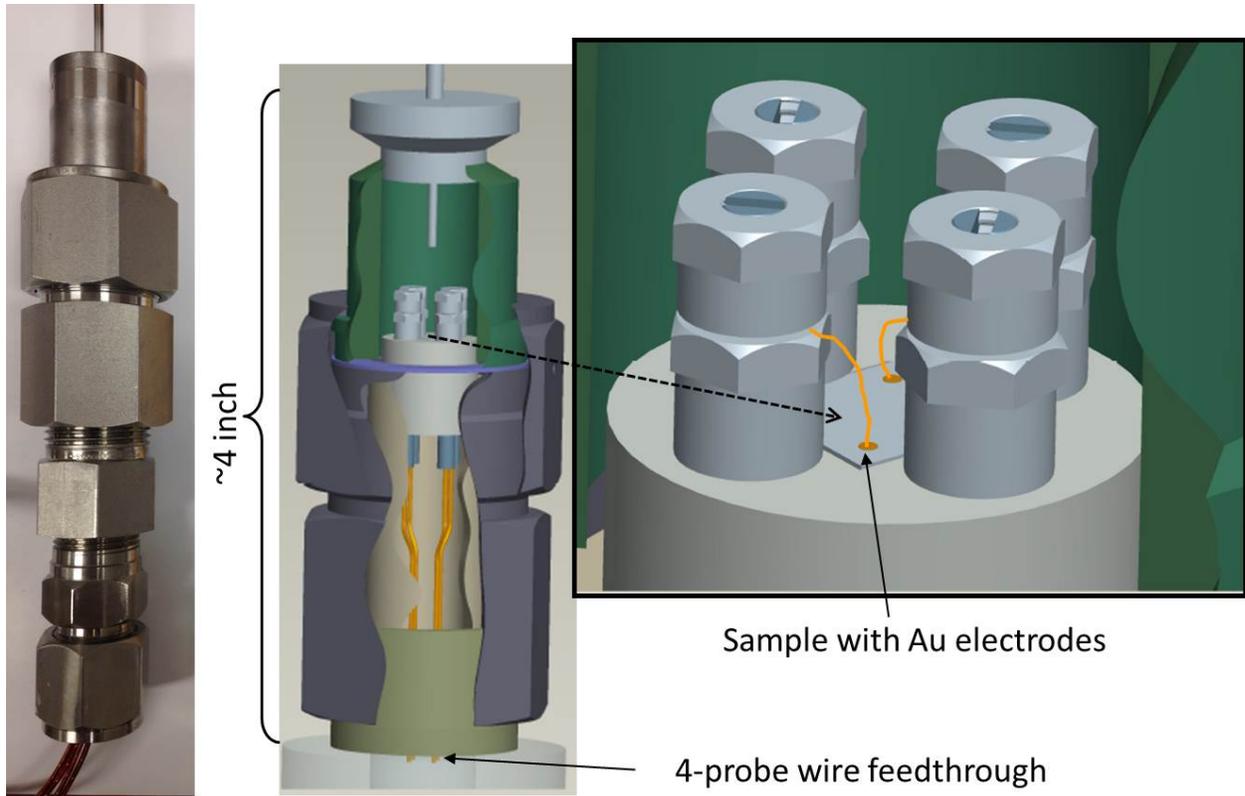


Figure 5: New betavoltaic hydrogenation cell design.

FY2014 Accomplishments

- Performed an extensive literature search to select potential tritium trapping materials
- Developed a method to measure resistivity in situ to confirm hydrogen loading of a thin film
- Demonstrated a proof of principal in depositing and hydrogen loading selected materials
- Made significant progress in development of a new hydrogenation apparatus that dramatically reduces the thermal mass (and hence provides better temperature control) over the previous apparatus

Future Directions

- Continue collaboration with betavoltaic manufacturing company
- Establish partnership with the University of South Carolina to provide additional film deposition expertise and refinement
- Creation of a Georgia Tech sub contract to allow SRNL access to multiple vapor deposition techniques is currently under way.
- Continue to refine hydrogenation methodologies

- Continue collaborating with the Savannah River Site Tritium Enterprise to tritium load the selected materials

FY 2014 Publications/Presentations

1. Staack, G., Gaillard, J. (2014, March). *Advancement of Tritium Powered Betavoltaic Battery Systems*. Presented at the Savannah River National Laboratory LDRD Mid-Year Review, Aiken, SC.
2. Staack, G., Gaillard, J., Teprovich, J., Colon-Mercado, H., Peters, B. (2014, April). *Next Generation Betavoltaics*. Poster presented at the Savannah River Tritium Enterprise PDRD Mid-Year Review, Aiken, SC.
3. Staack, G., Gaillard, J., Teprovich, J., Colon-Mercado, H., Peters, B., Coughlin, J., Fisher, C. (2014, October). *Next Generation Betavoltaics – Increasing Power Density*. Poster presented at the Savannah River National Laboratory LDRD Year End Review, Aiken, SC.

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1. L. C. Olsen, "[Review of Betavoltaic Energy Conversion](#)," in Proc. 12th Space Photovolt. Res. Technol. Conf, 1993, p. 256.

Acronyms

LDRD – Laboratory Directed Research and Development

PDRD – Plant Directed Research and Development

PVT – Pressure, volume, temperature

Patent Apps/ Patents Awarded

A provisional patent application has been drafted.

Total Number of Post-Doctoral Researchers

No Post-Doctoral researchers were used during FY14. One is anticipated in FY15.

Techneium Removal from Alkaline Liquid Waste

Project Team: Charles A. Nash,
(Primary), DOE Science Undergraduate
Laboratory Intern (SULI) Benjamin C.
Musall, Kimberly A. Roberts

Project Start Date: October 1, 2013

Project End Date: September 30, 2014

A reduction and precipitation process was examined using a wide variety of chemicals to discover improved technetium removal from radioactive salt simulants. One big challenge here is that the chemical removal is very difficult from pH 14 (highly alkaline) solutions. The simulants were of average SRS tank waste and were all at 5.6 M sodium and high (pH 14) alkalinity. Two chemical reagents were found to be fast and effective reductants of pertechnetate. Best adsorbents included certain forms of iron hydroxide and zirconium dioxide.

Two enhancing additives were also found to increase technetium removal substantially. Some of the chemistries that removed substantial technetium also removed soluble neptunium. Several metal reagents were also tested for iodide removal, but none of those tests indicated decontamination.

FY2014 Objectives

- Discover effective technetium adsorbents and reducing agents for pertechnetate.
- Demonstrate significant and rapid decontamination of technetium by reduction and precipitation/adsorption, in a room temperature process.
- Discover enhancing reagents.
- Explore iodide removal by precipitation with metals known to interact strongly with iodide.

Introduction

The nuclear waste isotope technetium-99 is receiving increased attention in the DOE Weapons complex, especially at Hanford and SRS, as well as in other countries because it poses increased problems for the environment. It has a long half-life at 211,000 years and is mobile in the soil as the pertechnetate ion. Leaking waste tanks in the DOE complex are increasing concerns about the need for fast and cost effective waste treatment processes. Tc-99 retention in high level glass is challenged by competing needs for melter redox chemistry. SRNL chemical discoveries further studied in this report would rapidly treat batches of liquid waste for Tc in mix-and-filter equipment similar to the Actinide Removal Process (ARP) at SRS [1]. This work is the subject of a patent application [2]. In addition significant removals of actinides like soluble Pu and U were seen in some cases. Development of this process should attract funding for Tc waste processing, especially at SRS and Hanford.

Past reviews have found that removal of pertechnetate from solutions is more difficult at high pH versus near neutral pH [3-5]. High pH (11-14) is typical of both waste tank supernatant liquid at Hanford and SRS, as well as the chemistry of Saltstone. This LDRD produced results that advance the capture and retention of technetium at high pH.

Approach

The approach to the work was to test both radioactive and nonradioactive (perrhenate) solutions, scanning adsorbents with the use of one proven reductant, then testing best adsorbents with several other reductants. Tests involved batch contacts as shown in Figure 1, and all solutions contained

chromate, which is present in liquid waste and is also removed, sometimes to a great extent, by the test chemistry.

Testing was also performed with the use of specific enhancing agents suggested by knowledge of technetium chemistry. Form of the chemical added was found to be important. One guiding principle was to add small amounts of reagent consistent with the use of monosodium titanate at SRS.

Monosodium titanate is typically added to liquid waste at a rate of 0.2 g/L [6].

The radioactive simulant in this research included about 25 mg/L iodide. One goal was to use precipitants such as silver or copper salts to see if the iodide could be removed. These metals are known for their affinity to form stable precipitates with iodide.



Figure 1. Radioactive Batch Tests and Incubator Box

Results/Discussion

The research was successful in finding combinations of reductants, adsorbents, and two separate enhancing chemicals that produce decontamination factors for pertechnetate at room temperature and at times ranging from 2 to 24 hours. Figure 2 shows the best decontamination factors from the testing. Such decontamination should be at practical levels for future SRS waste (current waste is blended to meet waste acceptance without technetium removal). Future technetium concentrations are expected to be higher and therefore requiring treatment.

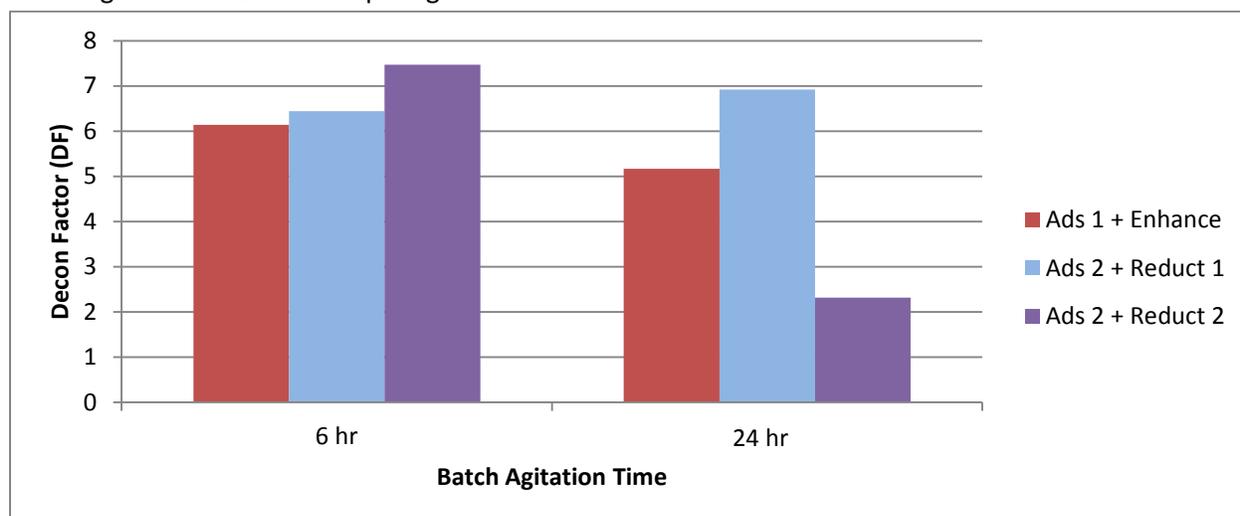


Figure 2. Best Decontamination Factors

Table 1 shows that reduction and precipitation chemistries remove other species. Chromate is reduced and adsorbed to decontaminations shown, and some tests measuring neptunium removal found significant decontamination there as well.

Table 1. Removals of Soluble Chromium and Neptunium in Selected Tests

Adsorbent and Chemistry	Species and Decontamination Found
Monosodium Titanate + Reductant	DF 9.6 in 2 hr, 12.5 in 6hr, Neptunium
Zirconium Oxide + Reductant	DF 15.5 in 2 hr, >23.4 in 6hr, Neptunium
Adsorbent 1 + Reductant	DF 5.9 in 2 hr, 35.2 in 6 hr, Chromium
Adsorbent 2 + Reductant	DF 3.8 in 2 hr, 6.6 in 6 hr, Chromium

FY2014 Accomplishments

- Adsorbent solids that are effective in removing technetium from a reductive process (precipitated iron, monosodium titanate, zirconium dioxide). Many others, mainly metal oxides, showed no effect.
- Effective reductants including stannous salts have been identified.
- Several inorganic enhancing reagents were found for the process, helping to provide decontamination (reductions in soluble technetium) of at least 6x in less than a day at ambient temperature.
- Significant and fast removals of soluble neptunium and chromium (chromate) were discovered during the work.
- No iodide removal was seen in precipitation/filtration methods tested here. Ion exchange may be a better option for iodine. This underscores the challenge of removing iodine species from caustic solution.

Future Directions

- Complete SRNL patent filing.
- Testing the newest and best chemistries for technetium removal using actual tank waste supernates.
- Effect of a double strike test: is decontamination multiplied?
- Testing at larger scale.
- Examination of various process times: does decontamination decline if unplanned delays occur before filtration?

FY 2014 Publications/Presentations

Slide package, midyear: C. A. Nash, "Technetium Removal from Alkaline Liquid Waste", presentation given April 29, 2014, at SRNL.

Final –TR- report: C. A. Nash, "Technetium Removal from Alkaline Liquid Waste using Reduction and Precipitation", SRNL-TR-2014-00249, r.0, 2014.

Acronyms

DOE – Department of Energy
LDRD – Laboratory Directed Research and Development
SRNL – Savannah River National Laboratory
SULI - Science Undergraduate Laboratory Intern

Patent Apps/ Patents Awarded

Nash, C. A., *Reductive Precipitation for Technetium Removal from Salt Waste*, SRS-14-008, March 2014, SRNS.

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2. Nash, C. A., “Reductive Precipitation for Technetium Removal from Salt Waste”, SRS Patent Application SRS-14-008, being processed in 2014.
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Patent Apps/ Patents Awarded

None

Total Number of Post-Doctoral Researchers

None

Laser-based Methods for Ultra-low Isotopic Analysis of Proliferant Materials

Project Team: J. Gray, S. Serkiz, P. O'Rourke, T. White, H. Colon-Mercado, B. Garcia-Diaz, R. Poland, and N. DeRoller

Project Start Date: October 1, 2013
Project End Date: September 30, 2014

Development of field-portable actinide isotopic analysis capabilities is an important need in the nuclear community for areas such as nonproliferation and safeguards, materials processing, remediation and storage, and post-detonation attribution. Current techniques such as thermal ionization mass spectroscopy require time-intensive multi-step sample preparation in order to isolate, dissolve and adjust the sample/instrument

conditions to optimal detection regimes. Not only are the sample preparation and analysis processes time consuming, but they require knowledge of the actinide concentration of the sample and the major ion chemistry. The proposed work seeks to investigate the feasibility of a field-deployable actinide isotopic analysis system based on High Performance InfraRed (HPIR) spectroscopy and solids fluorination. The HPIR system was successfully tested and integrated into existing laboratory test facilities and shown to significantly improve the resolution of the observed signals. Additionally, work was conducted with microcontrollers to enable the vision of a field-deployable automated sampling application.

FY2014 Objectives

- Set up a working HPIR system on the laboratory scale
- Demonstrate spectroscopic determination of fluorinated nuclear materials using UF_6
- Investigate enabling technologies for long-term remotely-deployable real-time isotopic analysis instrument

Introduction

Currently, analysis of post-detonation material generally involves continuous refinement where information is gained at various stages and timeframes [1]. Complete analytical determination is gained through a complex process of dissolution, ashing, particle and solids separation and isolation of non-nuclear debris. Dissolution is used to pre-concentrate the radioactive elements in the solid debris and is typically performed by liquid extraction. This extracted sample is used to measure isotopic composition by either radiometric counting or mass spectroscopic techniques. Over time various techniques have been used to expedite the analysis time and decrease the amount of hazardous chemicals and steps used for the sample preparation; however, alternative methods have only realized minor modifications to the well-established procedures. Typical non-selective fluorination of heavy metals, such as those in used nuclear fuels and relevant to the Comprehensive Nuclear Test Ban Treaty (CTBT) [2], consists of exposure to fluorine gas at temperatures of at least $300^{\circ}C$. In the last decade, fluorination experiments have focused on the use of less toxic and more temperature selective fluorination

agents in an attempt to separate the different components using the volatility of compounds such as UF_6 [3,4].

Grigor [5] demonstrated isotopic determination of uranium isotopes to about 5% accuracy using a high performance infrared spectrometer based on a tunable diode laser at 7.75 microns wavelength (1290 wave number [wn]). The isotopic shift between ^{238}U and ^{235}U is about 0.65wn at the vibrational combination band near 1291wn; however, the vibrational bandwidth was more than 10wn at the pressures and temperatures used in those experiments. The vibrational spectroscopy of the actinide (U, Np, Pu) hexafluorides is very similar, showing significant shift of the $\nu_1+\nu_3$ combination between the different elements with much smaller isotopic shifts within the elemental band. The wide vibrational bandwidth and narrow tuning range of the laser were limiting factors of the isotopic measurement. Currently available QCLs have tuning ranges of more than 75wn and power levels 50 to 100 times that of the diode laser used by Grigor. Hollow Core Wave Guide (HCWG) or resonant cavity technologies can be used to form robust, low-volume optical cells with path-lengths of tens of meters. These path lengths could be extended to 100's of meters using commercial QCL's because of their high power and low divergence. Long path lengths will give the sensitivity necessary for accurate isotopic measurements while the inherent high resolution will help avoid interferences from other infrared absorbing species.

The integration of HCWG and QCL technologies with automated fluorination techniques is explored here to produce a robust, field deployable device capable of highly accurate uranium/plutonium isotopic determinations. This work was focused on taking preliminary data for the development of an analytical tool using HPIR to make forensic analysis of materials characteristic of targeted nuclear applications. This work lays the groundwork for mobile isotopic detection of key nuclear materials in real-time with drastically reduced footprints.

Approach

The initial case considered presumed that the materials have been exposed to a fluorination process to render key species volatile or semi-volatile. The process assumed a front-end gaseous extraction process similar to those that have been developed for fluoride volatility separations and decontamination treatments, an example of which is recently funded work through the Fuel Cycle Research and Development program pursued in the DOE complex ^{Error!} ~~bookmark not defined~~, ^{Error!} ~~Bookmark not defined~~. The process would consist of a homogenization chamber where the sample is ground to micron/sub-micron size particles, followed by the gas-phase extraction in a heated fluidized bed in the presence of fluorination/carbonylation agents. Once the reaction is complete, it is possible that different compounds can be separated by a series of simple cold traps that will condense and freeze the volatile metal compounds while allowing the highly volatile compounds such as unreacted volatilization agents and major environmental volatile compounds like SiF_4 to be vented to waste. However, it would be much preferred to directly sample the volatile materials using the HPIR technique. We propose to use fluorinated or potentially carbonylated versions of materials characteristic of the target nuclear detection application. The envisioned system will not only reduce the sample preparation time and equipment footprint, but will also be able to reduce the number of steps used in typical liquid extraction from several dozen steps to approximately four steps, thereby minimizing the

susceptibility to experimental errors. SRNL has extensive experience with extraction and detection of radioactive materials from nuclear waste [6,7] and environmental samples [8] and plans to use this expertise.

Results/Discussion

In order to develop the laboratory scale HPIR analytical equipment, the major pieces of equipment which were required were a HCWG, a QCL and the IR Source Detector. These items were interfaced on a laboratory breadboard support tray to be interfaced with a manifold at SRNL built specifically to enable handling of UF_6 and other fluorinated materials. The integrated HPIR system is shown below in Figure 4, with the Deuterated Triglycine Sulfate (DGTS) detector on the left, the HCWG coiled in the interior, and the QCL IR source shown on the right. Not shown in detail here is the novel work used to incorporate the HCWG into the analytical apparatus involving custom-designed glassware fittings to house and seal the zinc selenide windows used.

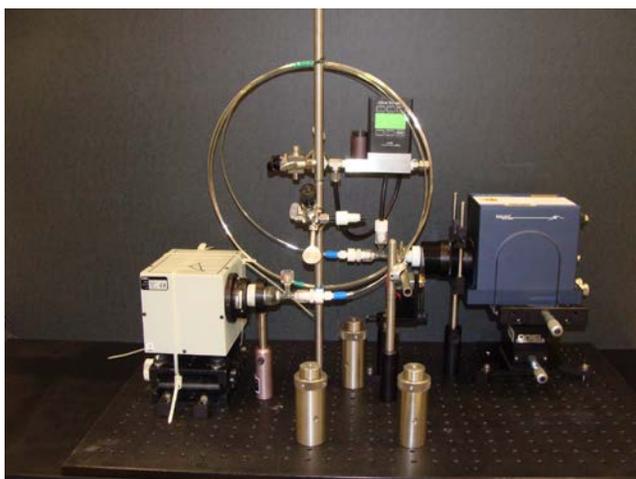


Figure 4. HPIR Laboratory System Including IR Detector, QCL IR Source, and HCWG Sample Volume

This system was first tested on one of the background fluorinating species proposed for selective separation of the nuclear materials of interest. The fluorinating species chosen was SF_6 , based on work previously conducted at SRNL on fluorination of UNF and the relatively inert chemical nature of this species. The IR signature collected is shown in Figure 5. This clearly shows the separated peaks for ^{32}S and ^{34}S as a function of the pressure in the HCWG. The calculated ratio of the two peaks is 4.4%, which matches the known natural distribution of these two sulfur isotopes. This result confirms the correct operation of the IR detection and analysis units in the assembled unit.

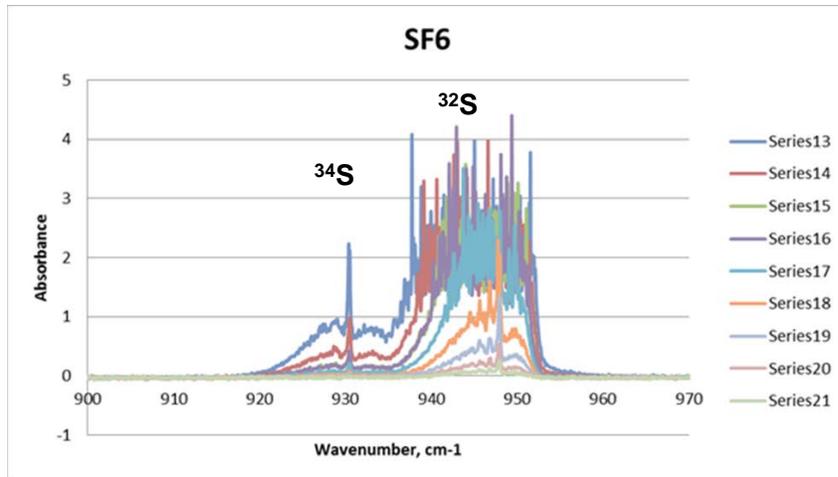


Figure 5. Infrared Spectroscopy Data for Sulfur Hexafluoride (SF6). Isotopic Ratio of 4.4% Measured as Predicted

The signal with the QCL is compared to the signal taken with a standard FTIR, shown below in Figure 6. For this analysis, the absorption peak of carbon monoxide (CO) was chosen at an absorbed concentration of 3ppm. It can be seen that the peak with the QCL source (shown as HPIR in red in the figure) is much sharper and defined in resolution, as opposed to the standard laser excitation (shown as FTIR in blue).

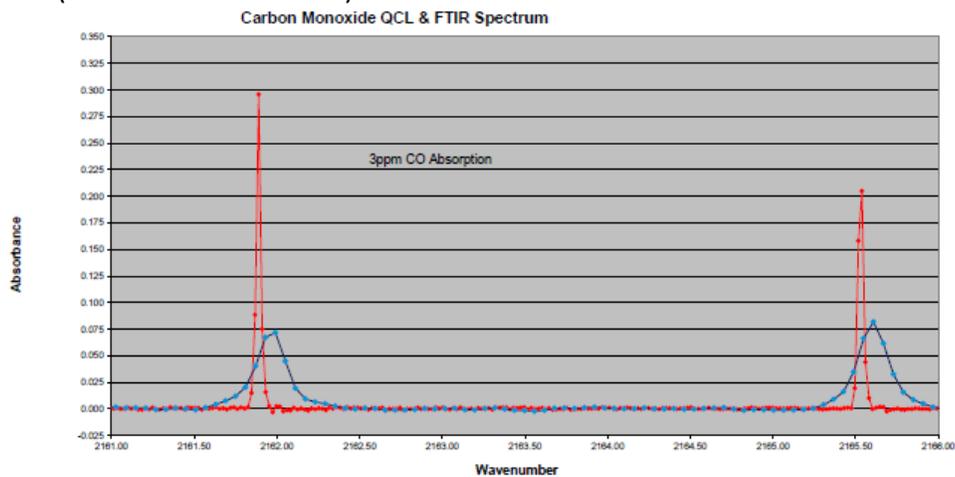


Figure 6. Comparison of Analytical Resolution for HPIR (red) vs. FTIR (blue) for CO Absorption Peak

Additionally, a sample of UF₆ was obtained from Oak Ridge National Laboratory which will be measured using the HPIR laboratory apparatus. This sample will seek to determine the isotopic resolution of the ²³⁵U and ²³⁸U peaks from the UF₆ sample, which is fluorinated using natural U in a similar manner as the SF₆ sample shown above in Figure 5.

FY2014 Accomplishments

- Demonstrated analysis of the IR spectra of SF₆ and matched the isotopic resolution to the naturally known ratio of 4.4%

- Assembled a laboratory scale HPIR system and interfaced the analytical unit with a custom-built manifold to handle fluorinated nuclear compounds
- Obtained a sample of UF₆ from ORNL for analytical measurement to confirm the improvement in isotopic resolution
- Developed microprocessor technologies to support field-deployable automated sampling capabilities

Future Directions

- Measure the isotopic distribution of the UF₆ sample and compare to the known distribution in naturally occurring uranium
- Obtain samples from colleagues at a commercial fuel vendor and use the measurements to determine the isotopic analysis for a varied set of samples

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Patent Apps/ Patents Awarded

None

Total Number of Post-Doctoral Researchers

None

Gas Adsorption Materials and Systems Development

Project Team: D. Tamburello (Primary), D. Anton, B. Hardy, K. Taylor-Pashow.

Subcontractor: M. Sulic (Greenway Energy), W. Lin (University of Chicago), R. Chahine (University of Quebec Trois Rivieres).

Project Start Date: October 1, 2013

Project End Date: September 30, 2014

At present, no national laboratory has the capabilities to model, design, build, and evaluate adsorption materials and systems. It is vital to develop laboratory capabilities and expertise for the evaluation of metal-organic framework (MOF) materials for gas adsorption; with particular emphasis on natural gas adsorption. The expertise thus gained can easily be used towards other technically relevant gaseous species, such as CO₂, H₂, deuterium, or tritium. Directed by SRNL, our partners modified commercially available or easily synthesized MOF compounds to increase their volumetric gas storage density, which is crucial to portable and light duty vehicle applications. These MOF compounds were

then evaluated at SRNL. In SRNL's current adsorption gas storage research programs, expertise has been limited to system modeling and design. An experimental program is crucial to expanding SRNL's adsorption research programs, and the backbone of any successful experimental program is the ability to characterize gas adsorption.

FY2014 Objectives

- Develop capabilities and expertise for the evaluation of metal-organic framework (MOF) materials for gas adsorption, with particular emphasis on natural gas
- Develop capabilities and expertise to synthesize and modify MOF materials for improved gravimetric and/or volumetric gas capacity and/or thermal conductivity

Introduction

Technical developments over the past decade have led to an exponential increase in discovering new domestic natural gas reserves. This abundant resource can now be economically extracted from shale beds using hydraulic fracturing (a.k.a., fracking). With increased availability, natural gas has found its way into numerous vehicular applications, including buses and short haul trucks. However, a number of technical hurdles need to be overcome before natural gas can be widely introduced into light duty vehicles. These hurdles include the development of inexpensive compression for home refueling and compact on-board fuel storage to maintain the passenger and cargo space.

One method of compactly storing gases is through adsorption, where gas molecules attach through low energy van der Waals' forces to the surface of a highly porous material as opposed to the more commonly used absorption process where gas molecules are chemically bonded to molecules at much higher energies. MOFs are a new class of low-density crystalline materials composed of a cage-like structure containing nano-scale pores. This results in MOFs' extremely high surface areas of over 3000 m²/g, allowing for greatly improved gas adsorption over common zeolites or activated carbons [1]. MOFs are also the lowest density solids currently known.

While SRNL has been awarded DOE programs in both hydrogen and natural gas systems development, SRNL is not responsible for any materials development or characterization. SRNL's participation on these programs is limited to system modeling and design. Currently available materials have limitations, especially related to their volumetric adsorption capacity. Thus, there is a strong need for adsorbent materials development and, based on existing DOE programs and partnerships, SRNL is well situated to make and exploit these improvements. SRNL is uniquely qualified with expertise on the development of the existing materials, what improvements should be pursued, and how to make the improvements. But, the key to these improvements is to first develop our adsorption evaluation capabilities. To quickly bring our adsorbent experimental capabilities up to world class standards, SRNL will partner with two of the leading adsorbent material development experts in the world, Prof. Richard Chahine of the University Quebec Trois Rivieres (Canada) and Prof. Wenbin Lin of the University of Chicago (formerly of UNC).

Approach

MOF materials incorporate metal sites connected by organic linkers to form a vast array of interconnected structures. The physical properties of MOF materials, such as surface characteristics, are controlled by the ligands, solvents, and their synthesis methods, and can be varied widely.

Many MOF materials have been shown to have high gravimetric gas storage capacities. However, their volumetric capacities are much lower than predicted based on the crystal density because they are often prepared as loose, low bulk density powders. Attempts have been made to increase the density for many materials by processing their powder form into pellets. However, the majority of MOF pellets have lower gravimetric capacities, likely due to pore collapse or amorphization of the material [2]. Although often offset by large increases in the volumetric capacity, developing a method for processing MOF materials into pellets without sacrificing gravimetric capacity would lead to a truly useful material. Attempts will be made to increase the MOF material density while retaining gravimetric capacity by utilizing methods previously reported to increase the permanent porosity of MOFs, such as solvent exchange and freeze drying [3].

Materials will be evaluated for gas adsorption both before and after densification using a Sievert's apparatus to generate pressure-composition-temperature (PCT) curves. Temperature control, monitoring, and stability are of critical importance to obtain accurate pressure measurements.

Results/Discussion

As mentioned previously, metal-organic frameworks characteristically suffer from low bulk density and thermal conductivity. To improve density of an adsorbent while simultaneously increasing the thermal conductivity of the overall system, the metal-organic framework $[\text{Cu}_3(\text{btc})_2(\text{H}_2\text{O})_3]$, more commonly known as HKUST-1, was grafted onto the carbon foam KFOAM[®] (commercially available carbon foam manufactured by Koppers). Figure 1 shows a series of images of a) pristine KFOAM, b) HKUST-1 grafted on KFOAM and c) magnified image of HKUST-1 grafted on KFOAM. After one treatment of HKUST-1 there was a 25 wt% gain, after two a 40 wt% gain, and 50 wt% gain after three treatments.

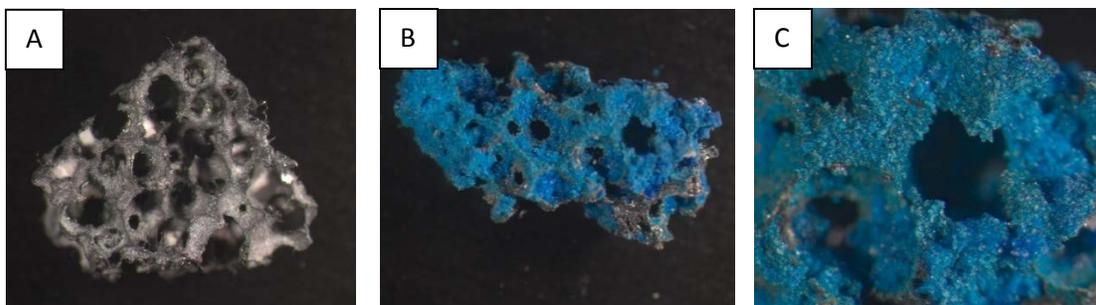


Figure 1: Images of carbon foam; a) pristine foam, b) after one treatment, c) after one treatment magnified.

Figure 2 shows the excess isothermal methane uptake of three deposition thicknesses (three levels of treatment) of HKUST-1 on KFOAM samples prepared by the University of Chicago and evaluated at SRNL. The overall excess uptake for each sample is quite low; however, it is vital to indicate that with each subsequent treatment the isotherms do confirm that more adsorbent is grafted onto the substrate (i.e. increase in capacity). The low excess adsorption measured is due to the limited sample volumes that were available for analysis. The small amount of overall sample, which in turn translates to even less HKUST-1 grafted onto the KFOAM substrate, posed difficulty in data acquisition. Larger sample batches with even more HKUST-1 treatments are needed to fully evaluate this approach. It is important to note that XRD did not show any changes in the HKUST-1 structure after any of the treatments (not shown); however, BET analysis did indicate that the adsorbent surface area dropped by at least 50% to approximately $1000 \text{ m}^2/\text{g}$.

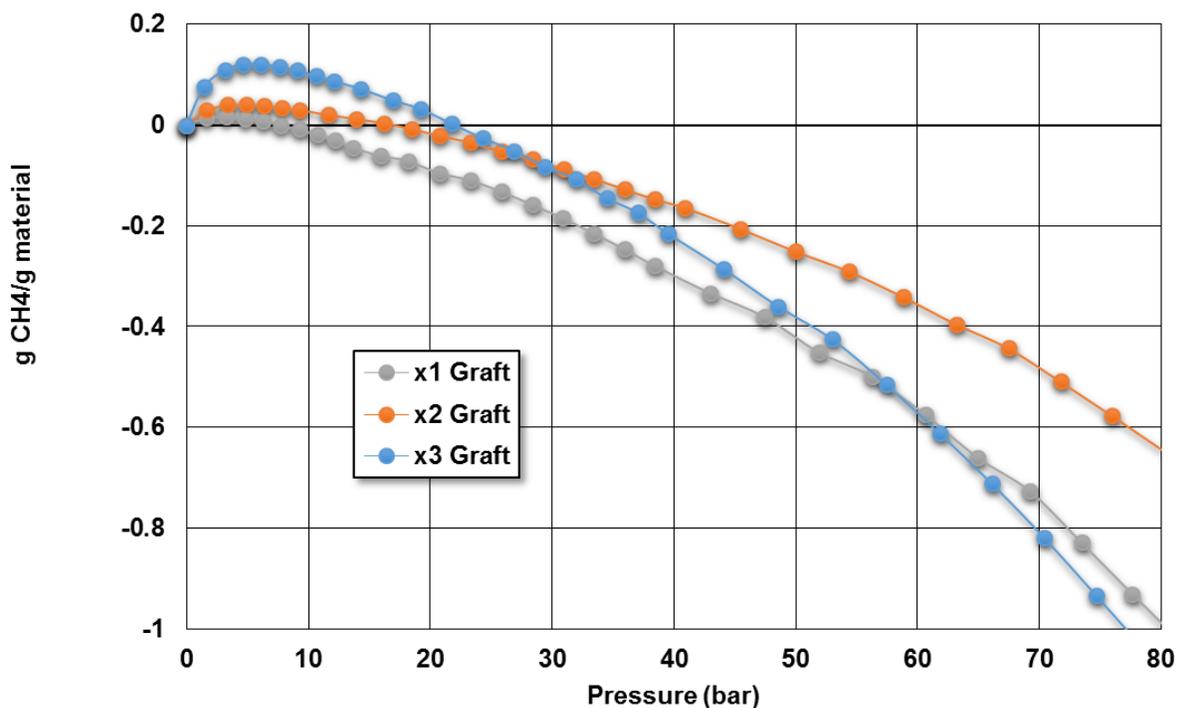


Figure 2: Excess methane adsorption of HKUST-1 on KFOAM after 1, 2 and 3 treatments.

In addition to examining improved densification and increase thermal conductivity, this project also evaluated a new novel adsorbent that had been reported to have high methane uptake at ambient temperatures. This improved uptake is attributed to its high branched, aromatic-rich nature of the bridging ligand, optimal pore size, and the open metal sites [4]. The high connectivity zinc based MOF was synthesized by the University of Chicago for SRNL, which SRNL dubbed UC02. Excess methane uptake was measured for UC02 over a range of 115 °C (-30 °C to +85 °C), Figure 3. As with HKUST-1 on KFOAM, uptake increases with lower temperatures, which is characteristic for adsorbents. However, unlike the reported data⁴, the excess methane uptake was not observed to follow the same pathway found in the reference until high temperatures, +85 °C.

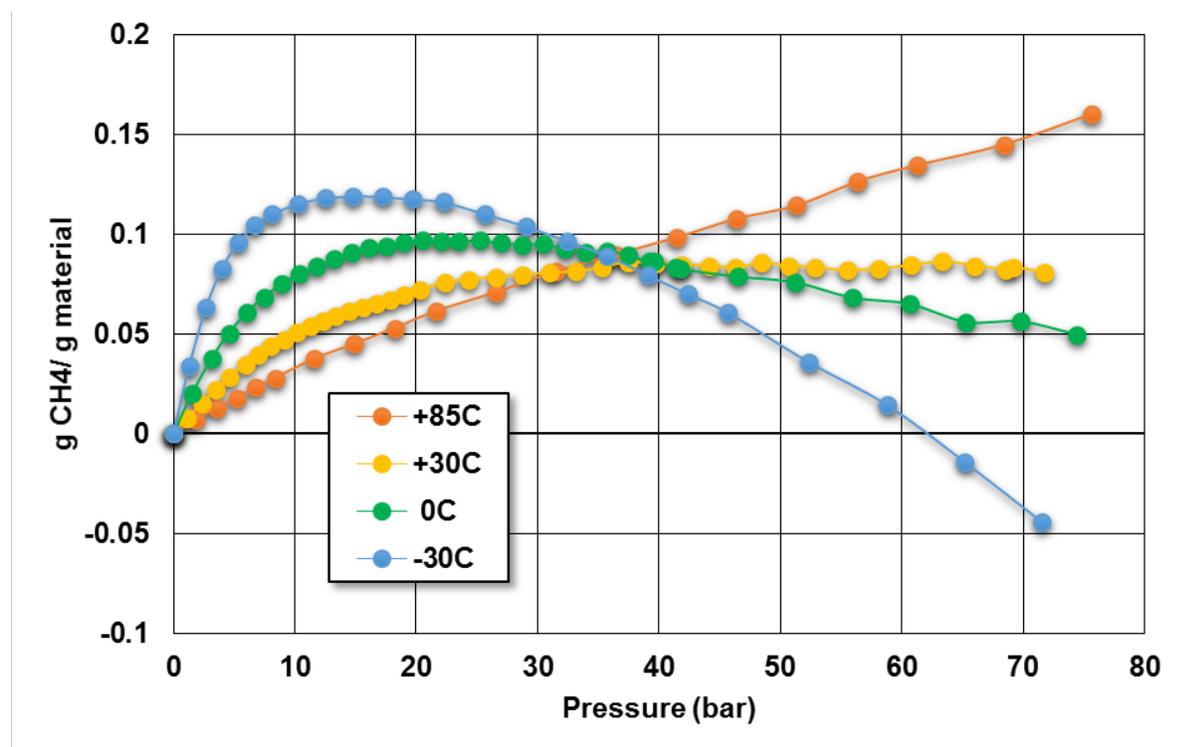


Figure 3: Excess methane adsorption isotherms of the UC02 high connectivity MOF over a 115 °C temperature range.

FY2014 Accomplishments

- Developed capabilities to model, design, build, and evaluate adsorption materials and systems on site.
- Even with the limitations in novel material and grafting technique that did not allow for sample preparations in quantities to precisely examine methane uptake over a wide range of temperature and pressure, repeatable accurate adsorption measurements were achieved.
- New high capacity adsorbent materials were developed, with guidance toward future generations in development.
- An adsorbent (HKUST-1) was grown on a thermally conductive substrate.

- Expanded on site SRNL capabilities for future material synthesis and evaluation over a wide range of temperatures and pressures.

Future Directions

- Increased aliquots of grafted HKUST-1 on KFOAM substrate (x4 and x5) in addition to larger sample preparation volumes for adsorption detection.
- Graft adsorbent to additional high thermally conductive substrates, such as aluminum.
- Graft higher capacity MOF to carbon or other thermally conductive substrates.
- Increase adsorbent density by directly depositing the adsorbent onto substrate through nucleation sites by exploring the relationship between substrate preparation (etched, shaped, etc.) and grafting capacity (layer thickness, strength of adhesion, etc.).
- Explore methane capacity at lower temperatures down to near LNG temperature
- Incorporate experimental data into models to validate for future predictions of new adsorbent materials with and without thermally conductive substrates

FY 2014 Publications/Presentations

1. The current document is the only report written about this work during FY2014.
2. A mid-year review presentation was given internally to SRNL personal on April 29, 2014.
3. A poster was created and presented at the LDRD Program Year End Review on October 15, 2014.

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Acronyms

MOF – Metal-organic Framework

PCT – Pressure-Composition-Temperature

XRD – X-ray diffraction

KFOAM – Trademark for carbon based foam from Koppers

BET – Brunauer, Emmett, and Teller theory

Patent Apps/ Patents Awarded

None

Total Number of Post-Doctoral Researchers

None

Stabilization of Radionuclides in Calcium Enriched Environmental Systems

Project Team: M. Millings, K. Taylor-Pashow, K. Roberts, M. Denham, D. Hobbs

Project Start Date: October 1, 2013
Project End Date: September 30, 2014

Strontium-90 (^{90}Sr), a hazardous radioactive fission product, is chemically similar to calcium (Ca), making it difficult to remove from Ca-rich contaminated water. A successful remedial technology must remove ^{90}Sr while minimizing Ca removal and have a cost/benefit ratio viable for large plumes. This study examined three types of materials (alginate, titanates and stable Sr/isotope

dilution) that prior research suggests may selectively remove ^{90}Sr from Ca-rich fluids. Tests were conducted using ^{85}Sr as a surrogate for ^{90}Sr . Results showed that titanate amendments removed $\geq 95\%$ ^{85}Sr in calcareous groundwater and cementitious pore fluid. Alginate and titanate showed $\leq 25\%$ ^{85}Sr removal in seawater. Stable Sr addition (isotope dilution) had the greatest ^{85}Sr removal in seawater (up to 95% removal with the addition of 0.02 M Sr and SO_4). Longer contact times and strontium sulfate seed crystals increased precipitation of Sr phases (and thus removal of ^{85}Sr) at low stable Sr concentrations (≤ 0.002 M Sr).

FY2014 Objectives

- Determine removal of ^{85}Sr (a surrogate for ^{90}Sr) from simulated seawater, Ca-rich groundwater, and cementitious pore fluid using:
 - Alginate (a polysaccharide derived from algae) – beads and shredded forms made from sodium salt alginic acid
 - Titanates – to include monosodium titanate (MST), MST modified with hydrogen peroxide (mMST), SrTreat[®] (manufactured by Fortum Engineering) and hydrothermally synthesized sodium titanate nanotubes (NaTONT)
 - Stable Sr addition (isotope dilution method)
- Evaluate chemical and physical properties that would be critical to deployment
- Evaluate relative costs and viability for use in large environmental plumes

Introduction

^{90}Sr is a radioactive fission product that contaminates groundwater at numerous DOE sites, some U.S. commercial sites, and international nuclear sites. It is also a contaminant of major concern at the Fukushima Daiichi site where it occurs in waters with relatively high calcium concentrations [1]. The hazard posed by ^{90}Sr is magnified by its mobility in groundwater and its tendency to concentrate in bone tissue after ingestion because of its chemical similarity to Ca.

Remediation of ^{90}Sr contaminated waters requires removal of stable naturally occurring strontium isotopes, as well as ^{90}Sr , because isotopic separations are not feasible in aqueous media at the scale of remediation targeted in this project. Stable strontium isotopes are present in mass concentrations that are many orders of magnitude greater than ^{90}Sr even in the most contaminated waters. Strontium is difficult to separate from calcium because of the similar chemical properties of the two alkaline earth elements. Thus, it is particularly challenging to remediate ^{90}Sr contamination in Ca-rich waters.

Ca-rich environments include aquifers with limestone (calcareous) components, cementitious wasteforms and their near-field environs, and seawater. Within the DOE complex, ^{90}Sr plumes occur in calcareous aquifers at Oak Ridge, Idaho National Lab, Hanford, and West Valley. Seawater contains about 50 times more Ca than Sr, and hence, the challenge to remediate large quantities of contaminated seawater at Fukushima. Likewise, many nuclear sites have trenches with ^{90}Sr comingled with cementitious materials that cause high calcium concentrations in pore fluids. A successful technology for treating ^{90}Sr in these environments must remove ^{90}Sr while minimizing removal of Ca. If the technology is not highly selective, large amounts of treatment media must be used to remove the requisite ^{90}Sr . Low selectivity results in large volumes of radioactive solid waste (secondary waste) from ex situ systems and presents engineering challenges to deploy the technology for efficient and cost effective in situ treatment.

Currently, permeable reactive barriers (PRB) using minerals as treatment media are deployed to treat ^{90}Sr plumes at West Valley (zeolite) and Hanford (apatite). The PRB at West Valley has 2000 metric tons of zeolite and is expected to remove 90% of the ^{90}Sr from the plume for ~5 years and keep effluent concentrations below 10,000 pCi/L for ~15 years [2]. The predicted life of the apatite PRB at Hanford is 300 years. Both PRBs operate in calcareous environments, but improvements in amendment selectivity for Sr over Ca would allow for more efficient future treatments. Furthermore, it is unclear how zeolite or apatite would perform in ^{90}Sr contaminated seawater. Hence, there is a pressing need for treatment media for both in situ and ex situ systems that are more selective for Sr in Ca-rich waters and have a cost/benefit ratio that makes them attractive for use in large clean-up efforts.

Approach

Titanates (MST, mMST, SrTreat[®], NaTONT) and alginate rely on sorption of ^{90}Sr with natural Sr, whereas the mechanism of sequestration is different for stable Sr (isotope dilution). This method exploits coprecipitation of ^{90}Sr with Sr when Sr minerals are forced to precipitate by addition of components that cause oversaturation of Sr minerals. This is particularly useful when waters are close to saturation with natural Sr. Added components may include a combination of Sr, sulfate, or carbonate to force precipitation of strontium carbonate (strontianite) or strontium sulfate (celestite) minerals. Figure 1 provides a general outline for initial laboratory tests.

All of the prepared simulants were spiked with approximately 30,000 dpm/mL ^{85}Sr . This radiotracer allowed for easy, quick and inexpensive analysis by gamma spectroscopy. Titanate sorption was tested with all of the simulants. Alginate sorption was tested only using the seawater simulant because it would most likely be applied or deployed in a seawater environment (as opposed to in-situ within an aquifer where plugging and biodegradation of the alginate would be potential concerns).

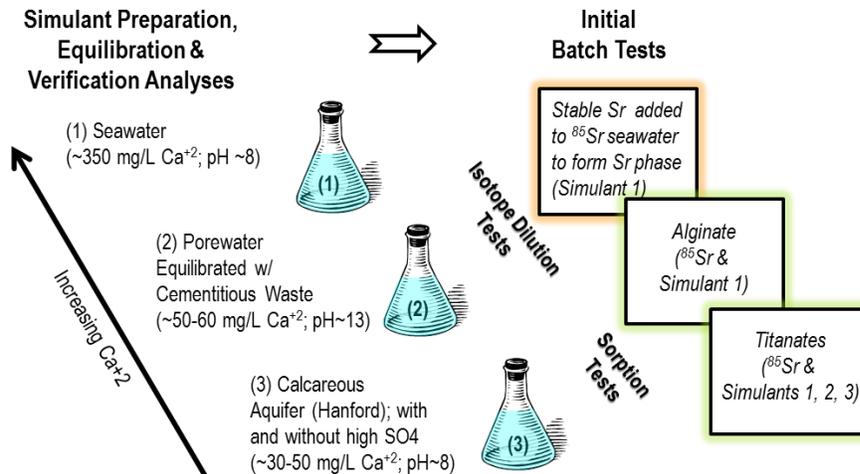


Figure 1. General outline of batch tests to assess each method's selectivity for ^{85}Sr removal under uniform geochemical conditions. Simulants included seawater, Hanford groundwater and cementitious pore fluid.

Results/Discussion

Calcareous Groundwater and Cementitious Pore Fluid

All of the titanate amendments removed $\geq 95\%$ ^{85}Sr from the calcareous groundwater and cementitious pore fluid solutions after contact times of 24 hours or more. MST and mMST showed the best performance overall even with the short (1 hour) contact times. Kinetically, SrTreat[®] and NaTONT showed slower uptake of ^{85}Sr compared to the MST and mMST. This slow uptake may be a function of the complex morphology of the individual particles and added time needed for the simulant to contact the various sites.

Seawater

The seawater simulant had the highest Ca concentration of all the simulants (approximately 100 times higher). Because of the higher Ca concentration, the titanate amendments showed less ^{85}Sr removal in the seawater compared to the groundwater and cementitious pore fluids. Analyses indicated that the titanates removed a large concentration of Ca with the small amount of Sr removed. SrTreat[®] had the greatest removal of all the titanate amendments (~25% at 1 week).

The 3 weight percent (wt %) alginate "wet" and "rehydrated" beads prepared with 0.1 M CaCl_2 showed highest ^{85}Sr removal for alginate tests (~21% at 1 week). Tests prepared with lower wt % alginate or with higher CaCl_2 exhibited less ^{85}Sr removal, which is likely due to fewer reactive sites being available. In these tests, the Ca concentration in the seawater increased from the addition of the alginate amendment.

Initial stable Sr (isotope dilution) tests run for 24 hours displayed greater ^{85}Sr removal when higher concentrations of stable Sr (and SO_4) were added. Removal varied from 50% to 95% with the addition of between 0.005 M and 0.02 M Sr and SO_4 , respectively. Much lower Sr removal (well below predicted removal by thermodynamic modeling) occurred upon addition of low amounts of stable Sr. Follow-up tests conducted for longer periods indicated increased Sr removal correlated with increased reaction time suggesting that the kinetics for precipitation of the Sr phases were slower than initially anticipated. Similarly, He et al (2014) found slow celestite precipitation in a recent study. Further testing using strontium sulfate seed crystals was also found to favor precipitation of Sr phases (and hence ^{85}Sr removal).

Upscaling and Viability

^{85}Sr and ^{90}Sr have very different specific activities, which should be considered together with the mass ratio of ^{90}Sr to natural Sr when upscaling to plausible remediation scenarios. For example, the mass concentration of ^{90}Sr will be higher than the mass concentration of ^{85}Sr in a water containing equal activity concentrations of ^{90}Sr and ^{85}Sr . If 90% of the activity of each isotope were removed, then 90% of the mass of each would be removed, but the absolute mass of ^{90}Sr removed would be higher.

A relative cost comparison was performed for the amendments assuming a seawater plume with 100 pCi/L ^{90}Sr and a target removal of 90%. The approximate amendment cost per cubic meter (m^3) of water treated was similar for alginate and stable Sr (isotope dilution) ($\leq \$200$). Relative to these removal methods, the titanate amendments cost four to eight times more. However, the cost per m^3 water treated will decrease, in terms of total mass removed, with increasing ^{90}Sr concentration. Although the titanates showed high removal of ^{85}Sr in calcareous groundwater and cementitious pore fluid, there is a need for optimizing titanate manufacturing to make it a cost effective option for extensive environmental plumes.

FY2014 Accomplishments

- Performed ~90 batch tests to determine radiostrontium removal from prepared simulants of seawater, calcareous groundwater and cementitious pore water using titanate amendments, alginate beads and an isotope dilution method.
- Evaluated methods and recipes for making alginate beads. The 3 weight percent (wt %) alginate “wet” and “rehydrated” beads prepared with 0.1 M CaCl_2 showed highest ^{85}Sr removal for alginate tests.
- Investigated the use of seed crystals as an enhancement for isotope dilution. For tests where low concentrations (0.001-0.002 M) of stable Sr (and in some cases sulfate) were added, the use of seed crystals increased ^{85}Sr removal between 10% to 18%.
- Evaluated kinetics associated with the precipitation of Sr phases (and thus the removal of radiostrontium) for isotope dilution. Longer tests (or contact times) correlated with precipitation of Sr phases and thus ^{85}Sr removal. Tests conducted for 3 weeks showed up to 30% greater ^{85}Sr removal than tests run for only 24 hours.
- Assessed upscaling and viability of using amendments for treating large environmental plumes. A cost comparison scenario (90% removal for seawater with 100 pCi/L ^{90}Sr) demonstrated that amendment costs were similar for alginate and stable Sr (isotope dilution) but the titanates were 4 – 8X higher in cost. For treating calcareous groundwater and cementitious pore fluid, there is a need for optimizing manufacturing costs of titanates to make them a cost effective option for extensive plumes.

Future Directions

- Evaluate less processed (i.e., less expensive) alginate products
- Evaluate isotope dilution in terms of biouptake factors rather than just percent removal
- Optimize cost of titanate manufacturing

FY 2014 Publications/Presentations

1. Presented project update to visitors from Japan National Institute for Environmental Studies (2/27/2014)
2. Presented poster (SRNL-MS-2014-00127) at SRNL Annual LDRD Year End Review

3. Millings, M., Taylor-Pashow, K., Roberts, K., Denham, M. and D. Hobbs. *Stabilization of Radionuclides in Calcium Enriched Environmental Systems Summary Report for LDRD-2014-00012*, SRNL-STI-2014-00458 (in draft).

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Acronyms

Ca	calcium
CaCl ₂	calcium chloride
dpm/mL	disintegrations per minute per milliliter
m ³	cubic meter
M	molar
MST	monosodium titanate
mMST	hydrogen peroxide modified MST
NaTONT	sodium titanate nanotubes
pCi/L	pico Curies per liter
PRB	permeable reactive barriers
SO ₄	sulfate
Sr	strontium
wt%	weight percent

Patent Apps/ Patents Awarded

None

Total Number of Post-Doctoral Researchers

None

Application of Radionuclide Signatures to Short Duration/Pulse Atmospheric Releases

Project Team: S. R. Chiswell (Primary), R. L. Buckley, R. J. Kurzeja, and D. W. Werth

Project Start Date: October 1, 2013
Project End Date: September 30, 2014

This project improves the ability to detect radionuclide emissions for non-proliferation monitoring and nuclear test ban treaty verification by developing signal analysis and mixed plume identification techniques with a multi-source/receptor model to separate atmospheric background signals from those related to a short pulse (explosion or unplanned) release. Source

attribution of radionuclides is dependent upon separating the signal of interest from background sources, which will be present in different ratios due not only to their differing sources, but also the period of time over which differing rates of decay have occurred. Increasing background source concentrations from nuclear power plants and medical isotope facilities make low signal-to-noise detection more difficult; therefore, the ability to improve the signal-to-noise ratio from existing measurements will have profound impacts on non-proliferation.

FY2014 Objectives

- Demonstrate improved detection and analysis of announced underground nuclear tests utilizing high resolution atmospheric transport and dispersion modeling capability combined with post-Fukushima observations.
- Determine the influence of known emissions on the observed radionuclide concentrations.
- Combine atmospheric numerical model predictions with spectral analysis of the background signal to allow a pulse event to be quantified.
- Apply resultant method to a location of interest to create a presentation and proposal for funding to DOE's NA-22 program (and potential WFO customers) targeted at defined proliferation detection mission areas to detect stages of weapons programs and locate and understand source term and propagation characteristics.

Introduction

The detection of radionuclide emissions is a key component of a non-proliferation monitoring framework, which must be able to discriminate transient emissions from ubiquitous background concentrations. The global background of detectable radioactive noble gases continues to increase, not only in concentration, but with greater variability. Significant sources of background radionuclides, in addition to reprocessing facilities, include medical isotope (MI) production facilities, and nuclear power plants (NPP). Most importantly, these combined background sources will contribute significantly to Comprehensive Test Ban Treaty Organization (CTBTO) and other measurements intended to characterize source and evolution from samples, including underground detonations where material may be sequestered for a period of time.

On February 12, 2013 the DPRK announced an underground nuclear test. Seismic monitors worldwide confirmed the location of the test with an estimated 10 kiloton yield. CTBTO measurements were not able to confirm the presence of radionuclides until 55 days later when Xenon measurements at Takasaki, Japan, and a few days later in Ussuriysk, Russia, revealed activity levels which were consistent with the assumed decay from the yield of the test [1] and the computed probable source region for the

plume. This event was chosen to demonstrate the value of improved background characterization for pulse events, and an opportunity to quantify detectability of proliferation activity as a result for this project.

Approach

The February 2013 nuclear test conducted by the DPRK presents a unique opportunity to investigate background source characterization utilizing known sources for radionuclides of interest. The period following the Fukushima-Daiichi disaster provided a unique test bed for this concept since only a single Japanese NPP was operational at the time. Global background concentrations were modeled from MI and NPP inventories provided by [2]. In addition to the CTBTO/IMS measurements from the Takasaki, Japan and Ussuriysk, Russia CTBTO locations, radiation counts from the Japan Nuclear Regulation Authority System for Prediction of Environment Emergency Dose Information (SPEEDI) network in Japan were analyzed. The SPEEDI network is a federated collection of approximately 218 local radiation sensors designed for detection of releases from nuclear power plants across Japan, and to provide radiation dose measurements for emergency response models. SPEEDI network sensors are raw radiation count (beta and gamma) sensors, which do not identify specific isotopes; however, the ten minute reporting frequency of the SPEEDI detectors provides significant information not only for the detection of a transient plume, but also to aid in interpreting longer sample duration 12- to 24-hour IMS measurements.

Atmospheric transport and dispersion models were used to model the period encompassing the time of the DPRK detonation through the CTBTO/IMS detection in April. A multi-source/receptor model was developed which was used with the model results for the event to confirm the CTBTO analysis that a plume detected beginning April 7, 2013 could have been emitted from the suspected test region, and that other nuclear emissions within the region could not explain the detected levels of radionuclides. A plume overlap algorithm combining multiple sources was then developed to identify preferred sampling regions in order to minimize ambiguity in quantifying sources of a plume. Utilizing a wavelet transformation, SPEEDI data were analyzed in order to detect and characterize signals in observed measurements which can be attributed to source region.

Results/Discussion

Quantifying the detectability of a proliferant signal amid known signals is accomplished from two metrics determined from high resolution transport and dispersion models to describe the signal-to-noise ratio and the ratio of plume overlap with known sources. These models can aid in unknown source detection by identifying the existing sensor locations most likely to detect a signal from a suspected source (Figure 1). Simulations of releases in the area surrounding the Sea of Japan with a high-resolution mesoscale transport model indicate that, despite the existence of other sources in the region, the source in Punggye, North Korea is discernable for much of the time. This supports the established use of transport modeling and indicates that a DPRK signal need not be significantly higher than the nearby sources to be detected.

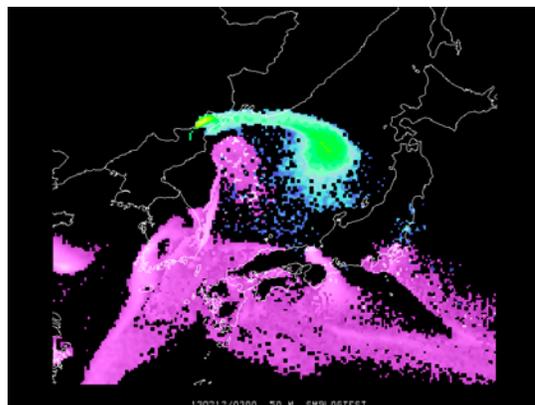


Figure 1. Detectability of a DPRK plume (green) is calculated using an index which includes over-lapping plume sources (pink). A multi-source/receptor transport model was developed to improve detection of emissions, even for signals near the background level.

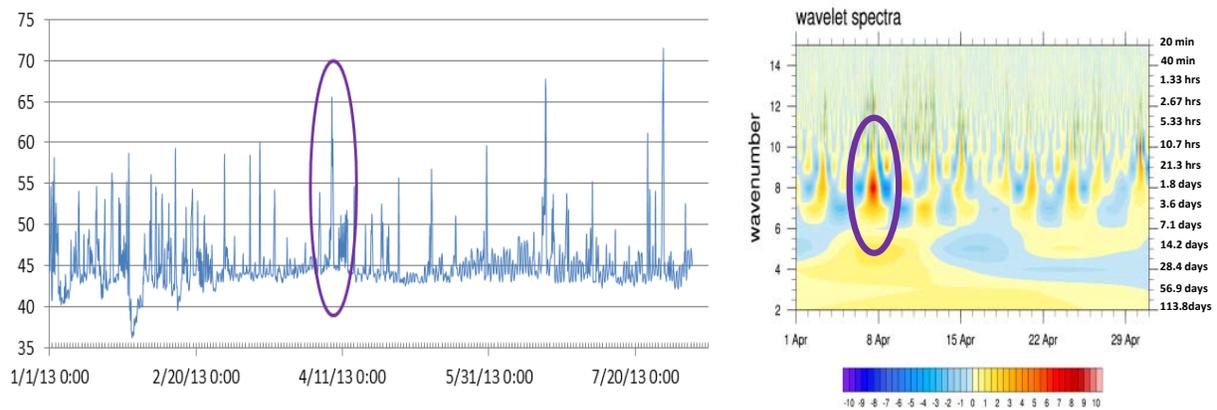


Figure 2. The time series of radiation dose at the Tatsunokuchi, Japan SPEEDI location (**Left**) illustrates the variability in detected radiation. A wavelet analysis for the period of the suspected DPRK plume passage (**Right**) shows increased contribution for longer time periods. The period of the DPRK plume is shown in the purple oval.

The projected plume path upwind of the CTBTO location was used to select the Tatsunokuchi, Japan SPEEDI location, which is seen to exhibit a maximum that not only coincides with the projected plume, but also exceeds all other peaks over the four month period centered at this time (Figure 2, left). A wavelet signal analysis method was applied to this period of data (Figure 2, right) in order to identify the wavenumbers comprising the observed data. Based on these results, the April 7th peak around wavenumber 8 can clearly be distinguished from other local maximas associated with higher order wave numbers. The higher order wave numbers can be attributed to higher frequency variability and therefore more localized variability. Since atmospheric mixing decreases high frequency variability with travel distance, the plume becomes more homogeneous. Thus, the distance of a plume’s downwind travel is characterized by its frequency distribution. Utilizing the broad spatial coverage of the SPEEDI sensors, the expanse of the suspected plume was found to be coherent across the west coast of Japan, with decreasing intensity away from the centerline (Figure 3). The location of the plume region is seen to correspond well with the plume path determined from the projected plume probabilities (Figure 4).

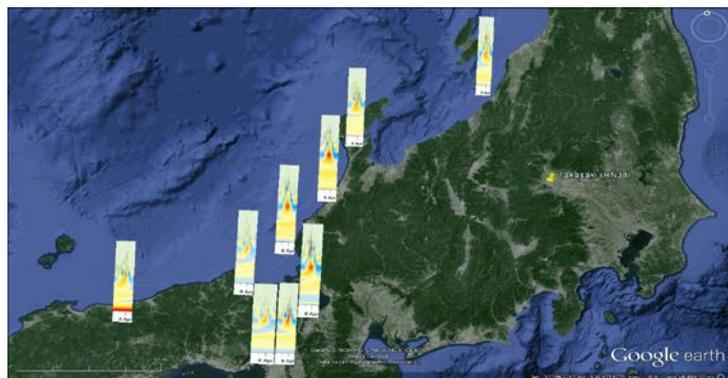


Figure 3. Analysis of SPEEDI radiation measurements in April, 2013, approximately 55 days after the DPRK test, identifies peaks in wavelet spectra consistent with the modeled plume trajectory from the suspected source region at locations upwind of the CTBTO/IMS location which detected the plume.

As a result of the verification of the CTBTO’s determination that measurements during the April 2013 time period were consistent with a DPRK pulse release, the period shortly after the detonation was examined to determine the likelihood that the Japan or Russian CTBTO sites would have been impacted by any release which may have occurred. Computed trajectories from the detonation location were found to rapidly shift from southeastward transport to a

period of eastward to northeastward transport, which would not be favorable for impacting the aforementioned CTBTO locations. The methods developed to verify the CTBTO identification of plume signatures from the DPRK test may provide a method identify embedded signals within the CTBTO data which may not exceed existing threshold criteria for detection above background. Proposed future research will utilize a similar method for analyzing the CTBTO data for signals, providing an independent method for detecting signatures within the data series.

FY2014 Accomplishments

- Atmospheric transport and dispersion models were used to analyze the period following the announced 2013 DPRK underground nuclear test.
- The SRNL multi-source/receptor model confirms the analysis by the Comprehensive Test Ban Treaty Organization (CTBTO) that a plume detected beginning April 7, 2013 could have been emitted from the suspected test region, and that other nuclear emissions within the region could not explain the detected levels of radionuclides.
- A wavelet signal analysis method was applied to Japanese radiation measurements which show the expanse of the suspected plume is coherent across the west coast of Japan, with decreasing intensity away from the centerline and corresponds well with the projected plume probabilities.
- A technique defining plume overlap from multiple sources was developed which can be used to identify sampling regions in order to minimize ambiguity in quantifying sources of a plume.
- A multi-laboratory NA-22 proposal for analyzing the fate and transport of radionuclide emissions, submitted at the end of March, leveraged results from this LDRD. This proposal received favorable review and is currently on hold status in NA-22 pending funding availability.
- A proposal based on project results was submitted to the National Counterproliferation Center (NCPC) Research, Development and Integration (RDI) fund in mid-July.
- Three publications are in preparation for submission to refereed journals.

Future Directions

Based on results obtained in the post-analysis of the 2013 DPRK underground nuclear test, follow on proposals have been developed to:

- Analyze the complete period from February to May, 2013 to identify additional signatures from the DPRK nuclear test. This analysis will provide a more detailed spatial and temporal picture of possible releases from the test site and also can be combined with the existing CTBTO record to determine the periods of time when the plume was present within the CTBTO sample volumes. This will enable us to focus on weak-signal periods, heretofore overlooked in the IMS data. We will quantify the significance of unexplained variance in the observed SPEEDI/CTBTO data using the multi-point/receptor model and compare to model predictions of releases from existing/known sources to ascertain the potential for releases of radioactive isotopes from the DPRK test prior to those which led to the April 7th-9th detection period announced by the CTBTO.

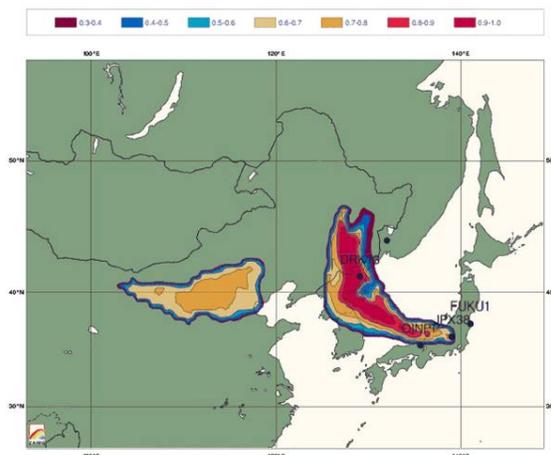


Figure 4. Possible source regions (correlation maxima) determined by Ringbom et al., 2014 for April, 2013 Takasaki radioxenon collections which include the DPRK test location and exclude other possible source regions.

- Apply signal analysis to historical observations to determine frequency characteristics of global sources. The result of this effort will lead to the development of spectral filters to improve signal-to-noise ratios. The wavelet technique demonstrated here allows for a large number of observations to be analyzed, while preserving the time and space dependency of detected signals.

FY 2014 Publications/Presentations

1. January, 2014 LDRD progress report update
2. March 27, 2014 LDRD NN Focused Review Presentation: Application of Radionuclide Signatures to Short Duration/Pulse Atmospheric Releases
3. May 6, 2014 LDRD Midyear Review Presentation: Application of Radionuclide Signatures to Short Duration/Pulse Atmospheric Releases
4. June, 2013 LDRD progress report update
5. SRNL-STI-2014-00496 LDRD poster session presentation
6. Characterizing the Detectability of Emission Signals from a North Korean Nuclear Detonation (Werth, peer review article in preparation)
7. The value of high frequency, low cost radiation measurements for nonproliferation and Comprehensive Test Ban Treaty analysis (Chiswell, peer review article in preparation)

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Acronyms

CTBTO	Comprehensive Test Ban Treaty Organization
DOE	Department of Energy
DPRK	Democratic People's Republic of Korea
IMS	International Monitoring System
MI	Medical Isotope
NCPC	National Counterproliferation Center
NPP	Nuclear Power Plant
RDI	Research, Development and Integration
SPEEDI	System for Prediction of Environment Emergency Dose Information
WFO	Work For Others

Patent Apps/ Patents Awarded

None

Total Number of Post-Doctoral Researchers

None

Functionalized Magnetic Mesoporous Silica Nanoparticles for U and Tc Removal

Project Team: D. Li (SRNL, Primary),
D. Kaplan (SRNL), S. Serkiz (SRNL), S.
Larsen (University of Iowa)

Subcontractor: University of Iowa

Project Start Date: October 1, 2013

Project End Date: September 30, 2014

Remediation of U and Tc remains an unresolved technical challenge because U adsorbs weakly to sediment minerals at $pH \leq 4$ (e.g., F-Area) and $pH > 8$ (e.g., Hanford, Idaho National Lab, and the former Yucca Mt. repository), and Tc has little or no adsorption to common environmental minerals. The overarching objective of this project was to develop novel and cost-effective functionalized magnetic mesoporous silica nanoparticles (MMSNs). The magnetite core allows for magnetic particle collection and the nitrogen and sulfur surface functionalization allows the engineering of

particles for ion selectivity and binding capacity. Mesoporous silica nanoparticles (MSNs) and MMSNs were successfully functionalized by grafting aminopropyltriethoxysilane (APTES), 3-Mercaptopropyltrimethoxysilane (MPTMP), N-(3-triethoxysilylpropyl)-4,5-dihydroimidazole (DIM), benzoylthiourea (BT) and polyaryloamidoxime (AD) functionalities. DIM-, BT- and AD-functionalized MSNs and MMSNs removed 2-6 orders of magnitudes greater amounts of U from $pH = 3$ or $pH = 9.6$ groundwater than unfunctionalized nanoparticles or silica. These results provide an applied scientific foundation for solving critical DOE and industrial issues related to nuclear environmental stewardship and nuclear power production.

FY2014 Objectives

- Synthesis and characterization of magnetite-core mesoporous silica nanoparticles (MMSNs).
- Surface functionalization of MSNs and MMSNs using selected surfactants and chelating agents.
- Batch sorption evaluation of the functionalized MSNs and MMSNs for aqueous U and Tc removal.
- Characterization of U and Tc bonding to nanoparticles by various spectroscopic and microscopic methods.
- Separation and regeneration of U- or Tc-sequestered nanoparticles and U extraction.
- Evaluating U extraction from seawater matrix using synthesized nanoparticles.

Introduction

U is the most common radioactive contaminant in the DOE complex, at U mine / processing sites, and fuel cell rod storage basins. There are two common oxidation states of U in natural environments and waste streams, U(IV) and U(VI). U(VI) is normally more mobile, bioavailable and toxic than its counterpart U(IV). The aqueous U(VI) species exists commonly in extremely acidic ($pH < 4$) or naturally-occurring basic carbonate ($pH > 8$) conditions. It has little or zero adsorption to sediments under $pH < 4$ or $pH > 8$ aqueous conditions due to repulsive surface charges between U species and sediment minerals, which leads to severe difficulties in its remediation. Existing technologies for U contaminant treatment include various biotic and abiotic reduction processes. However, these processes have several shortcomings in the field applications:[1] (1) electron donors (e.g., acetate, ethanol) need to be injected to stimulate the microorganism population for its sustainable effectiveness, (2) biogenic or chemical reduced U compounds (e.g., uraninite) are susceptible to re-oxidation in natural environments, and (3) they are not applicable to the extremely low pH systems.[2] There is, therefore, a great need to address this knowledge gap and to develop novel and cost-effective technologies for remediation of acid/base U contaminated systems.

Tc is a key risk driver at the Savannah River Site (SRS) and other DOE environmental management sites (most notably the Hanford Site and Oak Ridge National Laboratory). The anionic TcO_4^- is the dominant species under most of these environmental conditions, and is mobile and difficult to be immobilized through the use of sorbents.[3] For waste streams with a high content of TcO_4^- , reductant materials (Fe_3S_4 , soluble or structural Fe(II), zero-valence iron) and reducing bacteria can reduce Tc(VII) to Tc(IV) and remove Tc effectively.[4, 5] But like U(IV), the reduced Tc form (e.g., $\text{TcO}_2 \cdot n\text{H}_2\text{O}$) is susceptible to re-oxidation under most of natural environmental conditions and the mobile TcO_4^- will be released to the environments.[6] There are currently no demonstrated technologies that are highly efficient and cost-effective for separation of Tc-containing nuclear waste streams and remediation of aqueous Tc in the contaminated sites.

In this project, we synthesized surface-functionalized magnetic mesoporous silica nanoparticles (MMSNs) with a magnetite core. The ligands used to functionalize the MMSNs were selected to achieve a highly efficient binding of aqueous UO_2^{2+} or TcO_4^- , especially under extreme acid and base conditions.

Approach

Magnetite (Fe_3O_4) nanoparticle cores (<10 nm) were synthesized by controlled precipitation of FeCl_3 and FeCl_2 with ammonia hydroxide. MMSNs (<100 nm) were made by coating the magnetite core using surfactant-template self-assembling methods. In this synthesis step, the nano magnetite particles were mixed with cetyltrimethylammonium bromide (CTAB) and tetraethyl orthosilicate (TEOS) in water in a reflux flask and heated at a temperature of 80°C for 2 hours.[7, 8] Functionalized MSNs and MMSNs were made by grafting APTES, MPTMP, DIM, BT, and AD. A general procedure for functionalization was: calcined MSNs or MMSNs were added to toluene containing the functionalization surfactant or chelating agent; the reaction mixture was heated to 120 °C for 6 h and then was centrifuged; but for AD functionalization, it was done in methanol as the solvent at 65 °C. The solids were washed with dichloromethane and diethylether and dried overnight at 100 °C.[9-11] Some of the functionalization agents (e.g., BT and AD) required an immediate coupling agent (e.g., APTES) to be grafted onto nano particle surfaces.[11, 12] All synthesized nanoparticles were characterized using XRD, TGA, BET surface area, TEM, and ^{13}C solid-state NMR.

Functionalized MSNs and MMSNs were evaluated for U and Tc removal from pH = 3 and pH = 9.6 groundwater simulant under atmospheric ($P_{\text{CO}_2} = 10^{-3.5}$ atm) conditions using batch adsorption experiments. Adsorption coefficient (K_d , mL/G) and the equilibrium sorption capacity (q_e , $\mu\text{g/g}$) were calculated using formula 1 and 2, respectively:

$$K_d = \frac{C_0 - C}{C} \times \frac{V}{M} \quad (1)$$

$$q_e = \frac{(C_0 - C) \times V}{M} \quad (2)$$

where C_0 and C were U or Tc concentrations before and after adsorption, respectively, V was the total volume of liquid phase (i.e., groundwater), and M was the mass of nanoparticle sorbent. Oxidation state and chemical bonding of U onto the functionalized MSNs and MMSNs were investigated using synchrotron radiation X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS).

Results/Discussion

Adsorption coefficient (K_d) and equilibrium sorption capacity (q_e) onto the synthesized nanoparticles and natural silica in pH = 3.0 groundwater simulant are shown in Figure 1A and 1C, respectively. The K_d values for functionalized MSNs and MMSNs were 4-6 orders of magnitude greater than those of unfunctionalized nanoparticles and silica. Similarly, the K_d and q_e values for U onto functionalized MSNs and MMSNs in pH = 9.6 groundwater simulant are shown in Figure 1B and 1D, respectively. The K_d values for functionalized MSNs and MMSNs were 2-4 orders of magnitude greater than those of unfunctionalized nanoparticles and silica.

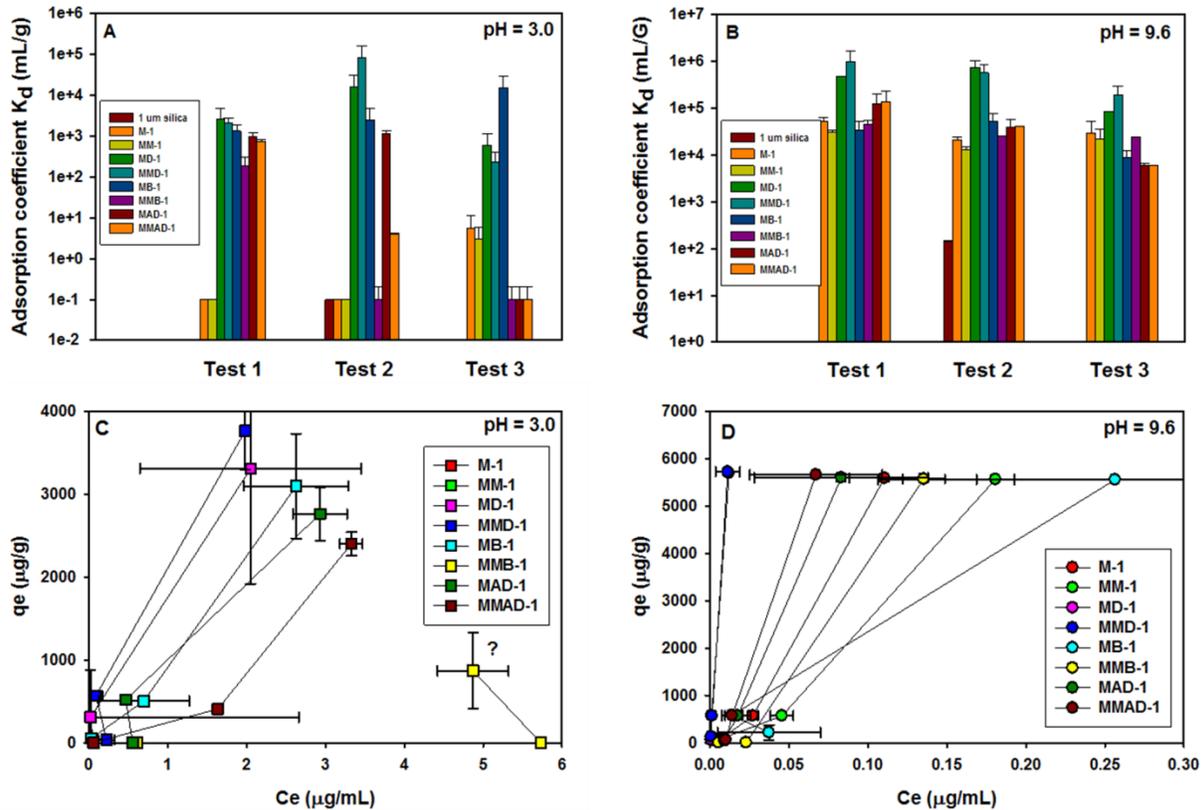


Figure 1. Adsorption coefficient (K_d) and equilibrium sorption capacity (q_e) onto functionalized MSNs and MMSNs in pH = 3.0 (A and C) and pH = 9.6 (B and D) groundwater simulant (Tests 1, 2 and 3 represented batches for the initial U/sorbent ratios of 5.95, 0.595 and 0.0595 mg/g, respectively).

U L3-edge XANES spectra of BT-MMSNs (# MMB-1) after U adsorption at pH 3 and 9.6 are shown in Figure 2, in comparison with those of uraninite (U(IV)) and uranyl acetate (U(VI)). They were representative of the U L3-edge XANES spectra of other series samples. With regard to the standards, three distinctive features distinguish U(IV) from the U(VI) spectra: 1) the U L3-edge peak is sharper and shifts toward lower energy by 2.5 eV for U(IV) than U(VI), 2) there is a “shoulder” at 17,188 eV for U(VI); 3) the peak at 17,215 eV is sharper and stronger for U(IV) than U(VI). The spectra of functionalized MMSNs after U adsorption clearly indicated that the sorbed U species was U(VI). EXAFS data of these MMSNs have been collected and detailed data analysis is under way to determine U chemical bonding to the functionalized MMSNs.

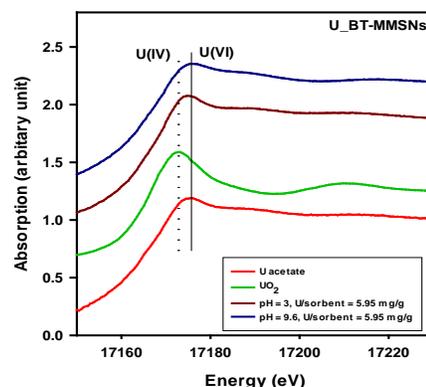


Figure 2. U L₃-edge XANES of BT-MMSNs (# MMB-1) after U sorption

The K_d values for Tc removal by functionalized MSNs and MMSNs in pH = 3.0 and pH = 9.5 groundwater simulant are summarized in Table 1. Unfunctionalized MSNs and MMSNs did not remove Tc from either pH = 3.0 or pH = 9.5 groundwater. The functionalized MSNs and MMSNs (except for BT-MMSNs) showed moderate adsorption capability of removing Tc from pH = 3.0 groundwater, but near zero adsorption of Tc from pH = 9.5 groundwater.

Table 1. Adsorption coefficient (K_d) of Tc onto functionalized MSNs and MMSNs in groundwater

MSNs samples	K_d (mL/g)		MMSNs samples	K_d (mL/g)	
	pH = 3.0	pH = 9.5		pH = 3.0	pH = 9.5
MSNs	0	0	MMSNs	0	0
DIM-MSNs	146	1	DIM-MMSNs	62	0
BT-MSNs	153	0	BT-MMSNs	0	11
AD-MSNs	228	0	AD-MMSNs	184	0
APTES-MSNs	36	0	APTES-MMSNs	29	6
MPTMS-MSNs	77	0	MPTMS-MMSNs	25	0.6

FY2014 Accomplishments

- DIM-, BT-, AD-, APTES- and MPTMS-functionalized MSNs and MMSNs have been successfully synthesized and characterized.
- Batch sorption experimental results demonstrated that DIM-, BT-, AD-functionalized MMSNs were very effective for U removal from pH = 3 or pH = 9.6 groundwater under atmospheric $P_{CO_2} = 10^{-3.5}$ atm.
- At pH = 3, U removal was as much as 99% with final U concentrations as low as ~100 ppb, K_d values increased by a magnitude of 4-6 orders compared to unfunctionalized MMSNs and silica.
- At pH = 9.6, U removal was nearly 100%, K_d values increased by 2-4 orders of magnitude compared to natural silica. Functionalized MMSNs removed U from pH = 9.6 groundwater to as low as <0.7 ppb, which is lower than the U Maximum Contaminant Level of 30 $\mu\text{g/L}$ regulated by EPA.

- DIM- and BT-functionalized MSNs, and AD-functionalized MSNs and MMSNs have been demonstrated to have moderate capability of Tc removal from pH = 3 groundwater simulant ($K_d > 100$ mL/g); but none of the synthesized nanoparticles were effective in Tc removal from pH = 9.5 groundwater simulant.

Future Directions

- Measuring adsorption capacity of the functionalized MMSNs for U removal.
- Identifying the influence of geochemical parameters (e.g., pH and competing ions) on MMSNs performance.
- Evaluating application of these sorbents for U extraction from seawater.
- Developing additional MMSNs functionalization approaches for Tc removal.
- Conducting spectroscopic and microscopic characterization of newly developed nanoparticles.
- Submitting a patent application and publications.

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Acronyms

AD	Polyaryloamidoxime
APTES	Aminopropyltriethoxysilane
BET	Brunauer–Emmett–Teller
BT	Benzoylthiourea
CTAB	Cetyltrimethylammonium bromide
DIM	N-(3-triethoxysilylpropyl)-4,5-dihydroimidazole
DOE	Department of Energy
EPA	Environmental Protection Agency
EXAFS	Extended X-ray absorption fine structure spectroscopy
FT-IR	Fourier transform infrared spectroscopy
MMSNs	Magnetic mesoporous silica nanoparticles
MPTMP3	Mercaptopropyl-trimethoxysilane
MSNs	Mesoporous silica nanoparticles
NMR	Nuclear magnetic resonance spectroscopy
SEM	Scanning electron microscopy
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TEM	Transmission electron microscopy
TEOS	Tetraethyl orthosilicate
TGA	Thermogravimetric analysis
XANES	X-ray absorption near-edge structure spectroscopy
XRD	X-ray diffraction

Patent Apps/ Patents Awarded

None

Total Number of Post-Doctoral Researchers

None

Field Detector Development for Undeclared/Declared Nuclear Testing for Treaty Verification Monitoring

Project Team: D.B. Hunter (Primary),
M.R. Kriz, T.N. Riley, R.K. Huffman,

Subcontractor: N/A

Project Start Date: October 1, 2013

Project End Date: September 30, 2014

Radioxenon is a critical part of the Comprehensive Nuclear Test Ban Treaty (CTBT) for the detection/confirmation of undeclared/declared nuclear weapons tests. Treaty verification monitoring for radioxenon is another application for post-event monitoring on-site; however, this is not currently conducted because there are no simple portable field devices for measurements. This project assessed the development of a small, robust beta-gamma coincidence counting system, which will combine collection and in

situ detection methodologies. This will be a significant advancement for field detection/quantification of short-lived xenon isotopes that would not survive transport time for laboratory analysis.

FY2014 Objectives

- Assess the design a small/robust beta-gamma coincidence system
- Initiate development of beta pulse processing system
- Develop a beta scintillation cell

Introduction

Radioxenon is a critical part of the Comprehensive Nuclear Test Ban Treaty (CTBT) for the detection/confirmation of undeclared/declared nuclear weapons tests. Noble gases are ideal signatures to detect clandestine nuclear events since they are very difficult to contain and can diffuse and migrate through soils due to their inert nature. Radioxenon is used instead of other radioactive noble gases due to the poor production rates, short half-lives, high background levels or issues with global scale monitoring of other noble gases [1]. There are four key radioxenon isotopes used in monitoring: ^{135}Xe (9 hour half-life), $^{133\text{m}}\text{Xe}$ (2 day half-life), ^{133}Xe (5 day half-life) and $^{131\text{m}}\text{Xe}$ (12 day half-life). By measuring the activity ratios of $^{133\text{m}}\text{Xe}/^{131\text{m}}\text{Xe}$ versus $^{135}\text{Xe}/^{133}\text{Xe}$, it is possible to distinguish between civilian sources (nuclear power plants and medical isotope production facilities) and nuclear explosions [2].

The International Monitoring System (IMS) currently uses large laboratory devices located throughout the world for xenon monitoring, such as the Swedish SAUNA (Swedish Automatic Unit for Noble Gas Acquisition), the French SPALAX (Système de Prélèvement d'air Automatique en Ligne avec l'Analyse des radioXenon), or the Russian ARIX (Analyzer for Xenon Measurements). The current systems are large laboratory devices that require a climate controlled building. Treaty verification monitoring for radioxenon is another application for post-event monitoring on-site; however, this is not currently conducted because there are no simple portable field devices for measurements. The objective of this research is to develop the necessary components for a portable beta-gamma coincidence counting system that would allow for on-site monitoring for radioxenon.

Savannah River National Laboratory (SRNL) is a leader in the field of gas collections and has developed highly selective molecular sieves that allow for the collection of xenon gas directly from air. Using these molecular sieves, SRNL has the ability to collect radioxenon on location, but the components of a portable beta gamma coincidence counting system required to count the xenon are not commercially available. This work has focused on the development of custom electronics for beta-gamma coincidence counting using a small, USB powered device. Beta-gamma coincident counting is

advantageous for two reasons. First, the measurement sensitivity is improved by a lower of the background, relative to gamma counting alone (Figure 1). Second, more isotopic information is available using beta-gamma counting as opposed to gamma counting alone (Figure 2).

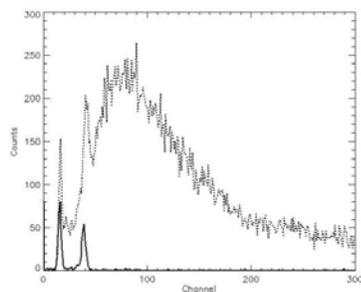


Figure 7: Spectra of ^{133}Xe showing background reduction in coincidence mode

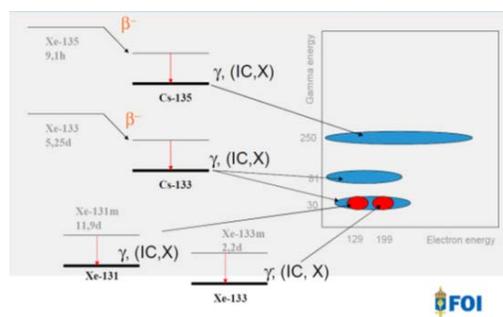


Figure 8: Conceptual 2D beta-gamma spectra [3]

Approach

This project is a collaboration of scientists and engineers. A four-step approach was taken to begin development of a small, robust/portable beta-gamma coincidence counting system:

Step 1: Demonstrate beta-gamma coincidence counting of xenon using COTS rack mount lab scale electronics.

Step 2: Use an Ortec digiBase to perform similar beta-gamma coincidence counting as the rack mount electronics.

Step 3: Design custom electronics to perform beta-gamma counting using one USB interface.

Step 4: Design and fabricate the gas scintillation cell.

The initial design for a portable field system consists of the custom electronics package developed electronics to perform beta-gamma counting using one USB interface, a gas scintillation cell fabricated from a plastic scintillator coupled to a photomultiplier tube (PMT), this scintillation detector is then inserted into a NaI(Tl) well detector. The plastic scintillator measures the beta/conversion electron signal while the NaI(Tl) detector measures the gamma /x-ray signal.

Results/Discussion

This project started the development of a small, robust beta-gamma coincidence counting system, which will combine collection and *in situ* detection methodologies. This will be a significant advancement for field detection/quantification of short-lived xenon isotopes that would not survive transport time for laboratory analysis. We have successfully developed the custom electronics enabling an Ortec digiBase to perform similar beta-gamma coincidence counting as commercially available rack mount technology, demonstrating a reduction in ambient background noise leading to improved sensitivity. The digiBase was designed for a portal monitoring system developed under DHS for registering timed gamma events between multiple detectors. The digiBase can also accept beta scintillation signals as triggers for gamma collection. Initial tests successfully demonstrated beta-gamma coincidence counting using an ^{181}Hf solution coupled to a PMT inside a NaI well detector with an Ortec digiBase, USB powered gate delay generator and PMT power supply, shown in Figure 3. A background reduction of more than 500x is possible for measuring beta-gamma coincidence signals over measuring gamma alone with an unshielded detector resulting in a sensitivity improvement of almost 25x, see Figure 4.

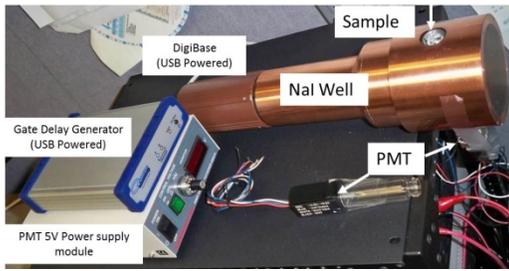


Figure 3:

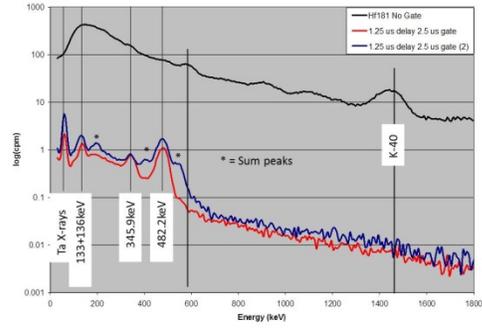


Figure 4: Spectra of ^{181}Hf using no gate delay and a 1.25 us gate delay, a $\sim 500\times$ background reduction is achieved

The next step was to develop the custom electronics necessary to enable an Ortec digibase MCA to perform beta gamma counting using one USB interface to connect the PC to the beta-gamma coincidence counting set-up. Additionally, the beta PMT timing properties need to be matched to the gamma PMT timing properties and the beta energies need to be recorded. The advantages of having a custom electronics for the communication is that they are specifically built for this application, all devices interface within one module, the PC will act as the data collection entry (but is not required during operation) and there will be better synchronization between the beta/digiBase events. Many electronic circuit configurations were evaluated for beta-gamma coincidence for applicability and two multichannel analyzers were identified with similar features and performance specifications, the Ortec digiBase (Figure 5) and the Amptek TB-5 (Figure 6). The Amptek TB-5 module was selected as the gamma spectroscopy interface due to the following factors:

- Operates directly from 5V power supply
- Supports gated list mode data
- Retains configuration settings in event of a power loss
- Supports preferred communication method (RS232 serial)

The Amptek DP5G module was selected as the beta PMT interface and it will perform a similar role as the TB-5 module used for the Nal gamma detector (Figure 7). Additional work needs to continue to resolve some of the gate enabled function timing issues (Figure 8).



Figure 5: Embedded controller with Ortec digiBase



Figure 6: Amptek model TB-5



Figure 7: Electronic components selected for beta-gamma coincidence system

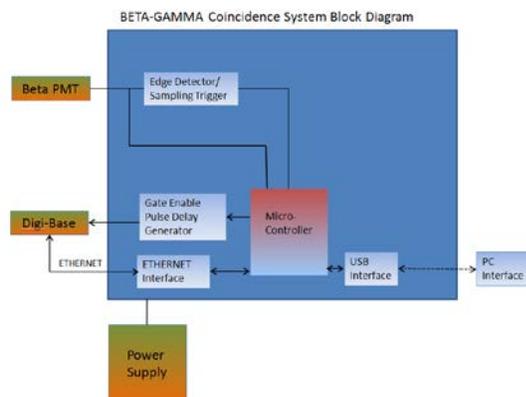


Figure 8: Beta-gamma coincidence system block diagram

To perform the beta-gamma coincidence counting in the field, a gas cell needed to be designed and fabricated to fit within the existing NaI well detectors used in the set-up shown in Figure 3. Two different plastic scintillators were identified for use, Eljen EJ-204 and EJ-212. These scintillators were chosen based on their overall properties and they are equivalent to other commercially available scintillators used in existing laboratory systems, i.e. EJ-204 is equivalent to the St. Gobain BC-404 plastic scintillator used in the SAUNA system. Two different geometry designs were fabricated: a circular cell and a square cell (Figures 9 and 10). The circular cell design was easier to fabricate and was found to hold gas without leaking; however, the square cell design encountered difficulties in assembling gas fittings and was not leak tested.



Figure 9: Exploded view of beta-gamma coincidence counting system

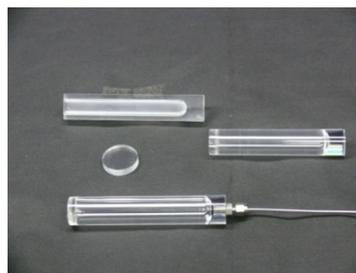


Figure 90: Gas cell prototypes

FY2014 Accomplishments

- Performed baseline xenon beta-gamma coincidence testing with lab scale electronics.
- Performed similar beta-gamma coincidence test with Ortec digiBase to verify capabilities of the digiBase MCA.
- Completed evaluation of electronic circuit configuration for beta-gamma coincidence counting.
- Selected Amptek TB-5 module for gamma spectroscopy interface and Amptek DP5G module for beta spectroscopy interface.

- Designed and built scintillation gas cell for evaluation.
- Made significant progress towards development of a fieldable beta-gamma coincidence counting system.

Future Directions

- This work will be continued in a funded FY15 LDRD “Phase II- Field Detector Development for Undeclared/declared Nuclear Testing for Treaty Verification”.
- The FY15 work will continue the work on the custom electronics developed in this LDRD and address the timing challenges and integration of electronics and data collection.
- Work will continue on the design of the gas cell, the calibration of the gas cell as well as the quantification of a radioxenon gas sample.

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Acronyms

ARIX: Analyzer for Xenon Measurements

COTS: Commercial off the shelf

CTBT: Comprehensive Nuclear Test Ban Treaty

DHS: Department of Homeland Security

IMS: International Monitoring System

MCA: Multichannel analyzer

PMT: Photomultiplier tube

SAUNA: Swedish Automatic Unit for Noble Gas Acquisition

SPALAX: Système de Prélèvement d’air Automatique en Ligne avec l’Analyse des radioxenon

SRNL: Savannah River National Laboratory

Patent Apps/ Patents Awarded

None

Total Number of Post-Doctoral Researchers

None

Technology Development for Water Detritiation and Volume Reduction

Project Team: Steve Xiao, Tommy Sessions, James Klein, Sharon Redd, Rob Lascola, Bill Spencer

Subcontractor: N/A

Project Start Date: October 1, 2013

Project End Date: September 30, 2014

This project investigated direct separation of HDO/H₂O experimentally as a potential process scalable for large volume water detritiation. More importantly, lab capabilities to study deuterium removal from water have been established. Tunable laser absorption spectroscopy was identified as the analytical method for trace level HDO analysis in water samples. Literature review and preliminary feasibility study support the SRNL concept as the best potential development. The work leverages the

SRNL expertise in isotope separation technologies to advance SRS's capabilities for environmental risk reduction.

FY2014 Objectives

- Assess SRNL and competing processes - literature search and review of existing processes in order to best address the SRNL technical concept.
- Test candidate column packing materials experimentally for isotope separation.
- Study process feasibility and applicability as how to engineering a continuous or semi-continuous process.
- Extend the research in a modified HPLC (High-Performance Liquid Chromatography) instrument, including necessary procurement and lab setup (additional scope).

Introduction

Water detritiation is very important for tritium production and reduction of environmental releases. Over the past four decades no breakthrough technologies have been developed to process tritium-contaminated water efficiently and economically [1-5] despite continuing interest and efforts. Combined Electrolysis Catalytic Exchange (CECE), water distillation (WD), and Girdler-Sulphide (G-S) processes are still among the leading processes to separate water molecules with different hydrogen isotopes. Both CECE and WD are very energy intensive and G-S uses toxic and corrosive chemical H₂S, which are problematic when combined with radioactive hazards. The potential for a direct isotope separation of water molecules is of considerable interest, as well as broad impacts to heavy water from SRS legacy moderator, TVA (Tennessee Valley Authority) cooling water, nuclear power industry, and environmental remediation, etc. The opportunity to clean up tritium contaminated water from damaged Fukushima Daiichi nuclear plant following 2011 Japanese earthquake is huge, but a practical separation technology on an industrial scale is needed.

Investigation of direct separation of HDO/H₂O was conducted experimentally in this project as a potential scalable process for large volume water detritiation. More importantly, SRNL has established capabilities to study deuterium removal from water, and one of the many expected challenges was identified as trace level HDO analysis in water samples. Literature review and preliminary feasibility study still support the SRNL concept as the best potential development.

Approach

Direct separation of H₂O/HDO was studied as a surrogate for tritium removal from water. The technology development is critical for the success of the SRNL concept and herein the focus of this project. Effective treatment of low-level tritiated water is technically very challenging due to the large volume that needs processing, however, the extremely low concentration also provides ample capacity for a column to remove tritiated water if the isotopic separation factor is adequate to establish a concentration profile. Once the isotope separation is confirmed with water molecules, catalytic isotope exchange will be developed in the future as the regeneration step of the separation column as well as to convert tritiated water to elemental hydrogen for tritium recovery.

Results/Discussion

Completed literature search that exceeded our expectations by discovering several scientific approaches that would enhance probability of success, including a SRNL patent and an industrial process having pilot plant data using tritiated water. The following four research pathways have been carefully identified as scalable water isotope separation processes based on the literature data: materials with isotopic effects for a packed column [6-8], Nafion membrane [9] (SRNL invention by Dr. Myung Lee, inventor of TCAP), media based separation [10] and composite membrane (Hanford) [11]. Each has its own merit and some even with tritium data. For example, Molecular Separation Inc. (MSI) reported significant tritium reduction on an ion-exchange resin loaded with aluminum sulfate, which has a greater affinity for tritiated water (HTO) over light water (HOH) in hydration waters [10]. However, the idea has been for a while with a fair amount of interest within the nuclear industry but not commercialized. Therefore, we need to understand if the claims are credible or what the actual issues are. By studying an independent evaluation [12], we came to an idea on how to engineering a semi-continuous process, in which the SRNL concept can solve both shortcomings of low capacity and potential short life of the material.



Figure 1. Lab setup for water isotope separation test

The lab testing capability was established to study HDO/H₂O separation. During the evaluation, analytical tools RGA (Residue Gas Analyzer by Mass Spec), FTIR (Fourier Transform Infrared Spectroscopy) and precision densitometer were tested for HDO concentration analysis. Figure 1 shows the lab testing equipment using 2 pumps, a separation column and FTIR detector. Tunable laser absorption spectroscopy was identified as the best tool to measure small variations of D/H ratios in water to the precision of +/- 0.05 ppm δ D from natural abundance (about 156 ppm). PICARRO L2130-i

Isotopic Water Analyzer was procured and received in FY14 (funded by tritium process development – NNSA). A HPLC instrument was also received to accelerate the following research work. Figure 2 shows these two instruments in our lab.

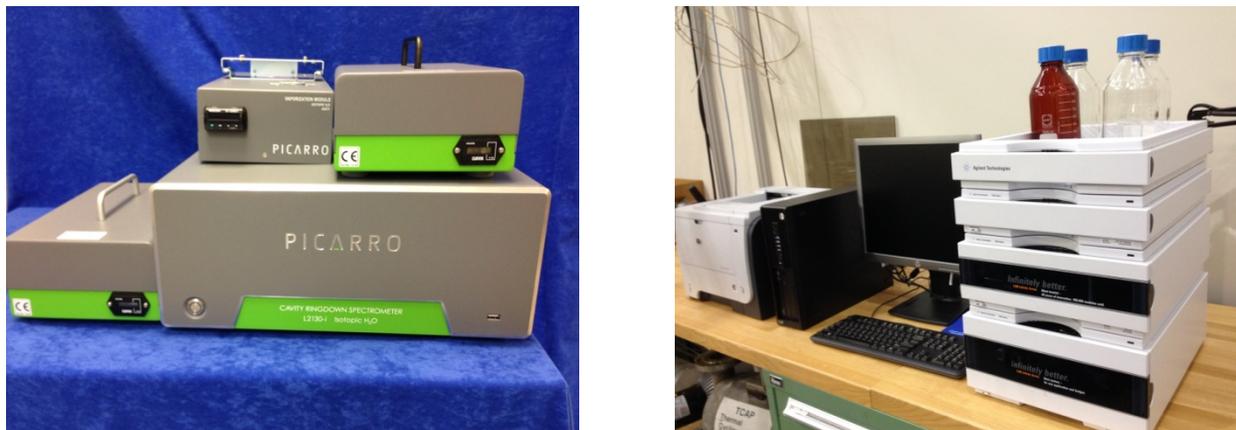


Figure 2. PICARRO Isotopic Water Analyzer (left) and Agilent HPLC (right)

FY2014 Accomplishments

- Completed literature review with 4 plausible technical pathways – exceeded our initial expectations.
- Established lab capabilities to study deuterium removal from water experimentally.
- Tested several candidate column packing materials in H₂O/HDO isotope separation.
- Studied feasibility and applicability (preliminary) of the SRNL concept in a semi-continuous separation process.
- Procured tunable laser absorption spectroscopy as the method for trace level HDO analysis in water samples, and a HPLC instrument for accelerated material screening (additional scope).

Future Directions

- Continue technology watch for new discoveries / concepts in this area.
- Perform material screening to rank their isotope separation efficiency.
- Conduct HDO/H₂O separation test for separation factor, capacity, theoretical stages, etc. basic information.
- Build a model with the experimental data and perform engineering feasibility study.

FY 2014 Publications/Presentations

X. Xiao, B. B. Looney, “Tritiated Water Challenge in Fukushima Daiichi”, Tritium Focus Group Meeting, Aiken, SC, April 22-24, 2014.

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12. P. Snead, S. Bushart, M. Naughton, R. Kohlmann, L. Furlong, *Evaluation of a Low Level Waste Technology – "A Media Based Tritium Removal Process"*, EPRI, Palo Alto, CA, and Progress Energy, Raleigh, NC: 2002. 1006710.

Acronyms

CECE - Combined Electrolysis Catalytic Exchange
 FTIR - Fourier Transform Infrared Spectroscopy
 G-S process - Girdler-Sulphide process
 HPLC - High-Performance Liquid Chromatography
 MSI - Molecular Separation Inc.
 RGA - Residue Gas Analyzer (by Mass Spectroscopy)
 SRNL – Savannah River National Laboratory
 SRS - Savannah River Site
 TCAP – Thermal Cycling Absorption Process
 TVA - Tennessee Valley Authority
 WD - Water Distillation

Patent Apps/ Patents Awarded

X. Xiao, "Decontamination of Tritiated Water", International Patent Application PCT/US13/69826, November 13, 2013.

Total Number of Post-Doctoral Researchers

None in FY14, future postdoctoral planned.

Reinventing the Nuclear Waste Chemical Processing Flowsheet using Advanced Continuous Chemical Reactors and Separations

Project Team:

D. P. Lambert (Primary)
Dr. J. R. Zamecnik / Dr. M. B. Gorenssek

Subcontractor: Proteaf Industries

Project Start Date: February 11, 2014

Project End Date: September 30, 2014

Process Intensification principles were used to identify two continuous reactors suitable for use in the Defense Waste Processing Facility (DWPF). An Oscillating Helical Reactor was chosen for the continuous reactor and two subcontracts were awarded to Proteaf to manufacture the equipment and provide technical support for this project. The equipment was delivered to SRNL on September 30, 2014.

Planned testing in FY15 will demonstrate the feasibility of using a helical reactor for chemical

processing of sludge. Key objectives are to demonstrate the mixing of the slurry, the neutralization of the sodium hydroxide with acid and the generation of offgas generated by carbonate and nitrite destruction and mercury reduction.

FY2014 Objectives

- Procure Helical Reactor. Setup continuous reactor (Ready for testing)
- Phase 1 – Demonstrate high solids mixing
- Phase 2 – Demonstrate slurry neutralization
- Phase 3 – Demonstrate mercury reduction

Introduction

The project objective is to determine the feasibility of using a continuous reactor for the chemical processing of sludge to replace the semibatch process in the Defense Waste Processing Facility. The first task was to identify continuous reactors that could be suitable for this testing. An oscillating helical reactor (Figure 1) was chosen as it has laminar flow and good mixing can be achieved due to the oscillation, leading to a much smaller volume reactor. An oscillating baffled reactor was not chosen primarily because it was too expensive for this project. Proteaf was selected to produce the experimental reactor and associated equipment

(Vessels, pump, oscillator, offgas de-entrainment equipment, etc.) with support from TNO. The equipment was delivered to SRNL on September 30, 2014 so no testing was completed in FY14.

Approach

The chemical processing of sludge is complicated due to chemical complexity and challenging rheology of the slurry, and the large offgas generation during processing. First the safety considerations will be addressed using SRNL's electronic Hazard Assessment Process and a Job Hazard Analysis. Initial testing will be completed with water to demonstrate the equipment works as planned. Next the processing of the slurry will be demonstrated by pumping a nitrite, carbonate and mercury free sludge simulant

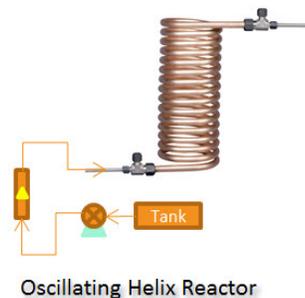


Figure 1. Schematic of Helical Reactor.

through the reactor system and demonstrate that adequate mixing can be accomplished. The testing will be followed by the neutralization of the nitrite, carbonate and mercury free slurry with nitric acid, so there will be no offgas generation. The last phase of testing will be testing of slurry containing carbonate, nitrite, and or mercury leading to offgas generation due to the production of carbon dioxide from carbonate destruction, oxides of nitrogen from nitrite destruction, and the production of carbon dioxide from the reduction of mercuric oxide to elemental mercury and carbon dioxide using a reducing acid (glycolic or formic acid).

Results/Discussion

The first accomplishment of this project was the identification of two continuous reactors that might be feasible for processing sludge in DWPF. The Oscillating Baffled Reactor (OBR) has been tested extensively by Professor Ni of Heriot Watt University. The Oscillating Helical Reactor has been tested extensively by Dr. Dirk Verdoes and his team at TNO. Nondisclosure agreements were established with both teams and with Proteaf, the US supplier of this equipment. The cost of the OBR exceeded the project budget so the oscillating helical reactor was chosen and a subcontract was established with Proteaf to supply the equipment. The equipment was delivered to SRNL on September 30, 2014.

FY2014 Accomplishments

- Triparty nondisclosure agreement with TNO and Proteaf
- Meeting with Bert Rietveld, Proteaf, Dr. Dirk Verdoes TNO at SRNL on April 2, 2014
- Design Test Reactor (Proteaf coordinating with TNO to complete design for equipment)
- Two subcontracts, (1) equipment and (2) technical support, awarded to Proteaf on July 31, 2014
- The equipment was delivered to SRNL on September 30, 2014

Future Directions

Plans for FY 15 include the following:

- Modeling the Helical Reactor – Max Gorenssek
- Complete Hazard Assessment and Procedure Development – Dan Lambert
- Set up the Helical Reactor System – Proteaf and SRNL
- Experimental – Dan Lambert, Jack Zamecnik and Technicians
 - Phase 1 -- Demonstrate high solids mixing – October 2014
 - DWPF slurries are rheologically thick mixture of insoluble solids and solution
 - Maintaining well mixed slurry is key in controlling chemical reactions
 - Laminar flow with oscillation is used for good mixing
 - Phase 2 – Demonstrate slurry neutralization – November 2014
 - The first and simplest chemical reaction is neutralization of NaOH with acid
 - Neutralization will be characterized to determine kinetics of reaction
 - Simple slurry with added acid will be used to demonstrate neutralization
 - Phase 3 – Demonstrate mercury reduction – December 2014
 - One of the more complicated reactions is reduction of mercury
 - This requires a reducing acid (any acid can neutralize NaOH)
 - Reduction demonstrates reaction producing offgas (carbon dioxide)
 - Sample Analysis and Report Writing – January 2015

FY 2014 Publications/Presentations

D.P. Lambert, Reinventing the Nuclear Waste Chemical Processing Flowsheet using Advanced Continuous Chemical Reactors and Separations, Midyear Review of Process Intensification and Smart Manufacturing Projects, LDRD-2014-00097, August 14, 2014.

References

None

Acronyms

DWPF Defense Waste Processing Facility

OBR Oscillating Baffled Reactor

SRNL Savannah River National Lab

TNO Essentially the national laboratory of Netherlands

Patent Apps/ Patents Awarded

None

Total Number of Post-Doctoral Researchers

None

Smart Manufacturing: replacing analytical sample control with model predictive control

Project Team: M.B. Gorenssek (Primary), D.P. Lambert, and T.B. Edwards

Subcontractor: C.-C. Chen (Texas Tech University)

Project Start Date: February 11, 2014

Project End Date: September 30, 2014

Liquid waste operations at SRS rely on sampling and analysis for product quality control, dictating long wait times and round-the-clock analytical staffing. We are working toward a detailed model of Sludge Receipt and Adjustment Tank (SRAT) and Slurry Mix Evaporator (SME) operations that could be used instead of sampling and analysis to control Defense Waste Processing Facility (DWPF) operations. This requires a firm grasp of sludge properties, since the model's predictions need to be at least as reliable as the analyses it is intended to

replace. We have teamed with a world-class electrolyte properties expert to build the best possible sludge properties model. Our team also includes one of the DWPF Product Composition and Control System (PCCS) developers who knows the uncertainties in the sludge sample analyses and their impact on product quality requirements. The work to date has focused on demonstrating this capability with bench scale sludge simulant experiments.

FY2014 Objectives

- Complete aspenONE® sludge properties model for use with formic acid flowsheet
- Quantify potential savings (cost and schedule) from elimination of sample-and-hold dead time
- Complete aspenONE® lab scale/simulant SRAT and SME process model
- Demonstrate lab scale/simulant SRAT and SME process model that can predict analyses used by PCCS with comparable or better confidence in real time

Introduction

Nuclear materials processing across the DOE complex uses traditional analytical sample control, relying on hold points at critical steps to verify by analysis that composition/properties meet product acceptability criteria. Waiting for analyses accounts for much of the processing time. Analyses also add cost and require round-the-clock laboratory staffing. SRNL sees radiochemical processes of the future as highly automated systems that take advantage of SM concepts, using advanced automation, process control, and information technology to optimize performance.

We are developing a model of the DWPF sludge treatment process that will provide material balances with sufficient detail to replace analytical sampling hold points. This includes an electrolyte properties model tailored to DWPF compositions, capturing only those components needed for process control. The model will be robust and fast enough to serve as the basis for a truly predictive control system. The immediate significance is that this has the potential to reduce batch processing times up to 40%, increasing DWPF capacity by up to 67%. Fewer analyses would be needed, and could be scheduled during normal working hours (as confirmation), reducing analytical costs and staffing needs. Finally, this will represent a first step toward implementation of SM concepts at SRS, leading the way toward similar improvements in other SRS facilities.

When fully implemented, SM would have the potential to allow global optimization of SRS operations, enabling rapid, effective response to any changes in manufacturing conditions (e.g., funding, mission, staffing, priorities, etc.) This requires good real-time models of SRS processes. SRNL has the opportunity to establish technical leadership in SM since it has direct access to actual nuclear waste operations and the requisite modeling expertise. The significant cost savings that could be demonstrated by application of this technology to DWPF operations should open up other funding opportunities.

Approach

DWPF was originally intended to use an on-line predictive PCCS to control glass composition using glass properties models and upstream analyses. However, due to the complex nature of the sludge, which encompasses much of the periodic table, the PCCS concept was reduced to an off-line spreadsheet still used in conjunction with manually entered treated sludge sample analyses to make processing decisions. Our objective is to create a process model that can provide stream property information to PCCS in real time instead of relying on time-consuming and expensive analytical measurements. This will allow the PCCS to be fully automated as originally intended and shorten batch processing times.

We are building the process model using sludge simulant as a starting point and to validate it against SRNL bench scale SRAT and SME data. This provides a well-characterized basis for the model and access to a broad range of experimental data for validation. The process model is being built using aspenONE® Engineering, and invokes the Chen Electrolyte NRTL model for sludge properties. We are teaming with Prof. Chau-Chyun Chen, author of the Chen properties model, to ensure success. Prof. Chen has a strong track record of successfully developing properties models for complex chemical systems. Correctly accounting for model and measurement uncertainties is another major challenge. Our team includes the statistician who helped write and now maintains the PCCS spreadsheet. He has unique knowledge of the uncertainties in the process measurements and laboratory analyses, and is responsible for quantifying the uncertainties in the model predictions.

Results/Discussion

Progress was significantly hurt by procurement issues. Specifically, the properties model subcontract with TTU was not placed until mid-June, forcing an unplanned, 4-month delay. Consequently, the aspenONE® sludge properties model could not be finished until September 24. It includes all necessary thermodynamic parameters for the aqueous electrolytes, covering phase equilibria for various volatile components and mercury. Soluble electrolyte species include: NaCl, NaF, NaNO₂, NaNO₃, Na₂CO₃, Na₂SO₄, NaCOOH, KNO₃, Ca(NO₃)₂, NaAl(OH)₄, NaOH, B(OH)₃, Cr(NO₃)₃, Na₂SiO₃, and Na₂C₂O₄. The following major subsystems were also explicitly modeled and compared with experimental data available in the literature: CO₂-H₂O and CO₂-H₂O-NaOH VLE, HNO₃-H₂O and HNO₃-H₂O-NaNO₃ VLE, HNO₂-H₂O and HNO₂-HNO₃-H₂O VLE, HCOOH-H₂O and HCOOH-H₂O-salt VLE, and H₂C₂O₄-H₂O VLE and SLE. A draft report was submitted to SRNL by TTU on October 1.

Experiments with sludge batch simulant SB6H were chosen as the basis for the bench scale SRAT and SME sludge processing model, because a wealth of data from these tests, which were conducted about two years ago, is readily available. Analyses of SB6H samples were used to prepare a stream composition for aspenONE®. The MIXCISLD stream structure was invoked, with solutes placed in the MIXED substream and insoluble solids in CISOLID, where they are treated as inert with respect to solubility equilibria. Figure 1 shows the resulting stream composition. A significant discrepancy between measured and calculated insoluble solids was found. Solids calculated from analyses are ~30% higher than those actually measured. This suggests an apparent disconnect between the assumed and

actual forms of Fe and Al species, which constitute the bulk of the insoluble solids. XRD and SEM analyses in process to resolve difference

Data sets for model demonstration have been identified and construction of an aspenONE® model of the bench scale SRAT and SME experiments is underway. An extension until January 31, 2014 due to the delayed start has been given.

FY2014 Accomplishments

- Chen electrolyte-NRTL sludge properties model for use in aspenONE® flowsheet model of the formic acid SRAT/SME sludge treatment process has been completed
- Sludge batch simulant SB6H experiments selected for model development and demonstration and sludge composition modeled in aspenONE®
- Flowsheet model development begun, on track for completion by January 31 deadline

Future Directions

- Extend subcontract with TTU to add glycolate chemistry to properties model for simulation of new glycolic acid flowsheet scheduled for implementation at DWPF
- Complete aspenONE model using ® formic acid flowsheet sludge properties model developed by TTU
- Prepare estimate of potential savings (cost and schedule) at DWPF from elimination of sample-and-hold dead time
- Demonstrate formic acid flowsheet lab scale/simulant SRAT and SME process model that can predict analyses used by PCCS with comparable or better confidence in real time
- Extend lab scale/simulant SRAT and SME process model to glycolic acid flowsheet

FY 2014 Publications/Presentations

1. Mid-year project review (Power Point presentation), SRNL/703-41A, Ellenton Room, August 14, 2014.
2. M.B. Gorenssek, D.P. Lambert, T.B. Edwards, and C.-C. Chen. "Smart Manufacturing: replacing analytical sample control with model predictive control," poster SRNL-STI-2014-00497, LDRD Year End Review and Poster Session, Aiken County Applied Research Center , October 15, 2014.

References

None

Acronyms

DOE	Department of Energy
DWPF	Defense Waste Processing Facility
NRTL	Non Random Two-Liquid
PCCS	Product Composition and Control System
SEM	Scanning electron microscope

Table 3A. SB6H insolubles			Table 3B. SB6H solubles			Table 4. Total Na distribution		
insoluble solids	MW	g/L slurry	soluble solids	MW	g/L slurry	assumed Na distribution	MW	(mole %)
Al(OH) ₃	78.00356	50.13489	NaAl(OH) ₄	118.0012	16.12812	Al(OH) ₄ ⁻	95.01145	11.50%
B ₂ O ₃	69.6202	0.577301	B(OH) ₃	61.83467	0.019737	COOH ⁻	45.01829	0.00%
Ca(OH) ₂	74.09268	1.255906	Ca(NO ₃) ₂	164.0879	0.030818	CO ₃ ²⁻	60.0103	14.71%
Cr(OH) ₃	103.0198	0.009383	Cr(NO ₃) ₃	238.0126	0.077678	C ₂ O ₄ ²⁻	88.0207	2.86%
Cu(OH) ₂	97.56068	0.43256	KNO ₃	101.1032	0.7452	Cl ⁻	35.45325	2.04%
Fe(OH) ₃	106.869	47.69634	Na ₂ SO ₄	142.0431	4.3464	F ⁻	18.99895	0.00%
HgO	216.5894	0	Na ₂ SiO ₃	122.0632	0.0399	NO ₂ ⁻	46.00609	35.75%
K ₂ O	94.196	0	NaCOOH	68.00751	0	NO ₃ ⁻	62.00549	8.49%
Mg(OH) ₂	58.31968	1.073373	Na ₂ CO ₃	105.9887	9.269774	OH ⁻	17.00789	19.50%
MnO ₂	86.93685	13.801	Na ₂ C ₂ O ₄	133.9991	2.279057	SO ₄ ²⁻	96.0647	5.15%
Na ₂ O	61.97894	0	NaCl	58.44247	1.41734	total		100.00%
Ni(OH) ₂	92.70468	5.540852	NaF	41.98817	0	soluble Na	27.3331	g/L slurry
PdO	122.4194	0	NaNO ₂	68.99531	29.32842			
Rh ₂ O ₃	134.9043	0	NaNO ₃	84.99471	8.576214			
RuO ₂	133.0688	0	NaOH	39.99711	9.274497			
SiO ₂	60.0843	0.239952	total		81.53318			
Sr(OH) ₂	121.6347	0	target		88.751			
TiO ₂	79.8788	0.07359	delta (%)		-8.1325			
Na ₂ U ₂ O ₇	634.0331	0						
Zn(OH) ₂	99.40468	0.035657						
ZrO ₂	123.2228	0.419825						
CaCO ₃	100.0872	0.324476						
MgCO ₃	84.3142	0.29682						
total		121.9138						
target		93.626						
delta (%)		30.2136						

Figure 1. Sludge batch simulant SB6H composition determined from analyses for use in aspenONE® model.

SM	Smart Manufacturing
SME	Slurry Mix Evaporator
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TTU	Texas Tech University
VLE	Vapor-liquid equilibrium
XRD	X-ray diffraction

Patent Apps/ Patents Awarded

None

Total Number of Post-Doctoral Researchers

One (Texas Tech University)

Investigation of In-Line Monitoring Options at H Canyon/HB Line for Plutonium Oxide Production

Project Team: L. Sexton, S. Branney, J. Wilson, P. O'Rourke, M. Holland, K. Fuller

Project Start Date: Feb., 2014
Project End Date: Sept. 30, 2014

H Canyon and HB Line have a production goal of 1 MT per year of plutonium oxide feedstock for the MOX facility by FY17 (AFS-2 mission). In order to meet this goal, steps will need to be taken to improve processing efficiency. Process intensification and smart manufacturing concepts could provide the needed tools to help meet H Canyon/HB Line production goals. One such concept is to implement in-line process monitoring at key measurement points within the facilities. In-line

monitoring during operations has the potential to increase throughput and efficiency while reducing costs associated with laboratory sample analysis. In the work reported here, we mapped the plutonium oxide process, identified key measurement points and data quality objectives, investigated alternate technologies that could be used for on-line analysis that are fit-for-purpose, and initiated a cost benefit analysis.

FY2014 Objectives

- Map the H Canyon/HB Line processing path for AFS-2
- Identify key measurement points for in-line monitoring
- Identify alternate technologies that may be used for in-line analysis
- Estimate the time saving gained for implementation of in-line analysis

Introduction

In-line process monitoring is a concept employed in process intensification and smart manufacturing concepts, which seeks to improve process efficiency, reduce footprint and operating cost, improve safety and quality, and increase sustainability through manufacturing processes and production technologies. The goal of this work was to develop a systematic approach for evaluating a processing path and identifying opportunities to conduct in-line sample analysis to increase throughput and efficiency while reducing costs associated with laboratory sample analysis. H Canyon/HB Line was used as a test bed to develop this strategy in an effort to use in-line monitoring to speed up the safe clean-up of legacy nuclear material from weapons production. The concepts developed during the study could also be applied to other DOE facilities.

In 2011, the H Canyon and HB Line facilities were chosen to begin dissolving and purifying excess plutonium oxide for initial feedstock material for the Mixed Oxide (MOX) Fuel Fabrication Facility (AFS-2 mission). The goal for production is to provide 1 metric ton (MT) per year of MOX feedstock by FY17. Meeting this goal will be challenging unless measures are taken to reduce waste and/or increase throughput. The process intensification/smart manufacturing concept of in-line process monitoring could provide the needed tools to help meet H Canyon/HB Line production goals.

For process monitoring and accountability, H Canyon and HB Line typically pulls samples at various points during processing, which are sent to F/H Laboratory or HB Line Laboratory for analysis. The analyses performed in F/H Laboratory can take several days to complete leading to pauses in production. Setting up in-line monitoring equipment at the key measurement points within the process

could lead to significant time savings and increased processing efficiency. Reducing the number of samples pulled for laboratory analysis would also lead to a reduction in cost for facility operation.

Approach

In order to complete the proposed work, five tasks were proposed. The first task was to map the H Canyon/HB Line processing path for plutonium oxide production. This included developing a flow chart of the process with current sampling locations and analysis techniques used at each point. The second task was to identify key measurement points during the process for quality control and accountability and identify any gaps in the current monitoring scheme. The third task was to identify alternate technologies that could be used in-line for process control and accountability to replace the currently used laboratory techniques. Task four was to perform a cost benefit analysis to provide an estimate of the potential savings in time and money resulting from implementation of in-line monitoring. The final task will be to provide an overview (conceptual outline) of the methodology that will be used to calibrate each proposed in-line instrument and to achieve traceability to SI for the measurement system (FY15 task).

Results/Discussion

Tasks 1-2, described above, were completed during the reporting period. The plutonium oxide production processing path in H Canyon and HB Line was mapped out using documentation on the AFS-2 mission and expert input from the facilities. Sampling points and analytical techniques used on collected samples were also identified. The key measurement points for process control and accountability were also identified through H Canyon/HB Line documents and interviews with personnel. Key measurement points/hold points identified in H Canyon include several tanks prior to transfer to HB Line that measure for Pu valence state, process related conditions (acidity, impurities, Pu concentration) and accountability (isotopics & Am-241). Several hold points for total Pu and acidity were identified in HB Line. Hold points were also identified on the back end of the process (i.e., solution returning to H Canyon from HB Line) for verifying the oxalate kill step was completed.

Task 3, which involves alternated technology identification, was at 80% completion at the end of the reporting period. Several technologies amenable to in-line utilization were suggested to replace the currently used laboratory techniques. These include:

- X-ray fluorescence (XRF) to replace inductively coupled plasma mass spectrometry (ICP-MS) for metal impurity analysis (F/H Lab),
- In-line gamma spectroscopy to replace isotope dilution mass spectrometry (IDMS) for Pu isotopics and total Pu (F/H Lab) and alpha spectroscopy and ChemCheck for Pu isotopic ratio analysis and U concentration (F/H Lab)
- UV-vis spectroscopy to replace free acid titration (F/H Lab) and oxalate titration (HB Line Lab) for acidity and Pu DAS for total Pu (HB Line Lab)

After identification of these technologies, XRF and gamma spectroscopy were selected for initial proof-of-concept studies. XRF spectra was taken of a liquid Pu sample and an evaporated sample on a thin polymer film (Figure 1). Liquid sampling shows good sensitivity however, the background is limited by Compton scattering from water. The evaporated sample shows much better sensitivity due to the reduction in background from the water. However with both samples a wide range of impurities can be detected and based on data obtained with multi-element standards the limit of detection is estimated to be around 10-50 ppm. Gamma spectra of a liquid Pu sample was obtained with a High Purity Ge (HPGe) detector (data not shown). Significant scatter background from Cs-137 obscured the Pu peaks in

the sample. Incorporating appropriate shielding into future measurement set ups will eliminate this problem and allow for the determination of Pu isotopics and concentration, with appropriate modeling.

FY2014 Accomplishments

- Created a flowsheet for the AFS-2 plutonium oxide production in H Canyon/HB Line and identified all sampling points and methods used at each point ;
- Determined key measurement points for process monitoring,
- Identified technologies that could potentially replace current methods and be used for in-line process analysis; and
- Conducted preliminary testing with two of the methods to determine suitability.
- Began process model to determine the increase in throughput that would result from utilization of in-line technologies identified.

Future Directions

- Create an overview of methodology for calibrating each instrument and achieving traceability to SI
- Further XRF testing of AFS-2 solutions to determine best method for sample loading.
- Further testing of gamma detection for Pu accountability. Initial measurements were inconclusive as a means of quantifying the Pu content of the AFS-2 material due to the high background at F/H labs and scatter from the Am-241 in the sample. Further testing could mitigate this with appropriate shielding for the detector and sample and appropriate collimation.
- Modeling to quantify Pu from gamma spectra. Modelling will be performed in order to calculate the mass of Pu present in samples in a range of geometries from a collected gamma spectrum. This is a necessary step if any quantification of Pu mass is to be derived from gamma spectroscopy.

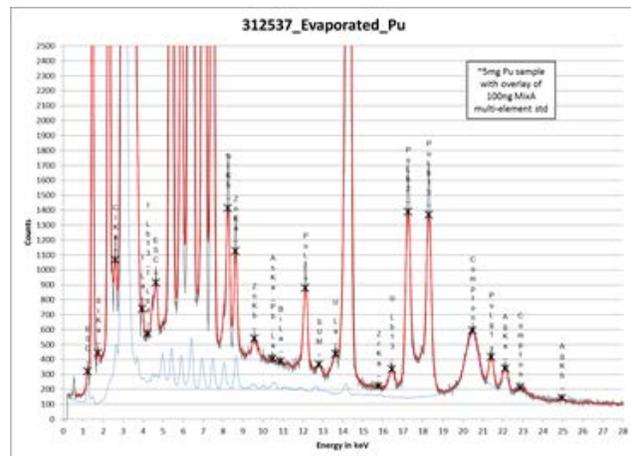
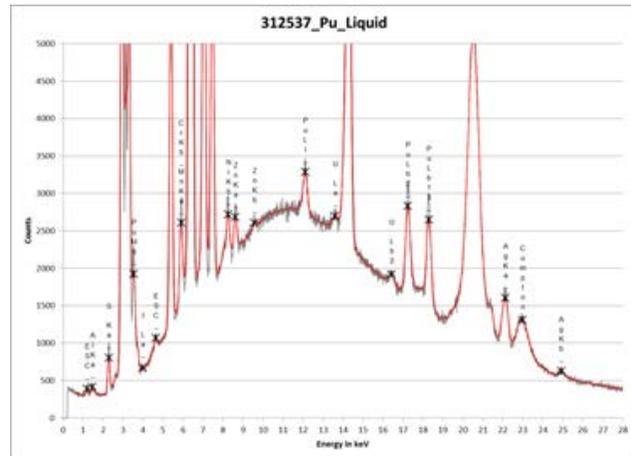


Figure 1. (top) XRF Spectra of liquid Pu sample from batch 3 of AFS-2 campaign, (bottom) XRF Spectra of evaporated Pu sample and a 100 ng mix multi-element standard

Acronyms

AFS-2	Alternate Feedstock – 2
HPGe	High Purity Germanium
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IDMS	Isotope Dilution Mass Spectrometry
MOX	Mixed Oxide
MT	Metric Ton
XRF	X-ray Fluorescence

Patent Apps/ Patents Awarded

None

Total Number of Post-Doctoral Researchers

1 - William Hardy

Reprocessing of Nuclear Fuels Using Chromatographic Separations

Project Team: D. T. Hobbs (Primary), T. Hang, T. S. Rudisill, J. A. Pike

Project Start Date: April 1, 2014

Project End Date: September 30, 2014

This project sought to evaluate reprocessing of nuclear fuels using continuous chromatographic separations. Chromatographic separations offer the opportunity to reduce facility footprint and secondary waste generation compared to conventional solvent extraction and ion exchange-based processes. Two flowsheet concepts were identified that use simulated moving bed chromatographic cycles to achieve the desired radiochemical separations. A commercial software modelling tool, Aspen Chromatography, was benchmarked against literature data and then used to develop a 2-cycle model demonstrating successful separation of cations and anions (Cycle 1) and separation of actinides and lanthanides (Cycle 2).

FY2014 Objectives

- Evaluate nuclear fuel reprocessing flowsheets that use chromatographic separation for the recovery and purification of radiochemical components in used nuclear fuels.
- Adapt commercially available software to model continuous chromatographic separations.

Introduction

Aqueous-based flowsheets have dominated nuclear fuels cycles for the recovery of uranium, transuranics (e.g., Pu, Np, Am, Cm) and fission products (e.g., ^{137}Cs , ^{90}Sr , and ^{99}Tc). Liquid-liquid extraction is typically used to provide the bulk separation of the desired element from other components and fission products that are present in the irradiated nuclear fuel matrix. Ion-exchange and precipitation processes are frequently used after liquid-liquid extraction to produce materials that are of high chemical and radiochemical purity. Typically, these separation processes are operated in batch mode in equipment of different sizes.

Due to the nature of these different separation processes, it is difficult to integrate all of the separation and purification techniques into a continuous process with a small footprint. Adapting chromatographic separation technology to reprocessing of nuclear fuels offers the opportunity to simplify the operational footprint of the reprocessing facility and the possibility of operating in a continuous mode that would allow smaller footprint. Reprocessing conditions could be adjusted relatively easily to adapt to the type of fuel being processed and to changes in the target analytes to be recovered and purified.

Two generalized flowsheet alternatives were considered in this evaluation. In both alternatives the nuclear fuel would be first dissolved in nitric acid. Following dissolution the uranium, plutonium and neptunium would be recovered in Flowsheet 1 by a liquid-liquid extraction. The raffinate from the liquid-liquid extraction separation would then be sent to the chromatographic separation stage for separation and recovery of the other nuclear fuel components. In Flowsheet 2, the liquid-liquid extraction is eliminated and only chromatographic separation cycles are used to separate and recover uranium, transuranics, fission products and other components in the dissolved nuclear fuel. To our knowledge, a continuous chromatographic flowsheet for nuclear fuel reprocessing has not been previously evaluated.

Approach

For this project, we assumed that the reprocessing facility would have a nominal operating capacity of 1000 mT/y using used light water reactor fuel that is cooled for 5 years after 50 gigawatt day per metric tonne of initial heavy metal exposure [1]. To simplify the modeling effort, we tracked fourteen key components of the dissolved fuel that represent actinides, fission products and activation products. Table 1 provides a list of the 14 components, representative ionic species and concentrations that would be present in the raffinate after liquid-liquid extraction of the uranium.

Element	Ionic Species	Raffinate Feed to SMB (kg/day)
Am	Am ³⁺	3.21
Ce	Ce ^{3+/4+}	18.0
Cm	Cm ³⁺	0.38
Cs	Cs ⁺	19.6
I	I ⁻ / IO ³⁻	0.04
Mo	MoO ₄ ²⁻	12.6
Nd	Nd ³⁺	30.7
Np	NpO ₂ ⁺ / NpO ₂ ²⁺	3.25E-03
Pu	Pu ⁴⁺	5.85E-04
Ru	Ru ⁴⁺ / RuO ₄ ⁻	8.59
Sr	Sr ²⁺	6.05
Tc	TcO ₄ ⁻	2.84E-02
U	UO ₂ ²⁺	0.14
Zr	Zr ⁴⁺ / ZrO ₂ ²⁺	25.49

Simulated Moving Bed (SMB) chromatography has been widely used in petrochemical, pharmaceutical and fine chemical separations. In this technique, chromatographic columns are arranged in a cyclic manner to separate feed into two product streams (extract and raffinate) with minimal used of an eluent (solvent). The process is operated with continuous feed/eluent injection and extract/raffinate collection (Figure 1). Recently Kawajiri, et al. have reported using this method to efficiently separate the chemically similar lanthanide ions, Nd³⁺ and Sm³⁺ [2]. Based on this work, they have proposed that the SMB technique is attractive for other difficult separations such as separating minor actinides from lanthanides and separating individual minor actinides such as Am and Cm.

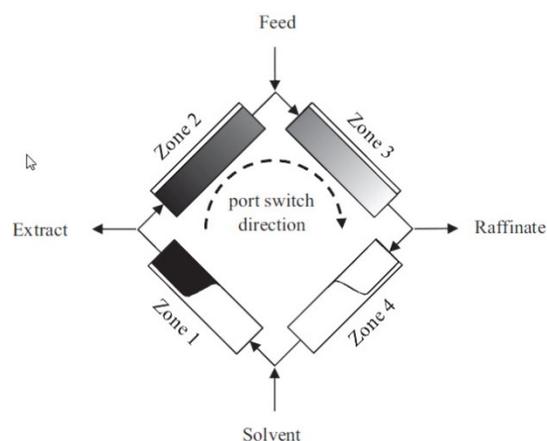
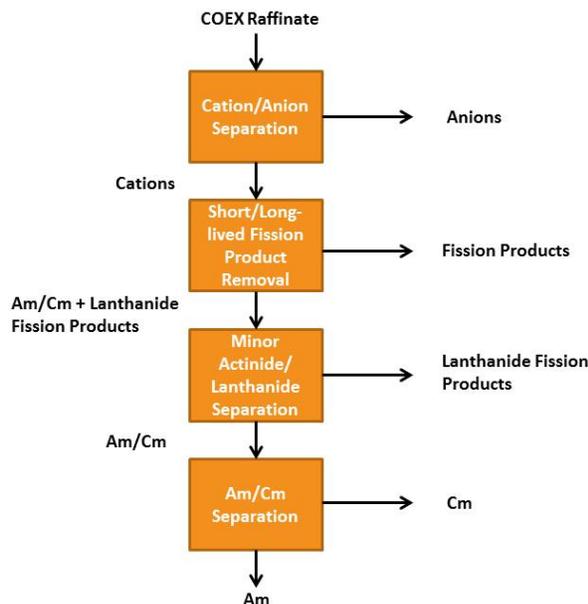


Figure 1 One-cycle SMB System with Continuous Feed Injection



The project explored a four-cycle SMB flowsheet as represented by the schematic in Figure 2. The first stage provides a bulk separation of cationic species (e.g., Am^{3+} , Sr^{2+} , Cs^+) from anionic species (e.g., I^- , TcO_4^-). The second stage separates cationic species having low charge (e.g., Cs^+ , Sr^{2+}) from more highly charged (e.g., Am^{3+} , Nd^{3+}) cationic species. The third stage separates actinides (e.g., Am^{3+} , Cm^{3+}) from lanthanides (e.g., Ce^{3+} , Nd^{3+}). The fourth stage then provides a final separation of the individual actinides (e.g., Am^{3+} and Cm^{3+}).

Figure 2. Schematic Four-Stage SMB Flowsheet

Results/Discussion

Aspen Chromatography software offered by Aspen Technology was selected to model the chromatographic stages. Aspen Chromatography provides a ready-to-use module for standard SMB simulations and was chosen since Aspen software (e.g., Aspen Plus, Aspen Custom Modeler) has been successfully used for process flowsheet modeling at several SRS facilities including processing of nuclear fuels.

The Aspen SMB process simulator was first benchmarked using the literature data for separation of the two lanthanide ions, Nd^{3+} and Sm^{3+} as reported in reference 2. Having established that the commercial software provided efficient separation of Nd^{3+} and Sm^{3+} , the next step was to add additional SMB cycles. Linking successive SMB modules had not been previously accomplished using the Aspen Chromatography software. Working with Aspen Technology, we successfully developed a two-cycle SMB process flowsheet model. The two-cycle model was then evaluated.

Figure 3 shows a series of snapshots over time for the extract and raffinate products with time for the first cycle in which cations are separated from anions. At this stage of flowsheet development, the simulations assume separation factors that will accomplish the desired level of separation. In Cycle 1 (Figure 3), process parameters (flow rates, switching time etc.) were adjusted to yield excellent results with purities of 87.6% and 99.999% for the raffinate and extract, respectively. Cycle 2 (Figure 4) was not fully optimized and, consequently displays poorer separation than in Cycle 1 (raffinate purity: 67.4% extract purity: 68.7%). Optimization of input parameters would significantly improve Cycle 2 performance.

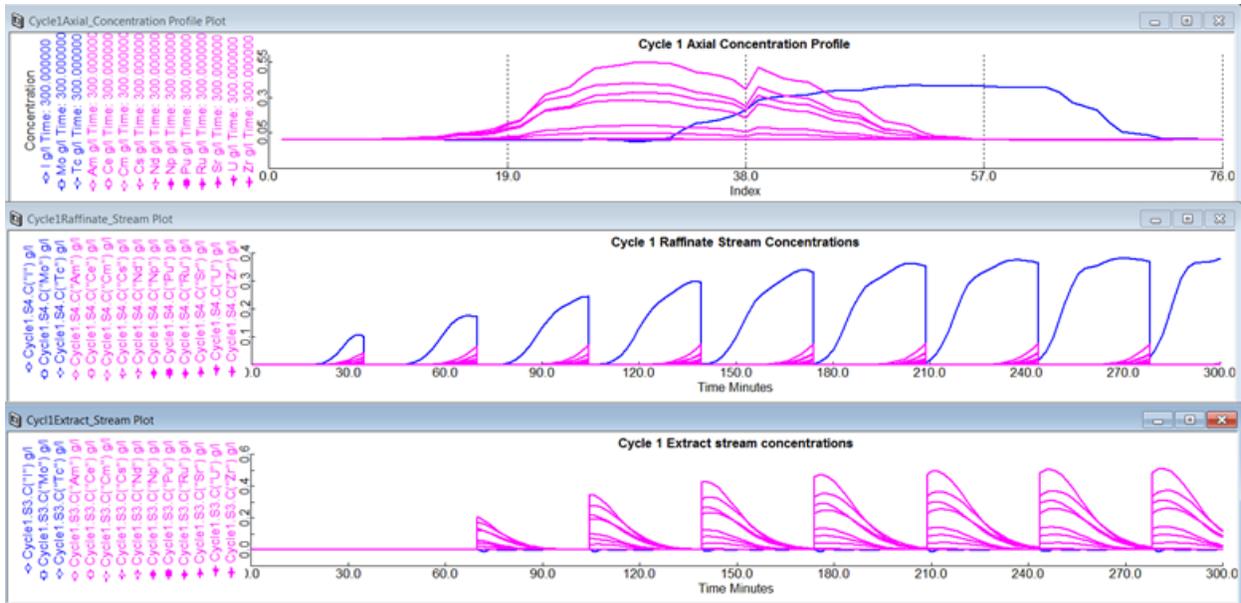


Figure 3. Cycle 1 SMB Model Result

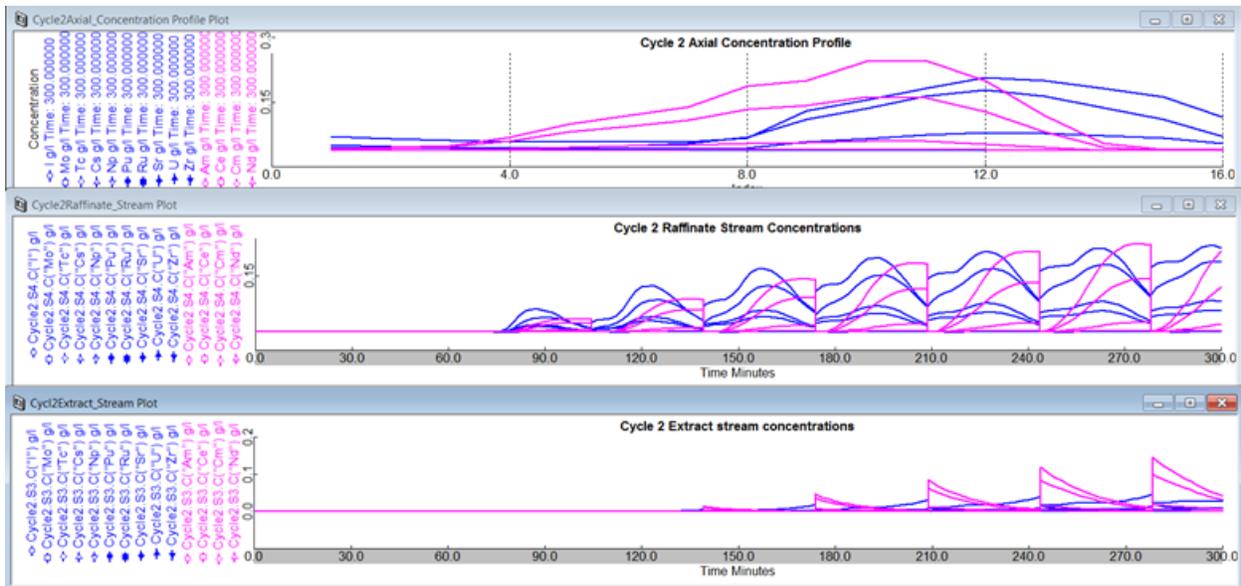


Figure 4A. Cycle 2 Model Result

FY2014 Accomplishments

- Identified two flowsheet concepts for the full recycle of used nuclear fuel
 - Flowsheet 1: combination of solvent extraction and chromatographic separations
 - Framework 2: all chromatographic separations
- Integrated literature data for lanthanide separation chromatographic separations into Aspen Chromatography module (commercial software)
- Developed 2-cycle SMB flowsheet using Aspen Chromatography module (first example of coupling of multiple SMB cycles)

Future Directions

- Complete flowsheet development for processing a COEX raffinate
 - Couple four separation stages; anion/cation, short-lived fission products, minor actinide/lanthanide, Am/Cm
 - Add stages for fuel dissolution in nitric acid and solvent extraction for U & Pu recovery (COEX)
- Develop conceptual Flowsheet 2 that eliminates solvent extraction and adds SMB-stage for co-recovery of U & Pu at front-end of process
- Perform parametric studies with both conceptual flowsheets to identify advantages and disadvantages for each flowsheet

FY 2014 Publications/Presentations

4. Presented poster (SRNL-STI-2014-00499) at SRNL Annual LDRD Year End Review

References

1. J.D. Law, et al. Separation and Waste Form Campaign Full Recycle Case Study, Idaho National Laboratory, FCRD-SWD-2013-000380, September 30, 2013.
2. Sreedbar, B., D. T. Hobbs, and Y. Kawajiri, Simulated Moving Beds Chromatography Designs for Lanthanide and Actinide Separations using Reillex HPQ™ Resin, *Separation and Purification Technology*, **2014** (136) 50-57.

Acronyms

SMB Simulated Moving Bed

mT/y metric tonne per year

Patent Apps/ Patents Awarded

None

Total Number of Post-Doctoral Researchers

None

Selective Electrochemical Extraction

Project Team: L. Olson (Primary), B. Garcia-Diaz, Hector Colon-Mercado, M. Martinez-Rodriguez, and J. Gray

Project Start Date: February 1, 2014

Project End Date: September 30, 2014

Nuclear separations and reprocessing using electrochemical methods in aqueous solutions is a challenging alternative to the more traditional PUREX methods. If workable, however, several advantages could be realized from such a change, such as waste reduction and easier removal of specific elements. Many fission products with half-lives over a year cannot currently be plated directly due to reduction potentials below the water stability limit. There are various other

electrodeposition methods however that may still allow for electrochemical separations. In this short-term LDRD project, researchers examined the feasibility of suppressing the water stability limit using tin doped indium oxide electrodes to electroplate molybdenum metal from a fission product waste stream. Fission product surrogates and simplified solution chemistries were used.

FY2014 Objectives

- Prove electrochemical separation as potentially viable for nuclear reprocessing using incremental approach.
- Predict thermodynamic parameters for specific electrochemical separation techniques
- Initiate study with electrode coating intended to suppress hydrolysis to allow for direct plating of elements. Initial studies will use molybdenum.
 - Molybdenum-99 precursor for technetium-99m is used heavily in medicine
 - Ability to selectively remove molybdenum continuously while leaving rest of fission products in place could potentially lead to dramatic cost savings.
 - Electrodeposition of a metallic molybdenum plate directly could potentially enable a host of industrial uses

Introduction

Electrochemical separations of fission products is challenging because many fission products cannot be directly electroplated within the water stability window in aqueous systems and engineering solutions to these difficulties have not been extensively studied. This work addresses this barrier by seeking to perform direct electrochemical separation of a fission product surrogate, molybdenum, by use of a novel electrode surface. Molybdenum has not previously been directly plated because molybdenum electroplating would occur below the water potential stability limit. However, direct plating of molybdenum from solution may be possible if hydrogen evolution can be kinetically limited through the choice of electrode materials. Electrode materials such as lead, tin, aluminum, and oxides such as indium tin oxide (ITO) have low hydrogen evolution exchange current densities which should allow for a lower water stability limit. Molybdenum co-plating was also studied as a lower risk alternative for electrochemical separation of molybdenum from a fission product waste stream. However, because co-plating of molybdenum requires use of a citrate bearing solution and Fe-group metals as dopants in the solution to aid in co-plating, this was a less desirable approach.

Fission Product Yield	
Yield (%)	Isotope
6.8	$^{133}\text{Cs} \rightarrow ^{134}\text{Cs}$
6.3	$^{135}\text{I} \rightarrow ^{135}\text{Xe}$
6.3	^{93}Zr
6.1	^{99}Mo
6.1	^{137}Cs
6.1	^{99}Tc
5.8	^{90}Sr
2.8	^{131}I
2.3	^{147}Pm
1.1	^{149}Sm

Table 1. Fission products from thermal neutron fission of U-235. FP yield below 1% ignored.

Molybdenum-99 is an isotope with a relatively short half-life that can be produced in relative high quantities from fission of uranium-235. Molybdenum-99 is also medically important because it is the generator of technetium-99m, which has a host of medical imaging applications. Technetium can be directly electroplated.

The current state of the art is that most transition metals can be electroplated, but molybdenum can only be co-plated with other metals and cannot be electroplated by itself. Fe-group metal intermediaries and a citrate solution must currently be used to co-plate molybdenum, further complicating potential process flows. If molybdenum could be directly electroplated, molybdenum and technetium could be electrochemically removed at high purities from current reprocessing cycles. Electrodeposition techniques have been shown to separate cesium, and may work for other fission products. Additional research would be required.

Molybdenum plating has many potential industrial uses that could further benefit from the ability to directly electroplate it. Although molybdenum cannot currently be electroplated by itself, it can be applied by other methods such as thermal spray. Uses for wear resistant and high lubricity molybdenum coatings range from applications inside jet engines to car engine components.

Approach

For direct molybdenum plating, a novel electrode was prepared with a surface intended to increase the water stability window thereby allowing for molybdenum to be directly plated. The electrode surface was sputter deposited ITO on a glass substrate. The ITO is a conductive oxide with low hydrogen evolution exchange current densities. Experimental solutions contained low concentrations of molybdenum salts, covered a wide pH range, used miniature cells to minimize waste, and primarily incorporated analytical voltametric tests such as cyclic voltammetry. Once the general plating characteristics were demonstrated, plating at constant potential was attempted at several pH's and increased molybdenum concentrations, with the subsequent electrode surfaces examined via SEM/EDS and other analytical techniques.

A lower risk option for electrochemical removal of molybdenum from a molybdenum bearing solution is by adding sodium citrate to the solution and co-plating the molybdenum with an iron-group metal. Co-plating was performed for comparison purposes in sodium citrate solutions near pH 7 containing sodium molybdate and nickel sulfate. Lead oxide coated carbon and bulk platinum electrodes were used for the co-plating studies to examine the effect of using a standard non-reactive electrode surface and one that should reduce the hydrogen exchange current density in a manner similar to ITO. Several plating potentials were used that were found in literature with analytical voltametric techniques used initially. Microcells were used to minimize waste. Once methods for co-plating were established, co-plating on both electrode surfaces was performed and evaluated via SEM/EDS.

Results/Discussion

Molybdenum was successfully plated directly on ITO electrodes over a select pH range but with the ITO coating attacked at low pH. Electrochemical and solution parameters were optimized to produce >1



Figure 10. Sputter deposited In-Sn oxide on glass slide.

micron thick molybdenum coatings on ITO sputter coated electrodes in 0.1 M Na_2MoO_4 solutions after being held at -0.65 V vs SHE for 1.5 hr at a current density of about 0.9 mA/cm^2 . Further optimization is likely possible. SEM/EDS verified the electrodeposition of molybdenum. The molybdenum rich coating is inferred to be pure molybdenum metal and not an oxide that was deposited. Further analysis such as grazing incidence x-ray diffraction, x-ray photoelectron spectroscopy, or Auger spectroscopy is needed to prove the exact chemical state of molybdenum. Major results from this research are 1) proof of hydrogen suppression and ability to electrodeposit molybdenum on an ITO coated electrode, 2) optimization of plating pH and 3) determination of the apparent lower limit for molybdenum plating on ITO. Furthermore, the plating efficiency was close to 100% based on the thickness observed in cross-sectional SEM and assuming a pure dense molybdenum metal was deposited.

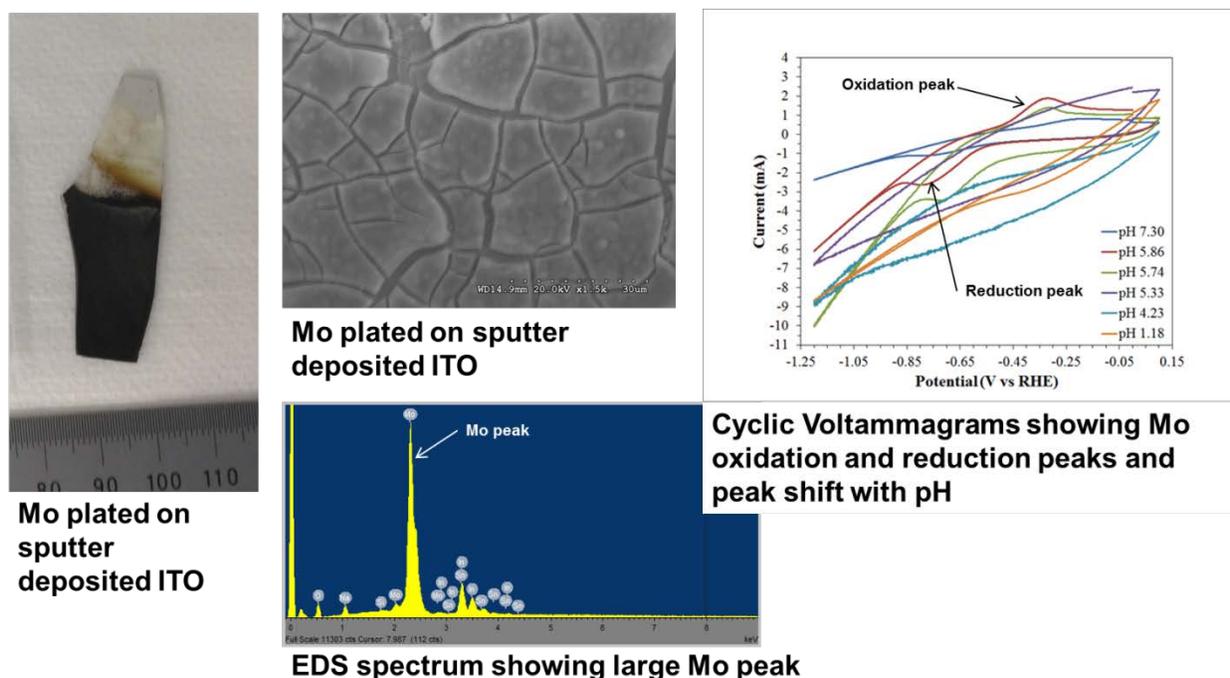
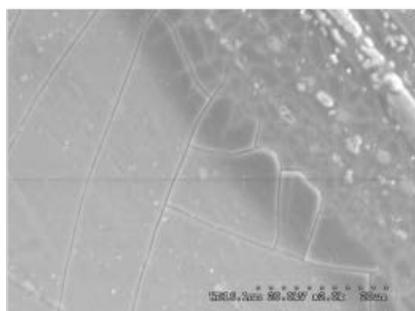
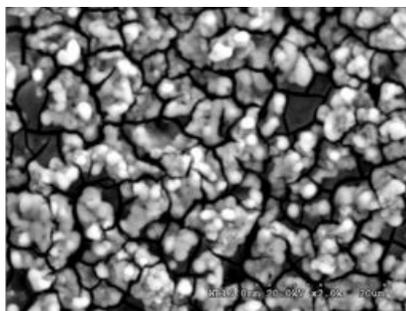


Figure 11. Plating results on ITO coated electrodes.

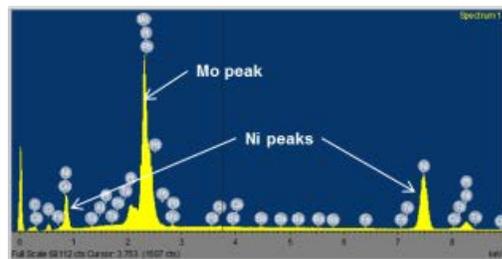
Molybdenum was successfully co-plated with nickel using conditions found in literature. Electrochemical and solution parameters were optimized to produce ~1 micron thick molybdenum-nickel coatings. SEM/EDS indicated successful electrodeposition of molybdenum-nickel. The ratio of molybdenum to nickel was found to vary depending on the electrode substrate material. The Mo:Ni ratio was 1:1 on the Pt and 2:1 on PbO. The plating efficiency on the PbO was ~5% based on the thickness observed in cross-sectional SEM and assuming a pure dense molybdenum-nickel alloy was deposited.



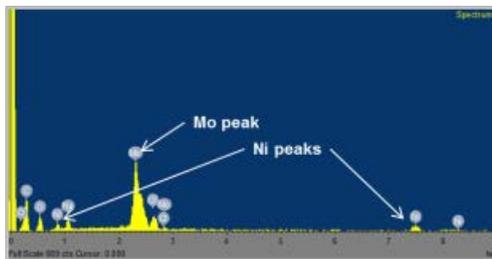
Mo-Ni Plated Pt



Mo-Ni Plated PbO



EDS spectrum showing large Mo and Ni peaks



EDS spectrum showing large Mo and Ni peaks

Figure 12. Co-plating results on Pt and PbO coated electrodes.

FY2014 Accomplishments

- Successfully electrodeposited a relatively thick molybdenum coating without any intermediaries on ITO sputter deposited electrodes from a molybdenum salt bearing solution.
- Achieved near 100% plating efficiency for molybdenum electrodeposit given available data and assumptions.
- Determined molybdenum electroplating is markedly more efficient than co-plating molybdenum-nickel.
- Proved molybdenum can be selectively removed from fission product bearing aqueous streams electrochemically, thereby demonstrating an additional waste treatment method with a simplified system and a fission product surrogate.
- Demonstrated electrodeposition of thick molybdenum-nickel layers from citrate, molybdenum, and nickel bearing solutions.

Future Directions

Future directions that would further enhance the concept of selective electrochemical separations are 1) more analysis of the deposited coatings, 2) further electrode substrate studies, 3) more realistic solutions, 4) research into electrodeposition methods for more fission products and actinides, and 5) testing in a hot cell with actual waste streams. Grazing incidence x-ray diffraction and x-ray photoelectron spectroscopy of the molybdenum coating could verify the oxidation state of the coating to determine if the molybdenum was electroplated in the metallic state, or electrodeposited as an oxide. Determination of adhesion properties of molybdenum coatings would prove valuable to enable their use in industrial processes. Quantification of maximum plating thickness achievable with current ITO coated electrodes would enable estimation of electrode and solution conditions necessary to achieve removal of molybdenum from specific solution volumes. A method of protecting ITO while

retaining hydrogen suppression could allow for wider useful electrode pH range. Fabrication of a high surface area electrode to more efficiently/quickly remove molybdenum from solutions would make the technique more practical. Such an electrode could be achieved by sputtering with ITO a thin sheet and folding it into a canister, or coating screens and placing in series in a canister. Other potential electrode substrates are also promising, and should be investigated. A prototype flow through cell for removal of molybdenum, technetium, cesium, and other fission products and actinides that are known to be electrochemically separable from stereotypical solution streams would further enable the selective extraction concept. Research into electrodeposition methods for other fission products and actinides is also needed. With sufficient support, electrochemical separation promises to be a lower waste producing alternative to conventional aqueous reprocessing methods.

FY 2014 Publications/Presentations

Presented poster at SRNL Annual LDRD Year End Review

References

N/A

Acronyms

ITO: tin doped indium oxide

PUREX: plutonium uranium redox extraction

Patent Apps/ Patents Awarded

None

Total Number of Post-Doctoral Researchers

None

Large Particle Titanate Sorbents

Project Team: K. M. L. Taylor-Pashow (Primary) and D. T. Hobbs

Project Start Date: March 1, 2014

Project End Date: September 30, 2014

This research project was aimed at developing a synthesis technique for producing large particle size monosodium titanate (MST) to benefit high level waste (HLW) processing at the Savannah River Site (SRS). The first application envisioned was the replacement of the current MST with MST of a larger particle size to increase throughput in the

current and future waste processing facilities by increasing filtration rate and decreasing downtime related to filter cleaning. The MST particle size was successfully increased 4-5 times by the addition of a surfactant to the sol-gel synthesis. This led to improvements in filtration rate as measured by a dead-end filter, with filtration rates 80 – 115% higher than that of the standard size MST. Sorption testing with the larger particle size material showed an increase in actinide removal and a slight decrease in Sr removal performance.

FY2014 Objectives

- Increase particle size of monosodium titanate (MST) to improve filtration performance (target 40 – 50 μm)
- Determine improvements to filtration performance obtained with larger particle MST
- Determine impacts of larger particle size on Sr and actinide removal performance
- Increase particle size of MST to enable column deployment (target > 100 μm)

Introduction

The high level waste (HLW) mission at SRS involves the processing of sludge and salt (supernate and saltcake). The sludge is incorporated in HLW glass during the vitrification process, while the salt is treated to remove Cs, Sr, and actinides. The separated radionuclides are incorporated into the HLW borosilicate glass along with the sludge during the vitrification process, while the decontaminated salt solution is disposed of onsite in a grout waste form referred to as Saltstone. The current salt treatment processes are performed at the pilot-scale Actinide Removal Process (ARP) and Modular Caustic-Side Solvent Extraction Unit (MCU) facilities. The larger Salt Waste Processing Facility (SWPF), currently under construction, is designed to have a throughput of about seven times that of the ARP/MCU facilities.

Filtration is the current throughput-limiting step in the ARP/MCU and SWPF. It is believed that the particle size and particle size distribution of the MST are significant contributors to low filtration fluxes that have been observed in the ARP facility. Current purchase specifications allow the vendor to supply MST powder that has as much as 10% of the material with a particle size less than 0.8 μm . The nominal pore diameter of the crossflow filter used in the ARP facility and SWPF is 0.1 μm , and a 0.5- μm filter was recently installed. Thus, the possible high fraction of fines less than 0.8 μm could be plugging the pores of the crossflow filter media resulting in reduced filtration flux. Increasing the particle size and narrowing the particle size distribution would be expected to increase the filter performance and,

therefore, the throughput of both facilities that use crossflow filtration to separate MST solids from supernatants.

Possible delays in start-up of the SWPF could cause an extension of the salt processing campaign, resulting in sludge processing completing prior to completion of the salt processing. The development of processes to either speed processing of salt through the current APR/MCU facilities or to supplement this and the SWPF facility with at-tank treatment processes would help to close this possible gap and allow for completion of salt and sludge processing at the same time. One technology that has been investigated to supplement the ARP/MCU facility is the use of a small column ion-exchange (SCIX) process performed at the waste tank. The proposed technology utilizes crystalline silicotitanate (CST) in a column for removal of the Cs. MST is added directly to the tank to remove Sr and actinides in a batch-contact fashion. The process could be improved by also deploying the MST in a column, either a mixed column with the CST or a separate column; however, the relatively small size of MST currently precludes its use in a column configuration due to very high pressure drop across the column. One objective of this project was to increase the particle size of MST through modification of the synthesis to generate material suitable for column deployment. An additional benefit to column deployment is more efficient use of the sorbent, resulting in less MST (i.e., titanium) being sent to the vitrification process. The solubility of titanium in the current borosilicate glass formulation is limited. Thus, it is likely that the DWPF glass formulation would have to be changed to accommodate increased titanium from the use of both MST and CST.

Approach

MST is synthesized using a seeded-growth sol-gel method optimized to produce spherical particles in the 1-10 μm size range. Researchers explored several changes to the MST synthesis to increase the particle size. Examples of variables that were evaluated included:

- size of seed crystals (i.e. using the current MST as a seed for growing larger particles),
- addition rates of reagents,
- ratio of reagents to seed crystals,
- concentration of seed crystals,
- use of surfactants,
- and reaction temperature.

A series of synthesis experiments were performed, systematically varying the parameters outlined above. The particle size distributions of the product obtained from each reaction were determined through dynamic light scattering (DLS) measurements. The filtration performance of the most promising samples was then determined using 0.45- μm dead-end filters, with results being compared to a sample of vendor supplied MST. In addition to filtration testing, batch contact testing with simulated waste containing Sr and actinides was performed to determine the impacts of the larger size MST on removal kinetics.

Results/Discussion

Of the modifications to the sol-gel synthesis tested, the addition of a surfactant was found to have the greatest impact on the particle sizes obtained. Four different surfactants were tested, a cationic

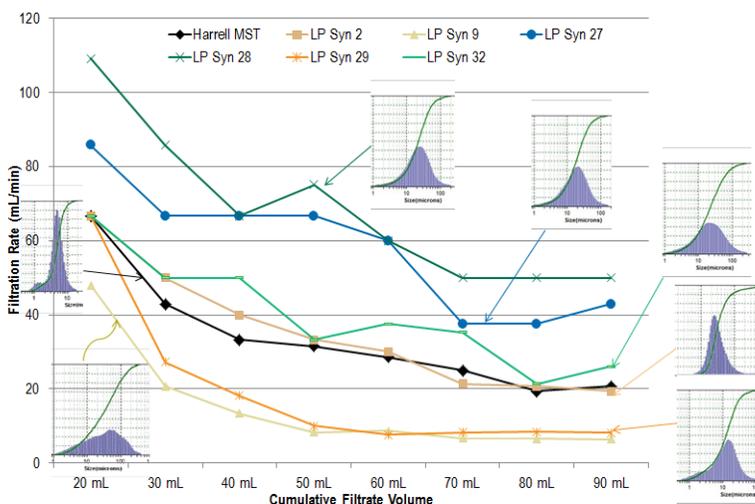


Figure 1. Filtration rates of several samples of varying size MST compared to the vendor supplied material (Harrell MST). MST concentration is 5 g/L; filter is 0.45- μ m Nylon membrane.

A sample of vendor prepared (Harrell Industries) MST was also tested. Initial testing at 0.4 g/L MST concentration did not show much improvement with the larger particle samples over the vendor material, but several of the much larger samples with broad distributions showed a decrease in filtration rate. Testing at 5 g/L showed more significant differences in filtration rates between the various samples and the vendor prepared material (Figure 1). Two of the samples prepared with the Tween 20 surfactant (LP Syn 27 and 28) showed much improved filtration rates over the Harrell MST.

In addition to showing improvements in filtration rate, it was also important to evaluate how the change in particle size affected the Sr and actinide removal performance of

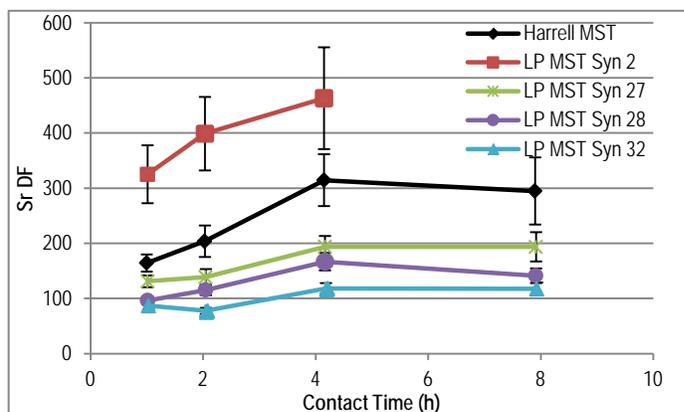


Figure 2. Sr DF versus contact time.

surfactant, an anionic surfactant, and two neutral surfactants. The neutral surfactants provided the most promising results, with Tween 20 providing the largest median particle size of all of the surfactants when the initial screening experiments were performed. Additional syntheses were performed using the Tween 20, varying the Ti:surfactant ratio, and the timing of the surfactant addition (i.e. before or after formation of the seeds). The samples that showed the most promising particle size distributions (i.e. large median size and narrow distribution) were then tested for filtration performance. Filtration testing was performed using a dead-end 0.45- μ m Nylon membrane. A

Table 1. Summary of Particle Size Data for Samples Used in Sorption Testing

Sample ID	M_v (μ m)	Geometric SD
Harrell MST	7.11	1.56
LP Syn 2	5.76	1.62
LP Syn 27	24.34	2.55
LP Syn 28	29.48	2.44
LP Syn 32	33.76	2.91

the material. Therefore, batch contact testing was performed using a simulated high level waste solution. The MST was added at a concentration of 0.4 g/L, and samples were removed after 1, 2, 4, 8, 24, and 168 hours to determine how the particle size influenced the kinetics. Table 1 provides a summary of the particle size distribution values for the samples tested for Sr and actinide sorption.

The Sr decontamination factors (DF) as a function of time are shown in Figure 2. As can be seen from the figure, synthesis 2,

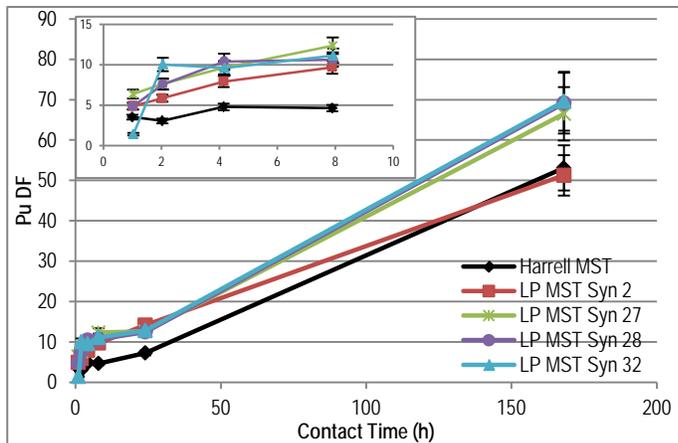


Figure 3. Pu DF versus contact time. Inset shows 1-8 h.

which was a lab prepared sample of normal particle size MST, had the best Sr removal performance. The three larger particle size samples that were tested had less removal than the vendor prepared MST (Harrell MST), and appear to have a lower capacity, not just slower kinetics, as there was not much change between 4 and 8 hours for any of the materials tested, indicating no additional uptake occurring. However, greater than 99% removal was still achieved with all of the materials tested within four hours. In contrast to Sr removal, the Pu removal of all of the lab prepared materials, both normal size MST and the larger particle

size samples, exceeded that of the vendor prepared MST as shown in Figure 3. Just comparing the lab prepared materials, the larger particle size samples showed greater Pu removal than the normal size MST. This trend was seen for the other actinides (U and Np) as well.

FY2014 Accomplishments

- The average particle size of MST was increased ~4-5 times over the standard MST by the addition of surfactant (Tween 20) to the sol-gel synthesis.
- Preliminary (dead-end) filtration testing showed improved filtration rates of 80 – 115% for the two most promising samples.
- Sorption testing with HLW simulant showed a decrease in Sr removal capacity for the larger particle size materials, but still greater than 99% removal (DF >100) by 4 hours.
- Sorption testing showed an increase in actinide removal capacity for all of the larger particle size materials.

Future Directions

- Prepare material suitable for column deployment
 - Modifications to the sol-gel synthesis proved unsuccessful at obtaining particles suitable for column deployment
 - Core/shell method has been identified where an inert core is coated with a layer of MST
- Column Demonstration
 - If successful the core/shell material will be tested in a column configuration using simulated HLW.
- Crossflow Filter Testing
 - Initial filtration testing using small scale dead-end filters has shown some improvement in filtration rate.
 - Testing on a crossflow filter will provide a better estimation of the amount of improvement that could be obtained if larger MST were deployed in ARP or SWPF.

FY 2014 Publications/Presentations

1. A presentation was given at the 248th National Meeting of the American Chemical Society (ACS) in San Francisco, CA August 10-14, 2014. The presentation entitled “Large particle titanate sorbents for treatment of high level waste” was given in the “Young Investigators in Nuclear and Radiochemistry” session of the Division of Nuclear Chemistry and Technology.

References

None

Acronyms

ARP	Actinide Removal Process
CST	Crystalline Silicotitanate
DF	Decontamination factor
DLS	Dynamic Light Scattering
HLW	High Level Waste
MCU	Modular Caustic-Side Solvent Extraction Unit
MST	Monosodium Titanate
SCIX	Small Column Ion Exchange
SRS	Savannah River Site
SWPF	Salt Waste Processing Facility

Patent Apps/ Patents Awarded

None

Total Number of Post-Doctoral Researchers

None

Low Temperature Waste Form Process Intensification

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Project Start Date: February 1, 2014
Project End Date: September 30, 2014

Low temperature waste forms are utilized for the immobilization of low activity waste and other hazardous materials. These waste forms benefit from the use of inexpensive raw materials (and materials that would otherwise be considered wastes themselves) and require a minimal amount of energy for processing. However, the volume of low temperature waste forms can be quite large

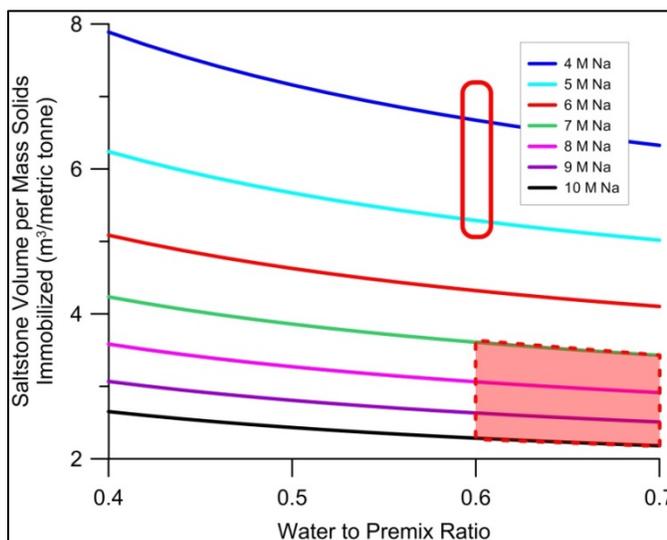
relative to the volume of waste immobilized within them. The process of immobilizing waste in a low temperature waste form would be significantly intensified by increasing the concentration of waste in the material. Improved understanding of the mechanisms of waste incorporation in low temperature waste forms will allow for volume reductions of 50% or more, which will greatly reduce the disposal footprint and cost.

FY2014 Objectives

- Apply *Process Intensification* principles to affect a step change reduction in disposal volume for low activity waste (LAW)
- Significantly concentrate waste while maintaining processing ability and performance of waste form
- Reduce waste form volume, and subsequently disposal costs, by a factor of 2-3

Introduction

The objective of this study is to develop a scientific understanding of the physical and chemical mechanisms by which contaminants are retained in low temperature, cementitious waste forms such that a step-change reduction in waste form volume can be achieved. The figure at right demonstrates this potential reduction in waste form volume. The area within the solid red outline represents the region of recent operation of the Saltstone Production Facility at the Savannah River Site. The area within the dotted and shaded red outline represents compositions tested by SRNL in a preliminary study for Hanford Cast Stone development, where it was shown that a waste form could be produced with a



concentrated feed material and retain acceptable properties. As shown in the figure, concentrating a LAW salt solution feed from 5 M sodium to 8 M sodium would reduce the volume of the waste form by approximately 50%, and would reduce mission life cycle costs by a similar percentage.

Approach

A series of cementitious waste form formulations were developed to characterize the influence of formulation on waste form properties and performance. Geopolymer precursors were added to the formulations to study their potential to better incorporate contaminants from the waste in complex, chemically durable structures. These precursors included metakaolin and fly ash in an alkaline medium. Dry blend powders were combined with simulated salt waste solution using elliptical paddle mixer to produce slurry for testing.

Fresh properties, which dictate the ability to process the waste form, were measured. These included slurry density, rheology, and the formation of bleed water. Performance of the waste form was characterized via several techniques, including isothermal calorimetry, density measurements, porosity measurements, compressive strength testing, determination of leach indices, and hydraulic conductivity measurements.

Results/Discussion

- Fresh properties indicate ability to process using current system at double salt solution concentration
- Identified influence of new premix components on processing of waste form
- Geopolymer additions show potential for rapid increase in curing
 - Curing time varies significantly as a function of dry blend composition
- Clay and geopolymer dry blends can be tailored for fresh properties that are similar to baseline
 - Indicates good ability to process with existing facilities

FY2014 Accomplishments

FY14 progress on this project has demonstrated the ability to significantly increase waste loading in low temperature waste forms via tailoring of the non-waste components.

- A series of novel waste form compositions was developed and fabricated in the laboratory.
- Demonstrated successful immobilization of wastes concentrated to 10 M sodium (double that of current process)
- Fresh properties, which dictate the ability to produce this waste form in an economical facility, have been measured and demonstrate the ability to process with existing equipment
- A manuscript has been submitted to a peer reviewed journal for review.
- The study supported a summer intern at SRNL.

Future Directions

- Measure additional cured properties of new waste forms
 - Curing periods of 30-60 days are needed for optimal performance. An EPA leachability index test method is the current reference for low temperature waste form performance.
- Measure thermal properties of new waste forms
 - A multi-station, isothermal calorimeter is being procured for this study. A matrix of test compositions has been developed and will be tested when a new instrument arrives.
- Study incorporation of new pozzolans in waste form composition
 - Initial results of the FY14 study have demonstrated benefits of including new pozzolans in the batch material for low temperature waste forms. Additional study is needed to determine the impact of these materials on the cured performance of the waste form, particularly with regard to hydraulic properties.

FY 2014 Publications/Presentations

1. K. M. Fox, A. D. Cozzi, K. A. Roberts, and T. B. Edwards, "Cast Stone Formulation for Nuclear Waste Immobilization at Higher Sodium Concentrations," *International Journal of Applied Ceramic Technology* (in press).

References

None

Acronyms

EPA	Environmental Protection Agency
LAW	Low Activity Waste
SRNL	Savannah River National Laboratory

Patent Apps/ Patents Awarded

None

Total Number of Post-Doctoral Researchers

None

Electrodialysis for Intensification of Aqueous Polishing and Other Separations

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Project Start Date: October 1, 2013

Project End Date: January 30, 2015

Aqueous polishing is the preferred method for separating and purifying Pu that is used in the fabrication of MOX fuel as well as other separation activities at SRS. Aqueous polishing is performed using an ion exchange resin that selectively absorbs Pu complexes and allows them to be separated from other fission products. HB-line can perform at SRS in a batch process, but the facility safety basis prevents adding a second resin bed that could make the process semi-continuous. This project investigates the creation of an electrodialysis process that will allow aqueous polishing to be carried out in a continuous operation. Membrane materials have been synthesized and tested for Pu

uptake selectivity and cells have been designed and fabricated for the process.

FY2014 Objectives

- Identify ion exchange membrane polymers that can selectively separate Pu and have sufficient ionic conductivity for electrodialysis
- Measure the partition coefficient for Pu for different ion exchange membrane polymers
- Design and fabricate an electrodialysis cell for aqueous polishing

Introduction

Aqueous polishing is a process where plutonium nitrate anionic complexes $\text{Pu}(\text{NO}_3)_x^{6-x}$ are selectively absorbed onto an ion exchange resin such as Reillex HPQ in order to separate them from other fission products and solution components. Aqueous polishing processes have been developed by LANL, AREVA, and others using ion exchange resins. Typically an acidic solution with a nitric acid concentration of at least 5 M containing Pu complexes is passed over the resin and they absorb. The resin is then washed with 5-8 M nitric acid to remove all remaining impurities. The Pu is then eluted using a mildly acid nitric acid solution.

Electrodialysis is a method commonly used for deionizing water that uses a combination of anion and cation exchange membranes coupled with an electrochemical reactions to drive separation. Electrodialysis techniques can be coupled with ion selective membranes to create a process that will separate specific components of a solution. Additional couples of anionic and cationic membranes can be added to a stack to increase the processing rate.

The process that is being developed will use anion exchange membranes that are selective for $\text{Pu}(\text{NO}_3)_x^{6-x}$ along with a proton exchange membrane such as Nafion to make an electrodialysis cell that creates a continuous aqueous polishing process. The creation of an electrodialysis cell based on the existing Reillex HPQ polymers is not straight-forward because the anion exchange membranes are not as available as membranes and the ionic conductivity of nitrate complexes through membranes of these polymers is not known.

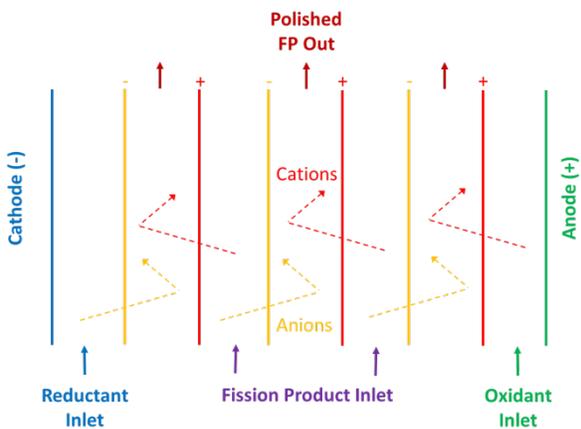


Figure 1. Schematic of an electrodedialysis cell for aqueous polishing

typically has a nitric acid concentration of 0.35 M. The residence time of the fluids in the bed in the batch process is typically 11.5 min. [1]. These design parameters are used as a starting point for cell design. Quarternized Poly-4-Vinylpyridine that is the main polymer component of Reillex HPQ is used as the baseline for investigating alternative polymers.

Approach

Figure 1 outlines the electrodedialysis process for aqueous polishing. The mixed fission product inlet streams are fed in from the bottom in alternating streams. The polished outlet come out in the outlet streams that alternate with the inlet streams. There is also a reductant and oxidant inlet that are for sacrificial solutions that enable the electrode reactions. The electrode reaction forces an ionic current between the anode and cathode. This ionic current carries the anions across the anionic exchange membranes and the cations across the cationic exchange membranes. The plutonium concentration that will typically be in the inlet solution is 5 g_{Pu}/L and the nitric acid concentration is 5-8 M. The outlet solution

Results/Discussion



Figure 2. Electrodedialysis stacks fabricated for proof of concept experiments

is successful.

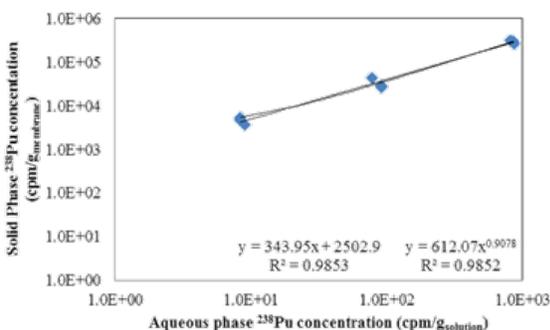
Figure 2 shows a photograph of the electrodedialysis cells that have been fabric. These cells have a 200 cm² active area. The polymers that are being developed by Clemson will be fabricated into circular membranes of 16 cm in diameter that will be used as the anionic exchange membranes in the stack. The designed processing rate through the cells is 5% of the processing rate from HB-line. This should enable relatively simple scale-up of this process through only needing to add more membranes to the stack. The scale-up of this process is planned to be demonstrated in future phases of the project if the proof-of-concept

Polymer Development

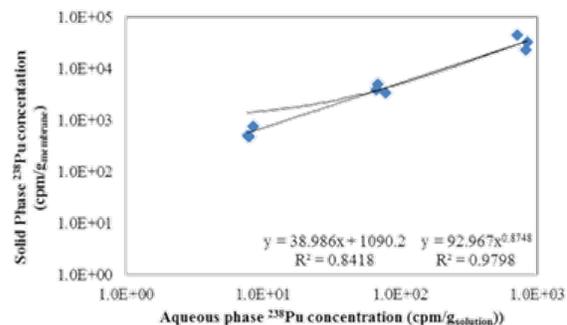
Batch sorption studies were performed to examine the uptake of ²³⁸Pu(IV) on the membranes. As the membranes were cast as one solid piece, they were cut into small sections of similar sizes for use in uptake studies. The pieces were weighed on a microbalance and were approximately the same size and shape. Four ²³⁸Pu(IV) solutions in 8 M HNO₃ were prepared with concentrations of 2.4 dpm/gHNO₃, 12.0 dpm/ gHNO₃, 112.5 dpm/ gHNO₃, and 1100.3 dpm/ gHNO₃. All solution and sample masses were determined gravimetrically and are reported in units of activity of moles per gram of solution or gram of membrane as noted. Each of the sorption isotherms are shown below in Figure 3. The LSC background is approximately 17 cpm. Thus the minimum detectable concentration for a 15 minute count time determined from the Curie equation was 2.8 cpm/mL. Thus none of the 1 cpm/mL data was above the

minimum level of detection within the limited count time. Due to the need to collect these data rapidly, longer LSC count times were not possible.

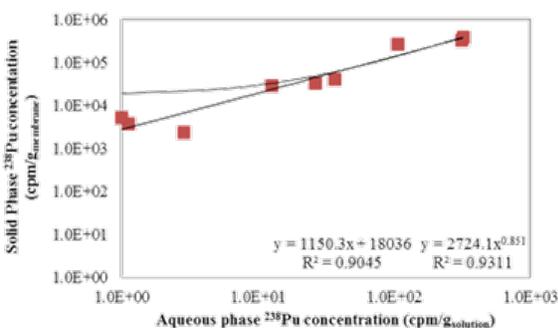
Pu(IV) sorption isotherm onto Poly(4-vinylpyridine) membranes with cross-linking



Pu(IV) sorption isotherm onto Picolyl substituted PVPy membranes with cross-linking



Pu(IV) sorption isotherm onto methylated Poly(4-vinylpyridine) membranes with cross-linking



Pu(IV) sorption isotherm onto cross-linked and aminated Clemson 1 membranes

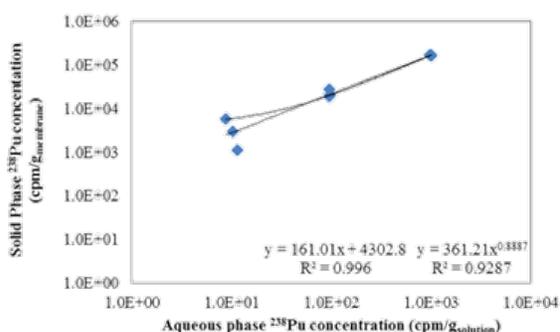


Figure 3. Figure 6: $^{238}\text{Pu}(\text{IV})$ sorption isotherm onto four different membranes

The K_d , K_f , and n values along with the associated R^2 parameters for each fit to the data are shown in Table 2. Generally the best fits to the data (as determined from R^2 values) were provided from the Freundlich isotherm expression. Both empirical models are capable of fitting the higher concentration data. However, in the lowest concentration samples (12 cpm/mL) the linear K_d model does not accurately approximate the data.

The methylated P4VP cross-linked membrane had the highest binding affinity with a K_f value of 2724 and a linear K_d of 1150. These K_f or K_d values were approximately 4x higher than control P4VP cross-linked membranes and approximately 20x greater than picolyl substituted P4VP. Due to time constraints, trouble-shooting issues with the picolyl substituted P4VP membranes was not possible and we believe higher K_f and K_d values may be attainable with further iteration. The cross linked PPO membrane had K_d and K_f values of 732 and 12 respectively. However, it is noteworthy that there was a significant amount of scatter in the data as evidenced by the poor R^2 values for both the linear and Freundlich approximations. The aminated PPO membrane also had a large amount of scatter in the data resulting in poor R^2 values of the approximations. The scatter in the data from the PPO based samples makes comparison of the aminated and cross-linked/aminated membranes with the baseline case difficult.

The fact that the two datasets with the most scatter are PPO based may be circumstantial. The scatter in the data does not appear to be an artifact from the small sample masses used in the experiments. The average masses of the membrane used in each experiment are listed in Table 3. While the two datasets with the highest amount of scatter (cross-linked PPO and aminated PPO) do have lower masses of membrane, there are two other datasets (cross-linked P4VP and aminated, cross-linked PPO) which also had small masses of membrane used but did not exhibit a significant amount of scatter. The synthetic methods for producing the quaternized PPO have also been refined since the collection of this data set, which may result in an increased K_f and K_d for this membrane type and improved reproducibility. The source of this scatter in the data will be examined in greater detail in the coming year.

FY2014 Accomplishments

- An electro dialysis concept was developed and a mass balance model was created to enable the creation of a bench-scale demonstration stack
- A survey of the potential anion exchange membrane materials was performed to identify candidate materials that could be used to have good selectivity for Pu and high ionic conductivity
- Pu uptake studies were performed on candidate membrane materials to characterize the partition coefficient of the membrane.

Future Directions

- Measure the ionic conductivity of membranes loaded with Pu nitrate complexes
- Fabricate membranes of cross-linked poly-4-vinylpyridine membranes for electro dialysis cells
- Integrate the poly-4-vinylpyridine membranes in the electro dialysis stack and operate the stacks using surrogate solutions.
- Characterize the ability of the electro dialysis method to separate surrogate materials using analytical methods.

FY 2014 Publications/Presentations

LDRD Year end poster session.

References

[1] E. Kyser, WSRC-TR-2000-00372.

Acronyms

N/A

Patent Apps/ Patents Awarded

None

Total Number of Post-Doctoral Researchers

2 graduate students at Clemson University

Process Intensification to Improve Long-Term Monitoring of Contamination in Groundwater and Reduce Costs

Project Team: C.A. Eddy-Dilek, M.E. Denham, M.R. Millings, B.B. Looney

Project Start Date: April 2, 2014

Project End Date: September 30, 2014

Abstract: *We evaluated a new approach to long-term monitoring of contaminated groundwater that emphasizes monitoring of hydraulic and chemical processes controlling contaminant mobility thereby significantly reducing the need for costly sampling and analysis of individual contaminants at numerous wells. The approach is most applicable to*

waste sites where the final remedy is monitored natural attenuation or other strategies that leave contaminants in the subsurface. The conceptual basis of the new paradigm is that monitoring the processes that control contaminant behavior is more efficient and effective than traditional strategies based solely on well measurements. This approach is a proactive rather than reactive decision process and is less costly. We demonstrated the effectiveness of this new paradigm by analyzing 30 years of monitoring data from a site with a history of remedial actions that changed the key hydraulic and chemical processes. In our analysis of this data set as if it were long-term monitoring data, we showed that parameters such as water levels, pH, and specific conductance reflected the changes to the key processes in each stage and predicted the observed changes in contaminant concentrations.

FY2014 Objectives

- Demonstrate a new paradigm for long-term monitoring of residual contamination at DOE waste sites that is proactive and reduces costs, waste production, and energy use
- Provide a validation of the innovative concept without monitoring a site for decades
- Provide a scientific basis to begin a dialogue with regulators and stakeholders on shifting emphasis of long-term monitoring toward new paradigm

Introduction

Long-term monitoring is the final phase in the life-cycle of an environmental waste site, done to ensure that the final remedy remains effective for a period of time negotiated among the waste site manager, regulators and stakeholders. As the use of in situ remedies become more widespread, the compliance periods required for long-term monitoring will become longer. This is particularly true for waste sites with metals and radionuclides that have been “immobilized” in the subsurface. Long-term monitoring will be done for centuries to millennia at these sites to ensure that contaminants are not remobilized and present a risk to human health and the environment. The current approach to long-term monitoring is the inefficient periodic, and often frequent, sampling for contaminants at multiple point sources (monitoring wells). This strategy leads to reactive rather than proactive decisions because detecting contaminants where they were not previously present, or increases in contaminant concentrations where they were, is perceived as a crisis. Furthermore, the cost of this monitoring approach projected over the large number of DOE waste sites and the long timeframes required is an enormous burden to taxpayers that can be reduced. Figure 1 shows the projected DOE budget through 2066 by program. Soil and groundwater remediation accounts for a large percentage of the out year budget and much of that will fund long-term monitoring of waste sites.

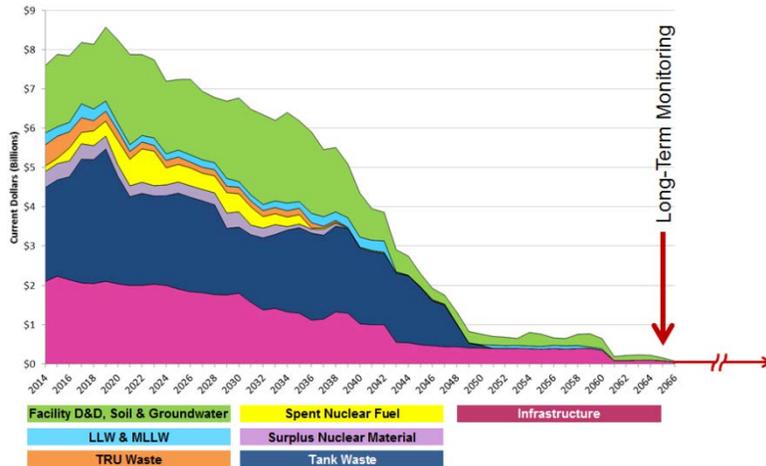


Figure 13: Projected future DOE-EM budgets by program.

We propose shifting the emphasis of long-term monitoring activities to predictive measurements that will indicate systemic changes to the waste site in order to predict mobilization of previously stabilized contaminants. Hydraulic and chemical processes control the movement of contaminants from waste site sources to the subsurface, as well as in groundwater. With knowledge of how these processes interact with stabilized contaminants, it can be predicted whether specific changes in these processes are likely to

mobilize the contaminants. Long-term monitoring of the hydraulic and chemical processes controlling contaminant behavior allows for proactive response to changes that warn of potential contaminant mobilization because it may be years to decades before these contaminants reach compliance points. In addition, measurement of these processes tends to be easier and less expensive than sampling and analysis for contaminants.

Hydraulic processes drive water through waste sites and groundwater through aquifers and are the physical processes that move contaminants. Changes to groundwater flow directions or the hydraulic gradient in an aquifer, after a waste site is closed, may indicate systemic changes that could mobilize contaminants. Hydraulic processes can be monitored by measuring water levels in an aquifer, rainfall/snowfall, stream stages, and evapotranspiration rates. Changes to wetland boundaries and major changes to vegetation types can also signal changes in the hydraulic processes. All of these measurements are relatively easy and inexpensive to acquire.

Chemical processes affect the partitioning of contaminants between the aqueous and solid phases, and hence the mobility of contaminants. These processes include adsorption/desorption and precipitation/dissolution. The effect of chemical processes on contaminant mobility is controlled by chemistry and mineralogy of the aquifer system. These processes are sensitive to pH and redox potential and, for some contaminants, alkalinity and total dissolved solids are important. Responses of most contaminants to changes in these parameters are well known. Thus, monitoring these parameters provides leading indicators of potential contaminant mobilization that are easily measured.

Our proposed new paradigm for long-term monitoring is to emphasize monitoring of the hydraulic and chemical processes that control contaminant behavior by combining inexpensive and easily acquired measurements with widely available information such as climate data and satellite imagery. Point source measurements of contaminant concentrations will still be required, but the number of points and frequency of sampling can be greatly reduced. The new paradigm will result in superior long-term monitoring at lower costs.

Approach

The challenge was how to demonstrate a long-term monitoring approach without monitoring a waste site for decades. We met this challenge by using an extensive set of monitoring data, spanning 30 years, from a waste site for which there was a known history of changes to the hydraulic and chemical processes. We then tested whether the changes to the hydraulic and chemical processes were reflected in the parameters we propose to monitor in the new paradigm. The data also provided an opportunity to demonstrate how changes that had not occurred, but would be commonly observed in long-term monitoring, would be reflected in the monitoring data.

The site chosen was the F-Area Hazardous Waste Management Facility (FHWMF) on the Savannah River Site. The FHWMF consisted of 3 unlined seepage basins into which approximately 7 billion liters of low-level radioactive liquid waste were disposed from 1955 to 1988. The waste solutions were predominantly acidic with relatively high concentrations of sodium and nitrate, as well as numerous radionuclides. This resulted in a groundwater contamination plume that migrated to a local stream that discharges into the Savannah River. The primary contaminants of regulatory concern in the plume are tritium, uranium, 90Sr, 129I, and nitrate.

The history of the waste site, shown in Figure 2, includes several discrete stages that had unique effects on the hydraulic and chemical processes governing contaminant behavior. During the operation of the FHWMF from 1955 to 1988 the system was dominated by large volumes of water with a very different chemical composition from the native groundwater entering the subsurface via the basins. From 1989 to 1991 the basins were closed and covered with a low permeability cap. This abruptly eliminated virtually all infiltration of water through the basins. In 1997, treatment of the plume began with a system that extracted water from the aquifer down gradient of the basins, removed dissolved contaminants – but not tritium -- with a water treatment system, and re-injected the treated water up gradient of the basins. The intent was to trap tritium in a continuous loop allowing it to decay before reaching the stream. This system was expensive, created radioactive solid waste, and by 2003 the effectiveness was diminishing. The pump-treat-reinject system was replaced by in situ treatment in 2004 using a funnel-and-gate system with injection of alkaline solutions in the gates to create enhanced sorption treatment zones for uranium and 90Sr. This remains the current remediation system.

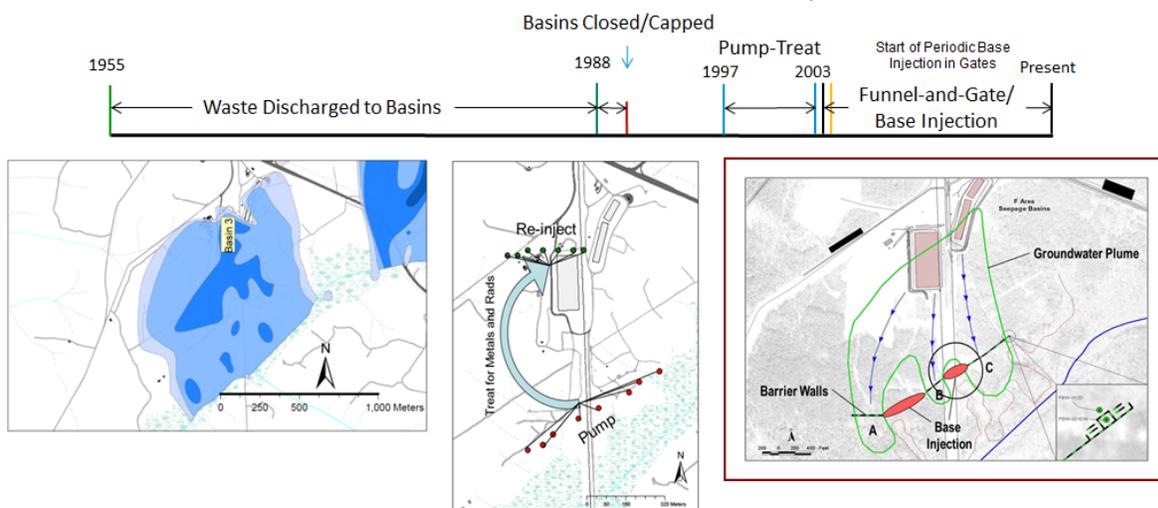


Figure 14: Timeline of stages in history of the F-Area Hazardous Waste Management Facility at the Savannah River Site. Time boundaries are color coded and correspond to figures below.

We analyzed 30 years of groundwater data from the FHWMF for temporal correlations between easily measured indicators of physical and chemical processes and transitions between stages in the history of the FHWMF. We also examined whether these correlations indicated changes in contaminant concentrations.

Results/Discussion

The results of the data analysis was generation numerous temporal trend plots showing that measurement of water levels, specific conductance (related to total dissolved solids), and pH correlate to the stages in the history of the FHWMF. A selection of these is presented here.

Figure 3 shows a comparison of the topography of the water table during four stages of the FHWMF history. The colored lines are contours of the elevation of the water table and the black arrows show general groundwater flow directions. During operation of the basins, the high infiltration rate of water created a water table mound beneath the site and groundwater flow was both lateral to the basins and

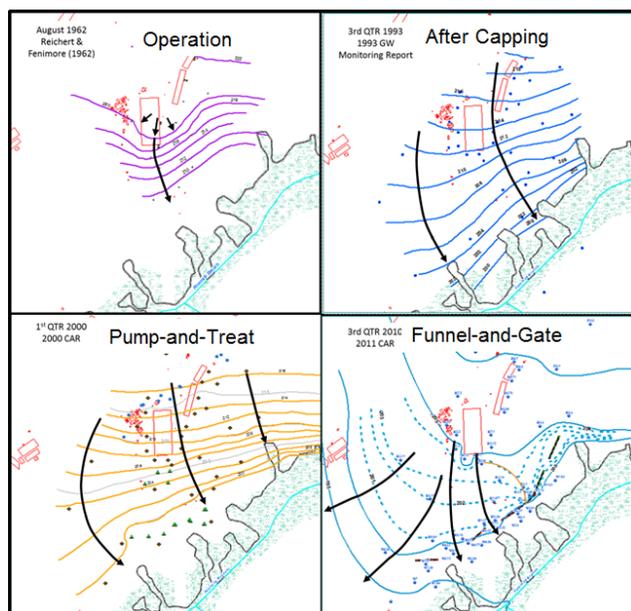


Figure 15: Water table topography and groundwater flow directions during four stages in the history of the F-Area Hazardous Waste Management Facility.

toward the stream. Flow direction after basin closure was predominantly toward the stream. When the pump-treat-reinject system began operation, the flow directions remained the same, but the water table gradient steepened toward the stream resulting in faster groundwater flow. Finally, when the funnel-and-gate was installed, groundwater flow directions were significantly changed so that there is now a substantial component of flow to the west of the site.

The changes observed demonstrate that water levels provide vital information on hydraulic processes during long-term monitoring. For example, steepening of the water table gradient would suggest that a plume that had been stable or shrinking because of natural attenuation might begin to advance. This situation would call for additional contaminant monitoring, investigation of whether the cause of the steepening could be mitigated, and possibly reassessment of the ability of natural attenuation to prevent

contaminants from reaching receptors.

Figure 4 shows three time series plots from two wells that illustrate the ability of simple chemical parameters to reflect changes to the chemical processes controlling contaminant behavior. The top plot on the left shows the effect of the various stages of FHWMF history on specific conductance and pH at well "A". After the basins were closed (marked by the red line) specific conductance decreased rapidly because of the elimination of water infiltration through the basins. The pH increased for the same reason – the influx of acidic water to the groundwater was reduced by the basins closure. The blue line marks the start of the operation of the pump-treat-reinject system, though the volumes extracted and

injected were relatively low until 1999. Specific conductance increased approximately 3 years after start-up of the treatment system and the time of the increase corresponds approximately to the time it took for groundwater to travel from the injection wells. The treated water being injected had a higher specific conductance than the ambient groundwater, and hence, the increase in specific conductance at the monitoring well pictured here. The trend in pH changes at the same time as specific conductance increases. This may be because the injection pH of treated water varied considerably. In contrast, the plot on the right shows that uranium concentrations did not increase with the increase in specific conductance, because the treatment system was removing uranium. This illustrates the importance to effective long-term monitoring of understanding the site history.

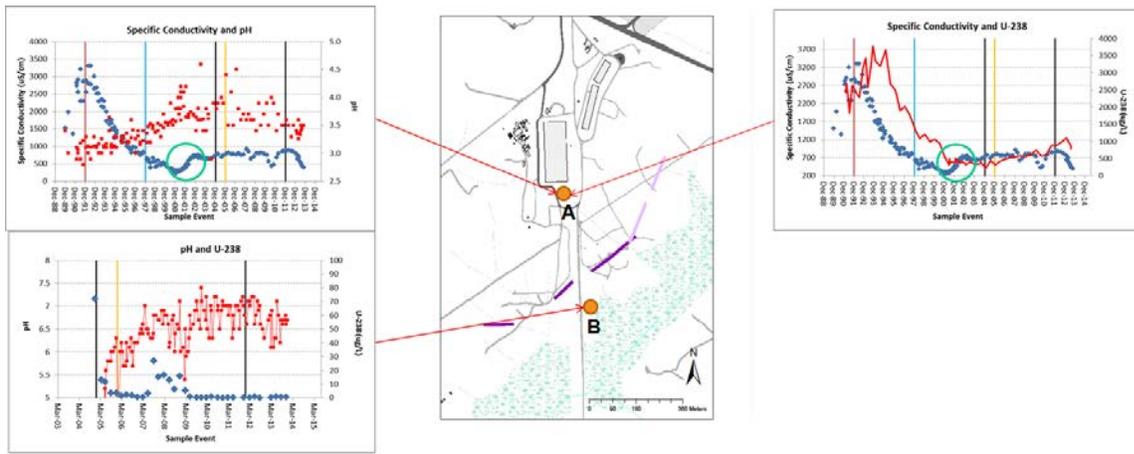


Figure 16: Time series plots from monitoring two wells at the FHWMF; top left, specific conductance (blue diamonds) and pH (red squares); top right, specific conductance (blue diamonds) and uranium (red line); bottom left, pH (red squares) and uranium (blue diamonds).

At the lower left of Figure 4 is a time series plot of uranium concentration and pH measured at well “B”, located just down gradient of a pH treatment zone associated with the funnel-and-gate. Prior to the injection of alkaline solutions the groundwater pH was less than 5 and the uranium concentration was greater than 70 ug/L. As pH increased, from base injections, uranium concentrations decreased. This indicates the utility of measuring pH during long-term monitoring, rather than individual contaminants, at a site where it is known that pH is the master variable controlling mobility of those contaminants.

FY2014 Accomplishments

- Demonstrated effectiveness of an innovative approach for long-term monitoring
- Analyzed 30 years of monitoring data from a waste site with complex history
- Developed technical basis for presentation to regulators to begin dialogue on transitioning long-term monitoring toward the new paradigm

Future Directions

- Submit paper for publication of results to peer reviewed journal
- Meet with South Carolina Department of Health and Environmental Control to discuss implementation of approach at FHWMF

- Present conceptual basis to meeting of the Interstate Technology and Regulatory Council and other federal agencies including EPA Superfund
- Continue work on new long-term monitoring paradigm with funding from DOE-EM-12 to be applied at other waste sites at SRS as well as the larger DOE complex including DOE-Office of Legacy Management

FY 2014 Publications/Presentations

1. Mid-term review talk
2. Invited tech talk to SRNS Environmental Compliance & Area Completion Projects group
3. Final poster presentation

References

N/A

Acronyms

FHWMF – F-Area Hazardous Waste Management Facility

SRNS – Savannah River Nuclear Solutions

Patent Apps/ Patents Awarded

None

Total Number of Post-Doctoral Researchers

2 graduate students at Clemson University