

2007

## University of Nevada, Las Vegas Transmutation Research Program Annual Report Academic Year 2006-2007

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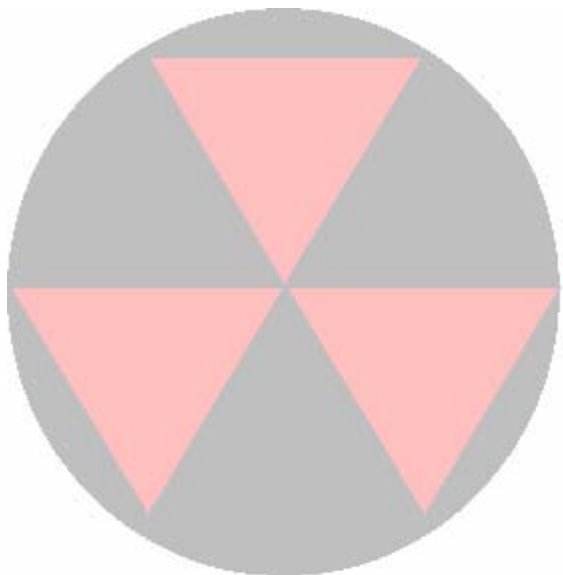
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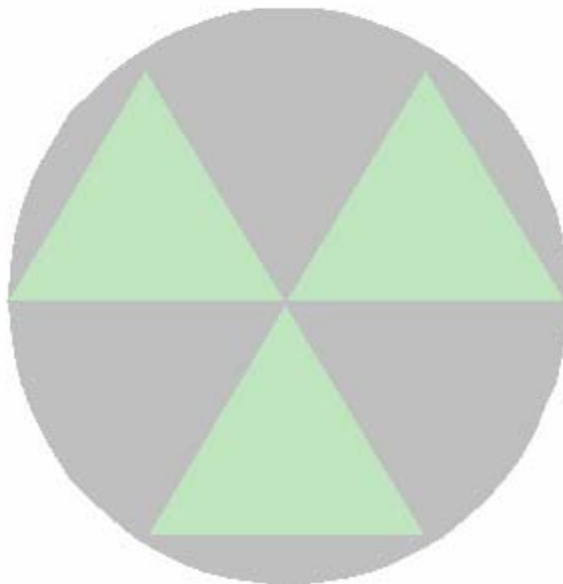
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**University of Nevada, Las Vegas**  
**Transmutation Research Program**  
**Annual Report**  
**Academic Year 2006-2007**



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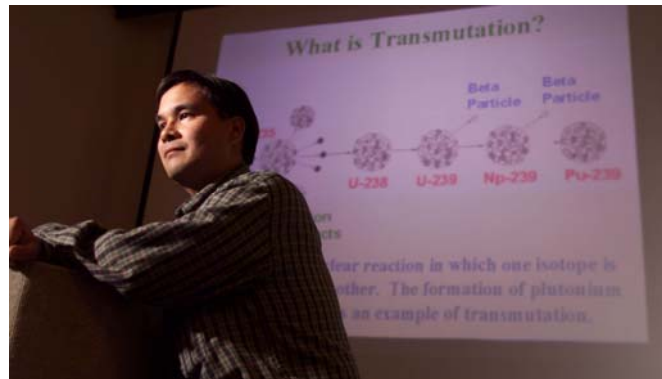
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# Letter from the Director



Anthony E. Hechanova, Ph.D.  
Director, UNLV Transmutation Research Program



It is my pleasure to present the UNLV Transmutation Research Program's sixth annual report that highlights the academic year 2006-2007. Supporting this document are the many technical reports and theses that have been generated over the past five years, which can be found on our program's website at <http://aaa.nevada.edu>.

In the sixth year of our program, we continued to see growth in the Radiochemistry Ph.D. program with a total of 13 students in the third year of the program (we anticipated eight in the program proposal). Since our inception, the program has sponsored to their conclusion 42 M.S. and 4 Ph.D. degrees. The program supported 39 graduate students, 17 undergraduates, and seven post-doctoral scholars in six academic departments across the UNLV scientific and engineering communities in the academic year 2006-2007.

Our research tasks span the range of technology areas for transmutation, including separation of actinides from spent nuclear fuel, methods of fuel fabrication, reactor-accelerator coupled experiments, corrosion of materials exposed to lead-bismuth eutectic, and special nuclear materials protection and accountability.

We continued our emphasis on molten metal technology and actinide chemistry in our enhancements to UNLV this year to build a foundation in areas that are in line with UNLV's strategic growth and our ability to address student-appropriate research in the transmutation program.

Finally, I believe that through the Transmutation Research Program, UNLV has established itself as the core university participant in transmutation research with active collaboration with national laboratories, universities, and international institutions.

I congratulate our students and faculty on a job well done and I look forward to the opportunities and challenges of this exciting research endeavor.

Sincerely,

*Anthony E. Hechanova*



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# UNLV Transmutation Research

The UNLV Transmutation Research Program was established in March 2001 as part of the national transmutation program (currently called the Global Nuclear Energy Partnership of the U.S. Department of Energy, Office of Nuclear Energy) to develop the technologies necessary for the ecological and economical treatment of spent nuclear fuel.

The goal of the UNLV program is to develop a sustainable and robust research community at UNLV that is able to contribute to and support the national effort through faculty-supervised, student-conducted research. In establishing the UNLV program, four basic principles were followed: peer review, program focus, integration with the national program, and commitment to the long-term goals of the university.

The primary role of the UNLV program in the national effort is the training of post-doctoral fellows and graduate and undergraduate students in nuclear engineering and other related fields to support the augmentation of the human infrastructure for transmutation technologies. However, the research conducted by UNLV faculty and students is also an integral part of the national research effort. This is accomplished through the direct involvement of students in collaborative research supporting the national transmutation research and development program.

Twenty-two independent student research tasks, supporting 39 graduate students and 17 undergraduates, were initiated, ongoing, or concluding this academic year. The UNLV program includes the involvement of 26 faculty in 6 academic departments.

UNLV research tasks span the range of technology areas for transmutation: separations of used fuel materials, fuel fabrication, accelerator design, materials corrosion and performance, neutron multiplicity and transport simulations and experiments, research in lead-bismuth eutectic technology development, and a recently-



*UNLV Radiochemistry graduate students Amber Wright and Sherry Stock (2nd and 3rd from left) staff a nuclear promotional booth at the Vegas Grand Prix with Newman Wachs Racing driver J.R. Hildebrand (left). Students and faculty helped staff the booth April 6-8, 2007.*

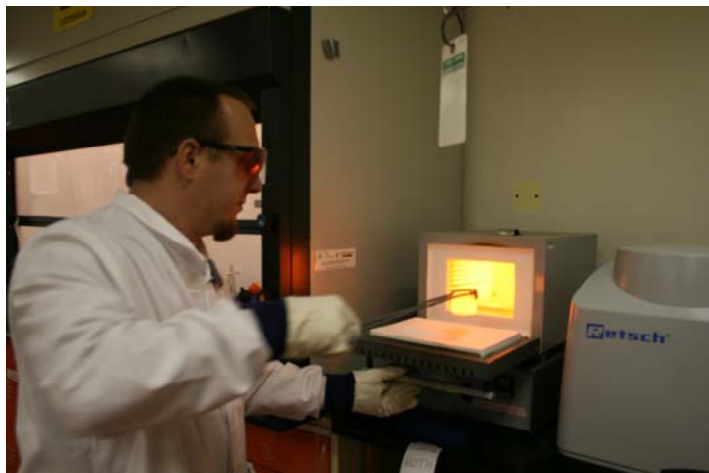


*M.S. Nuclear Engineering students Timothy Beller and Ryan Le-Counte set up the High-Power Reactor-Accelerator Coupled Experiment Target experiment at the Idaho Accelerator Center. The beam tube from the 20-MeV electron linear accelerator is on the left.*

added priority area on material protection, accounting, and control and waste forms.

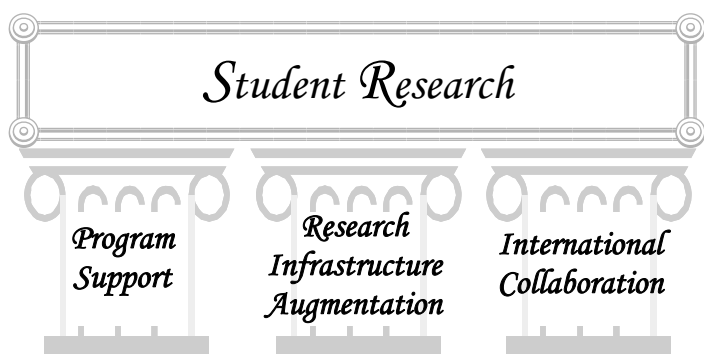
Student research and training is the primary focus of the UNLV Transmutation Program. To support this focus, the student research program is augmented by the remaining components of the UNLV Transmutation Research Program: Research Infrastructure Augmentation, International Collaboration, and Program Support.

These components are responsible for all aspects of the program that are not directly related to the student research projects, including the expansion of the research faculty, bringing new research equipment to campus, assisting in the development of new student research projects, coordination with the national and inter-



*Radiochemistry Ph.D. candidate Kiel Holliday making glass in his laboratory at UNLV.*

# Program Overview



## *UNLV Transmutation Research Program Components*

national programs, as well as handling the administrative details required for a program of this size.

The primary goals of these components are to support the current UNLV research efforts in transmutation technologies, to augment faculty and staff, and to increase research infrastructure necessary for the strategic growth of the UNLV research mission.

Through the international collaborations component, the program hosted a two Russian faculty members from the Institute for Nuclear Power Engineering in Obninsk, Russia. In addition, the project entitled "Preparatory Work for the Systematic Measurements and Evaluation of Minor Actinide Nuclear Data" was completed by the Research Coordinative Center on the Problem of Muon Catalyzed Fusion and Exotic Quantum Systems in Moscow, Russia, and a new project entitled "Safeguards Instrumentation Upgrade of Neutron Measurement System" was initiated with the V.G. Khlopin Radium Institute in St. Petersburg, Russia.

The program support component sponsored a number of workshops and meetings this year between UNLV researchers and



*UNLV Chemistry Professor Allen Johnson (left) being entertained by American Nuclear Society President Harold McFarlane (right) during McFarlane's visit to Las Vegas, October 4, 2006.*



*Radiochemistry pioneer Darlene Hoffman (third from the left) with UNLV Radiochemistry Ph.D. students and post-doctoral researchers at the American Chemical Society meeting in Chicago, IL, March 25-29, 2007.*

scientists from our national laboratory partners and the international community for the development of transmutation technologies, as well as sponsoring the participation of UNLV students in the American Nuclear Society Student Conference at Oregon State University in Corvallis, Oregon and the American Chemical Society's Spring Meeting in Chicago, Illinois.

The 2006-2007 academic year was a busy year that included extracurricular activities organized by the students such as a field trip to Los Alamos National Laboratory August 20 to 23, 2006; a Radiochemistry Recruiting week in February 2007; and, several middle school and high school outreaches.



*Students and faculty host six prospective students for the Radiochemistry Ph.D. program, including a hike of Red Rock Canyon on February 24, 2007.*



# Transmutation at a Glance

## Introduction

Over 20% of the electricity generated in the U.S. is provided by nuclear power reactors. It is estimated that the amount of used nuclear fuel in the U.S. will reach 140,000 tons by the end of the operational period of current reactors.

Many countries take different approaches to the management and recycling of used nuclear reactor fuel. The U.S. is pursuing a strategy of waste management that would place used nuclear fuel in deep geologic repositories for a long time, separating it from the biosphere and allowing the radioactive isotopes of the waste to decay to more stable progeny.

Transmutation is an alternative waste management strategy undergoing research and development in the U.S. The new national program was authorized by Congress to begin in fiscal year 2001, as the Advanced Accelerator Applications program. In fiscal year 2002, the national program was continued and expanded by Congress, and renamed the Advanced Fuel Cycle Initiative (AFCI). In February 2006, the Bush administration announced a broad program named the Global Nuclear Energy Partnership (GNEP) that effectively expanded the AFCI program (which was renamed Advanced Fuel Cycle Research and Development) and accelerated the development of commercial-scale facilities. The goals of the GNEP program are to:

- Provide abundant energy without generating carbon emissions or greenhouse gases.
- Recycle used nuclear fuel to minimize waste and reduce proliferation concerns.
- Safely and securely allow developing nations to deploy nuclear power to meet energy needs.



The Global Nuclear Energy Partnership logo. More information about the national program can be found at [www.gnep.energy.gov](http://www.gnep.energy.gov).

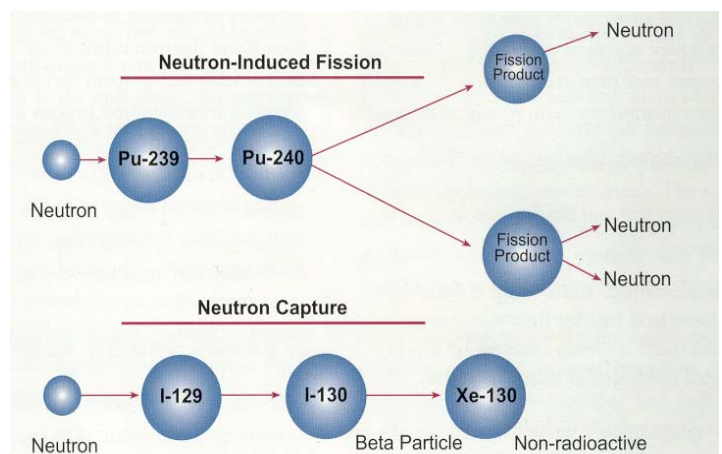
- Assure maximum energy recovery from still-valuable used nuclear fuel and reduce the number of required U.S. geologic waste repositories to one for the remainder of this century.

This concept could provide a dramatic shift in the U.S. waste management strategy by lessening the inventory of residual radioactivity, allowing recycling of fuel, providing optimization of final waste forms, and potentially removing much of the material from Nevada.

## What is Nuclear Transmutation?

For centuries, alchemists have been trying to transform elements into other elements, primarily lead into gold. With modern nuclear science, we can finally accomplish this. Scientists are using nuclear transmutation to change one isotope into another more favorable isotope by changing its nuclear structure. This process for waste management is aimed at plutonium, other actinides, and long-lived fission products, with the ultimate goal of converting them into short-lived isotopes that can be managed over a reasonable timeframe.

Transmutation can be done with two different processes: neutron-induced fission and neutron capture. Both processes start with the target nucleus absorbing an incident neutron. After the neutron is absorbed by the target nucleus, the nucleus can either fission (splitting of the nucleus) or go through another nuclear transmutation process such as radioactive decay. Both processes lead to the same final result: transmutation of waste. These processes are illustrated in the figure below.

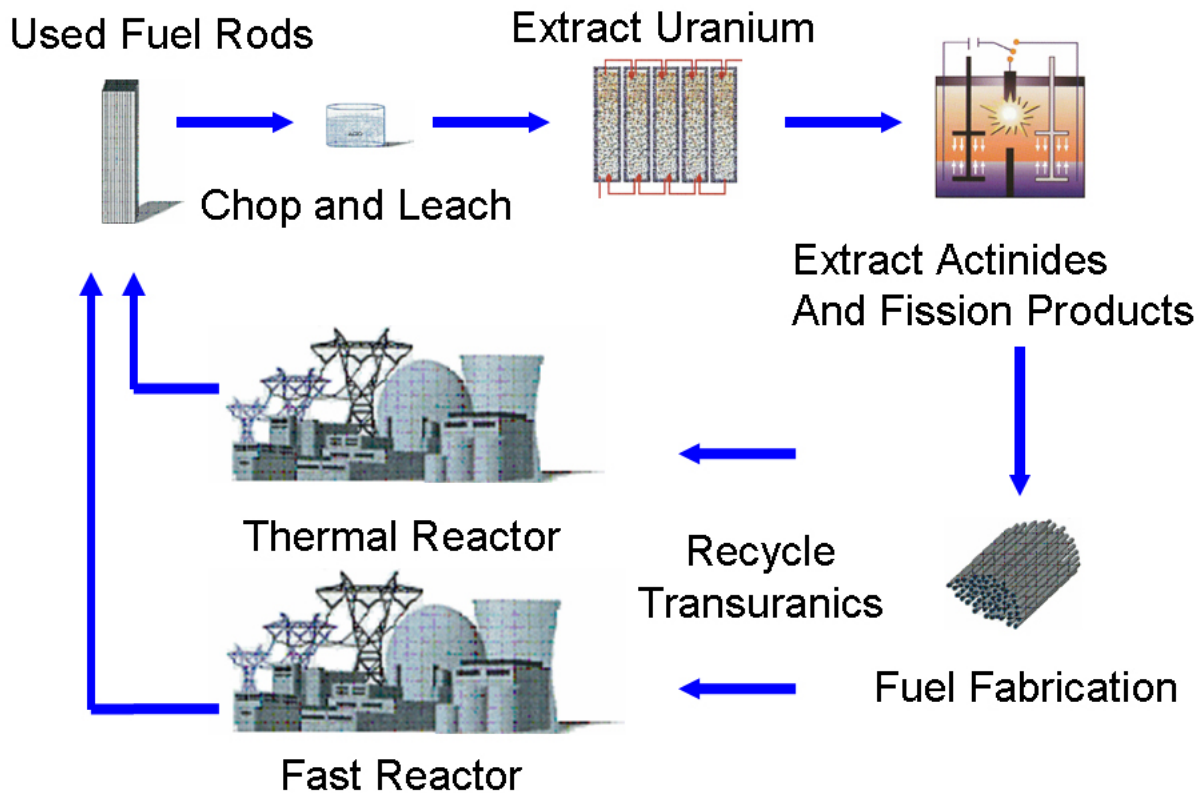


This picture illustrates how neutrons are used to transmute actinides and fission products.

*Neutron-Induced Fission (top): a neutron is captured by a fissile actinide (e.g. Plutonium-239) and is induced to split (or fission).*

*Neutron Capture (bottom): a neutron is captured by a nucleus (e.g. Iodine-129). A new nucleus is produced, Iodine-130, which decays into Xenon-130 which is a stable isotope (i.e., not radioactive). This decay process is complete within a few days.*

## Multi-tier Transmutation Concept



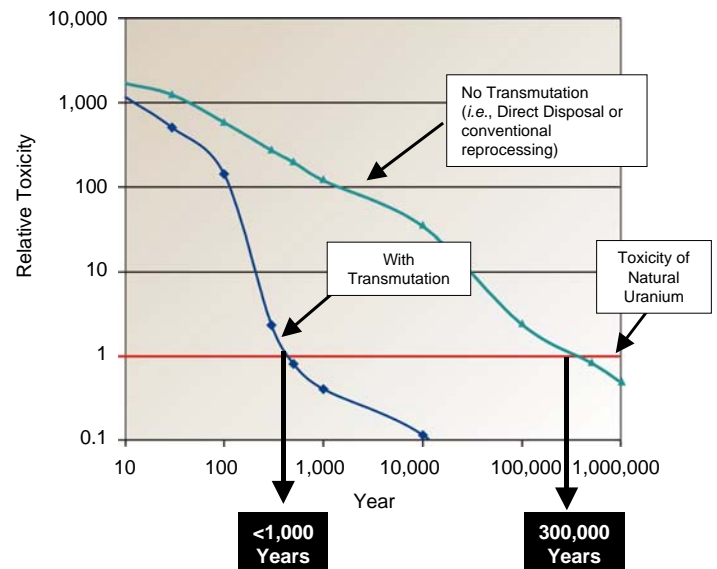
The above figure shows how used nuclear fuel could be managed under a multi-tiered transmutation strategy. In the first tier, plutonium (and other fissile actinides) would be recycled from used fuel and transmuted in an advanced thermal reactor. In the second tier, remaining long-lived radioactive isotopes would be transmuted using a fast spectrum reactor. The GNEP program is currently focused on sodium-cooled fast burner reactors to transmute the recycled transuranic actinides (such as plutonium and americium).

## RECYCLE, REDUCE, RESEARCH

### Benefits from Transmuting Nuclear Waste

Many benefits are obtained from transmutation of nuclear waste. Some of them are:

- (1) The initial amount of high-level radioactive waste will be reduced by virtue of separation (only two percent of used nuclear fuel is highly radioactive, the rest, if separated, can be classified as low-level or non-radioactive).
- (2) The radiotoxicity of the residual waste will be reduced such that it could be less radiotoxic after 300 years than direct disposal of used nuclear fuel after 100,000 years.
- (3) Usable energy is produced by destroying hazardous components of used nuclear fuel. Plutonium and other isotopes can be continuously recycled.
- (4) Someday other used nuclear fuel materials, such as uranium, may be reused. It is possible that other isotopes separated from nuclear waste could have a useful purpose in medicine and industry.



Incentives for recycling used nuclear fuel and "closing" the nuclear fuel cycle include lowering the radiotoxicity of the residual waste, shortening the time frame of concern, smaller amounts of radioactive waste, the elimination of plutonium, and the ability to make optimized waste forms.

## Task 1

# Design and Analysis of a Process for Melt Casting Metallic Fuel Pins Incorporating Volatile Actinides

Y. Chen, D.W. Pepper, and R. Clarksean

## BACKGROUND

The incorporation of non-fertile actinides into a fuel matrix for a transmuter blanket is of interest to the Advanced Fuel Cycle Initiative. One of three proposed candidate matrices for the transmuter is a metallic alloy fuel matrix. Metallic fuels are an outstanding candidate for a transmutation fuel due to excellent irradiation performance and ease of fabrication. However, incorporating a volatile constituent during fabrication of these or other fuel pins presents a challenge.

Volatile actinides, particularly americium, are susceptible to rapid vaporization during the traditional metal fuel casting processes. The actinide vapors boil off, and flow out of the system into the off-gas recovery system, resulting in only a fraction of the volatile actinide charge being incorporated into the fuel pins. The loss of these actinides from the fuel greatly complicates the task of preparing them for transmutation, requiring additional recovery and fuel fabrication steps to try to incorporate the volatile actinides into the transmuter fuel.

## RESEARCH OBJECTIVES AND METHODS

The goal of this project was to investigate the casting processes for metallic fuels to help design a process that minimizes the loss of the volatile actinide elements from the fuel. The research effort centered on the development of advanced numerical models to assess conditions that significantly impact the transport of volatile actinides during the melt casting process and represents a joint effort between researchers at UNLV and Argonne National Laboratory (ANL). Assessing critical equipment and process variables is required to build a successful system that will operate efficiently.

## RESEARCH ACCOMPLISHMENTS

Development of the induction-heating model: Modeling efforts centered on the development of the governing equations, incorporating these equations into computer codes, setting up a test problem, and making preliminary calculations for the geometry of interest. Detailed analyses were conducted for an induction skull melter previously built and tested by ANL.

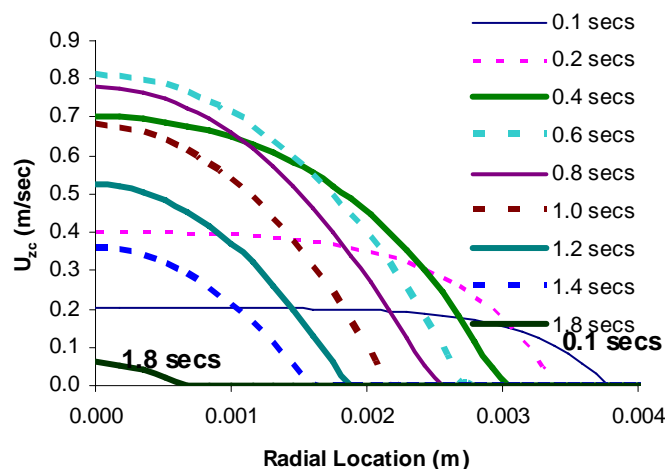
Modeling of casting process: Efforts continued to improve a model for the casting of fuel pins. Work considered the flow of the melt into the mold and heat transfer into the mold during solidification (after flow has stopped). Results from an energy balance model indicate that the thermal mass would typically be greater than needed to solidify the melt within the mold. The results of this simple model have aided in designing a mold to

hold and solidify the fuel pins. Detailed flow and heat transfer models show how the melt flows into the mold and ultimately solidifies.

In order to test the impact of process parameters (temperature, pressure, alloying elements, etc.) on the casting process, parametric studies were carried on different processing parameters. These studies centered around model development and analysis of the impact of mold preheating on heat transfer into the model. Results will assist with determining which process parameters are critical in manufacturing a suitable metallic fuel pin.

Americium Transport Models: A model that analyzes the transport of americium from the melt to the vapor phases above the crucible was also developed. The model considers mass transport in the melt, vaporization at the surface, and transport through the vapor phase. Parametric studies were performed to evaluate the impact of different properties or situations on the transport of americium from the melt.

Develop Prototype Furnace Design: A preliminary furnace design that can be built and tested with surrogate materials is critical in order to assess the viability of metal fuels. A preliminary analysis of potential surrogate materials was completed. Manganese appears to be an acceptable surrogate material. Discussions will be held with Argonne National Laboratory staff members to insure that no health and safety issues prevent manganese from being used.



*Axial velocity profile for constant inlet pressure of 20 kPa (Mold temperature = 400°C, initial melt temperature = 1500°C, interfacial heat transfer coefficient = 2,000 W/m<sup>2</sup>-K).*

## TASK 1 PROFILE

Start Date: June 2001

Completion Date: June 2004

### Theses Generated:

Xiaolong Wu, M.S., Mechanical Engineering, "Design and Analysis for Melt Casting Metallic Fuel Pins Incorporating Volatile Actinides," August 2002.

Taide Tan, M.S., Mechanical Engineering, "Design and Simulation of an Induction Skull Melting System," May 2004.

### Journal Article:

T. Tan, R. Clarksean, Y. Chen, S. Hsieh, and M. Meyer, 2004, "Simulation of the Casting Process for Melt Casting a Metallic Fuel Pin," submitted to *Nuclear Engineering and Design*.

### Conference Proceedings:

T. Tan, R. Clarksean, Y. Chen, S. Hsieh, and M. Meyer, "Analyzing afor Casting Volatile Actinides," 6th International Topical Meeting on Nuclear Reactor Thermal Hydraulics, Operations and Safety, Nara, Japan, October 4-8, 2004.

T. Tan, R. Clarksean, Y. Chen, S. Hsieh, S., and M. Meyer, "Numerical SimulationInduction Heating Processin an Induction Skull Melting Furnace," International Symposium

on Advances in Computational Heat Transfer, Norway, April 19-24, 2004.

T. Tan, R. Clarksean, Y. Chen, S. Hsieh, and M. Meyer, "Simulating the Casting Process for Melt Casting a Metallic Fuel Pin," 12th International Conference on Nuclear Engineering (ICONE-12), Arlington, VA, 25-29, 2004.

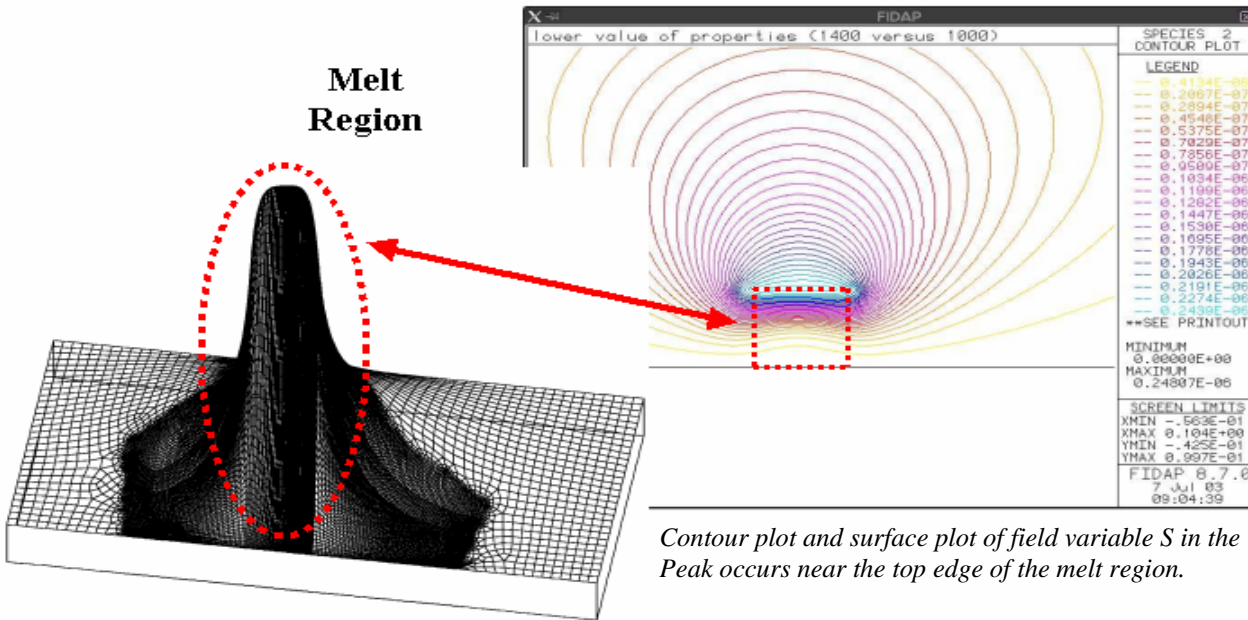
T. Tan, R. Clarksean, Y. Chen, S. Hsieh, and M. Meyer, "Simulating the Induction Heating Process in an Induction Skull Melter for Casting Metallic Fuel," ICONE-12, Arlington, VA, April 25-29, 2004.

T. Tan, R. Clarksean, Y. Chen, D. Pepper, and M. Meyer, "Simulation and Analysis for Melt Casting a Metallic Fuel Pin Incorporating Volatile Actinides" International Mechanical Engineering Congress and Exposition, Washington, DC, November 16-21, 2003.

X. Wu, R. Clarksean, Y. Chen, D. Pepper, and M.K. Meyer, "An Analysis of the Melt Casting of Metallic Fuel Pins," International Mechanical Engineering Congress and Exposition, New Orleans, LA, November 17-22, 2002.

X. Wu, R. Clarksean, Y. Chen, and D. Pepper, "Design and Analysis for Melt Casting Metallic Fuel Pins Incorporating Volatile Actinides," International Youth Nuclear Congress, Daejeon, Korea, April 16-20, 2002.

X. Wu, R. Clarksean, and Y. Chen, "Design and Analysis for Melt Casting Metallic Fuel Pins Incorporating Volatile Actinides," International Congress on Advanced Nuclear Power Plants, Hollywood, FL, June 9-13, 2002.



Contour plot and surface plot of field variable  $S$  in the induction field. Peak occurs near the top edge of the melt region.

### Research Staff

Yitong Chen, Principal Investigator, Associate Professor, Mechanical Engineering Department

Darrell W. Pepper, Professor, Mechanical Engineering Department; Director, Nevada Center for Advanced Computational Methods

Randy Clarksean, Adjunct Professor, Mechanical Engineering Department

### Students

Taide Tan and Xiaolong Wu, Graduate Students, Mechanical Engineering Department

Yulien Chen and Paul Lawson, Undergraduate Students

### Collaborators

Mitchell K. Meyer, Leader of Fabrication Development Group, Nuclear Technology Division, Argonne National Laboratory

Steven L. Hayes, Manager of Fuels & Reactor Materials Section, Nuclear Technology Division, Argonne National Laboratory



## Task 2

# Modeling, Fabrication, and Optimization of Niobium Cavities

R.A. Schill, Jr., M.B. Trabia, and W. Culbreth

## BACKGROUND

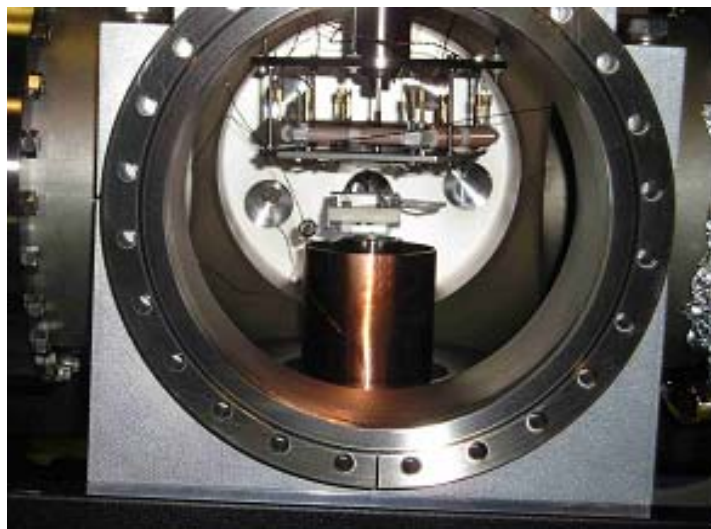
One of the key technologies for the deployment of accelerator-driven transmutation systems is the accelerator itself. Elliptical superconducting niobium cavities are used to increase the efficiency of the high-power accelerators needed to support the transmutation mission.

One of the major sources of energy loss from a superconducting accelerator cavity is a process known as multiple impacting (or “multipacting”) of electrons. This phenomenon limits the maximum amount of energy and power that the niobium cavity can store. As a result, the maximum power available for accelerating the desired charge, as well as the overall performance of the accelerator is reduced. Furthermore, the energy absorbed as a result of multipacting eventually turns into heat. This negatively impacts the performance of both the superconducting cavity and the accelerator.

## RESEARCH OBJECTIVES AND METHODS

This project was tasked with examining the impacts of the design and fabrication technologies for these elliptical niobium cavities on their performance. Niobium was selected primarily due to its behavior at low temperatures.

One objective of this study was to experimentally model the fluid flow resulting in the chemical etching of niobium cavities with the aid of a baffle. Numerical analyses tend to show that the current etching process with a baffle does not uniformly etch the cavity surface. Multiple cavity cell geometries were investigated. Optimization techniques were applied in search of the chemical etching processes, which would lead to cavity walls with near



*Side view of the secondary electron emission system. The components from top to bottom are: electron gun end, electron beam tube, particle position detector, micro-channel plate stack, business end of the manipulator arm, top of cryostat, and cryostat thermal guard.*

ideal properties.

A Monte Carlo secondary electron emission (SEE) code was modified to provide a statistical study of electron impact from Los Alamos National Laboratory (LANL) cleaned niobium samples at near cryogenic temperatures in an ultra high vacuum environment. A one-of-a-kind secondary electron emission test stand was developed to study, in part, the dynamics of the emitted particles subjected to an electron beam. Coordinating code studies with experiments offers a wealth of knowledge regarding the surface physics of the material that can enhance modeling codes at LANL.

Modeling codes, optimization techniques, and experimentation provided UNLV researchers with a well-rounded study to examine existing and novel niobium cavity designs and cleaning processes for the superconducting radio frequency high-current accelerator.

## RESEARCH ACCOMPLISHMENTS

Monte Carlo SEE Code Development and Modifications: A Monte Carlo secondary electron emission code based on the “Single Scatter” approach was obtained from Dr. David Joy of both Oak Ridge National Laboratory and the University of Tennessee. The “Single Scatter” approach follows the primary electron and each generation of secondary electron through the entire cascade. The code was modified to allow for surface layer contaminants in the hopes to verify experimental studies. The code only offers approximate results since the inherent mechanisms internal to the code are valid at higher primary beam energies. A SEE code was used to study the initial particle trajectory conditions of the secondary electron released by the primary electron impacted niobium sample. Results were compared with experiments.

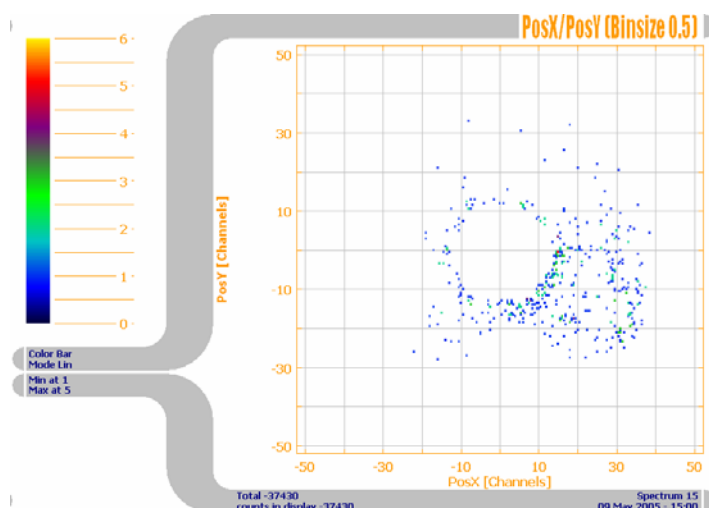
SEE Studies: Niobium samples were cleaned both at LANL and Cornell University and used for experimentation. Two types of cleaning procedures have been used: electro-polishing and buffered chemical polishing. *In situ* pictures of the sample surface were taken with a long-range light microscope for future comparisons.

The experimental setup is unique offering further insights to the SEE process not attained elsewhere. Individual electrons are detected and mapped over the detector surface. With the aid of particle tracking codes, knowledge of the final condition of the electron suggests a family of initial particle trajectory conditions of the emitted electron. Using the Monte Carlo SEE code, the family of initial conditions were evaluated. By March 2004, many of the components of the experimental study reached UNLV with some assembly accomplished. The first SEE measurement was made from the surface of a Faraday cup in September 2004. In December of 2004, the software for the particle positioning detector was finally up and running. The integrity of the code and detector were fine-tuned and initial experiments were completed by April 2005. Experiments on the



surface cleaned samples were completed in May of 2005 experimental studies were completed on the samples provided by LANL.

**Revised Etching Process:** The current etching method, which uses a baffle to direct the etching fluid toward the surface of the cavity, partially succeeded in achieving its task. However, flow was restricted to the right half of the cavity with very limited circulation in the left half. An alternative design was proposed and modeled. The exit flow is now parallel to flow inlet. Results show that flow circulation was eliminated. The flow is now closer to the surface of the cavity. Optimization techniques were used to improve this design.



*Typical secondary electron emission detected when a 100 ms pulse, 1 keV electron beam impinges on a 30 degree incline, virgin surface of niobium before in situ sample baking. Each pixel represents a spatial bin on the detector. The color of the pixel corresponds to the number of electrons detected at that position. The sample was buffered chemically polished. Single count events have been removed to enhance the scattering tendency.*

**Developed Flow Visualization System:** To confirm the predictions from the fluid flow models used to analyze the etching process, the UNLV team developed and deployed a flow visualization system. A complete experimental setup, including a computer-controlled x-y traverse and digital camera, was assembled. Flow visualization experiments using a plastic prototype of the niobium cavity used dye injection. Dye injection provided quantitative verification that laminar flow exists within the niobium cavities during etching. Additionally, it verified the absence of re-circulation pockets within the cavities.

## TASK 2 PROFILE

Start Date: June 2001

Completion Date: July 2005

### Theses Generated:

- Qin Xue, M.S., Mechanical Engineering, "Modeling and Simulation of the Chemical Etching Process in Niobium Cavities," August 2002.
- Satish Subramanian, M.S., Mechanical Engineering, "Modeling, Optimization, and Flow Visualization of Chemical Etching Process in Niobium Cavities," May 2004.
- Anoop George, M.S. Electrical and Computer Engineering, "Study of Secondary Electron Emission from Niobium at Cryogenic Temperatures," August 2005.

### Conference Proceedings:

- A. George, R.A. Schill, Jr., R. Kant, and S. Goldfarb, "Secondary Electron Emission from Niobium at Cryogenic Temperatures," International Conference on Plasma Science 2005, Monterey, CA, June 20-24, 2005.
- M.B. Trabia, W. Culbreth, S. Subramanian, and T. Tajima, "Optimization of Chemical Etching Process in Niobium Cavities," *Proceedings*, American Society of Mechanical Engineers 2004 Design Engineering Technical Conferences and Computers and Information in Engineering Conference, Salt Lake City, UT, September 28 – October 2, 2004.
- M. Holl, M. Trabia, and R.A. Schill, Jr., "Optimization of a Five-Cell Niobium Cavity," Sixth International Topical Meeting on the Nuclear Applications of Accelerator Technology, San Diego, CA, June 1-5, 2003.
- Q. Xue, S. Subramanian, M. Trabia, Y.T. Chen, and R.A. Schill, Jr., "Modeling and Optimization of the Chemical Etching Process in Niobium Cavities," International Congress on Advanced Nuclear Power Plants, Hollywood, FL, June 9-13, 2002.

### Special Commendation:

- A. George and R.A. Schill, "Preparation Studies for Secondary Electron Emission Experiments on Superconducting Niobium," American Nuclear Society Student Conference, April 1-4, 2004, Madison, WI. (Outstanding Student Paper Award)

### Research Staff

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 William Culbreth, Associate Dean for Research, College of Engineering

### Students

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### Collaborator

Tsuyoshi Tajima, Team Leader, Accelerator Physics & Eng., LANSCE-1, Los Alamos National Laboratory

## Task 3

# Corrosion of Steel by Lead Bismuth Eutectic

*J.W. Farley, A. Johnson, and D.L. Perry*

### BACKGROUND

There is an active international interest in lead-bismuth eutectic and similar liquid lead systems because of the relevance to the transmutation of nuclear waste, fast reactors, and spallation neutron sources.

Materials in these systems must be able to tolerate high neutron fluxes, high temperatures, and chemical corrosion. For lead-bismuth eutectic (LBE) systems, there is an additional challenge because the corrosive behaviors of materials in LBE are not well understood. Most of the available information on LBE systems has come from the Russians, who have over 80 reactor-years experience with LBE coolant in their Alpha-class submarine reactors. The Russians found that the presence of small amounts of oxygen (on the order of parts per million) in the LBE significantly reduced corrosion. However, a fundamental understanding and verification of its role in the corrosion of steels is incomplete.

### RESEARCH OBJECTIVES AND METHODS

This research program has analyzed various steel samples that have been exposed to lead bismuth eutectic as part of the national program to develop LBE and allied technologies. The goal of this research was to understand the basic science of corrosion in the steel/LBE system. This information will be paramount in developing engineering efforts to control, avoid, and/or minimize the effect of corrosion of steels by LBE in transmuter and LBE systems. Additionally, this program provided UNLV researchers with hands-on experience that will be crucial in developing the UNLV molten metal program.

Investigators performed post-experiment testing and analysis on steel samples that have been exposed to lead bismuth eutectic. Surface analysis techniques were employed that included

scanning electron microscopy, energy dispersive X-ray spectroscopy, X-ray photoelectron spectrometry, and laser Raman spectrometry.

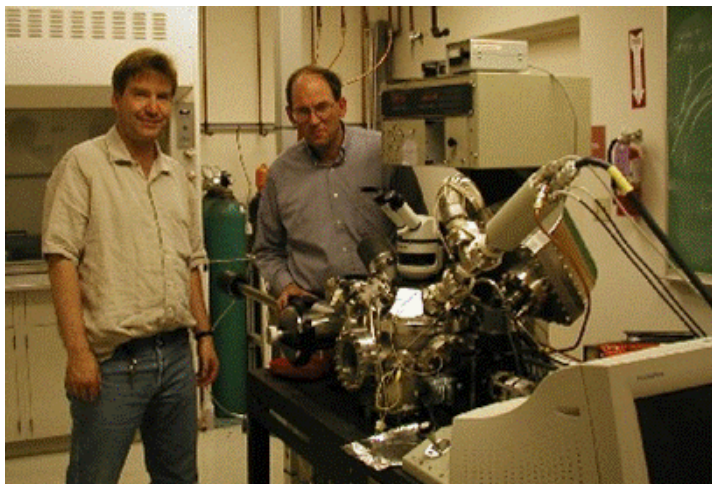
These techniques, applied to the steel surface, have probed the surface morphology, elemental composition, and oxidation states as a function of position. Chemical alterations and resulting chemical species were studied at the steel surface. Additionally, the experimental facilities at the Advanced Light Source (Lawrence Berkeley National Laboratory) and the Advanced Photon Source (Argonne National Laboratory) were used to characterize the systems. This allowed spectroscopic characterization of the stainless steel before and after interaction with LBE to determine its composition.

### RESEARCH ACCOMPLISHMENTS

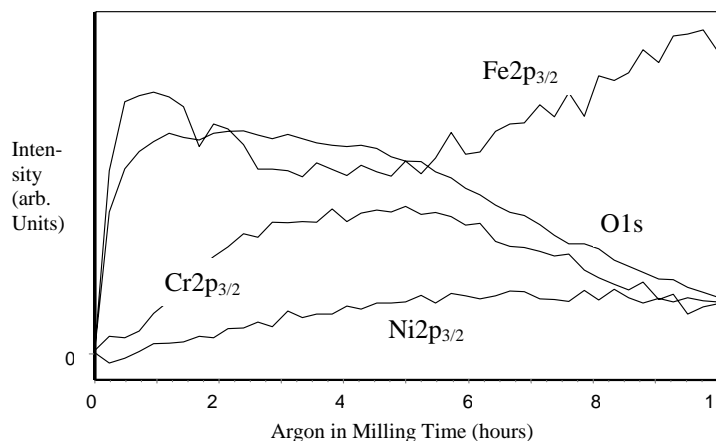
Several samples were compared having the same or similar compositions (standard nuclear grade 316/316L) but different surface preparation, including cold-rolled, annealed and a special low-corrosion treatment, "D-9." The cold-rolled sample had an order of magnitude less corrosion (i.e., both lower oxidation and less weight change) than the annealed sample.

Sputter depth profiling of the exposed annealed sample and cold-rolled sample showed a marked difference in oxide layer composition between the annealed and cold-rolled sample. The annealed sample showed a complex oxide structure (iron oxide over chromium/iron oxide mixtures) of tens of microns thickness, while the cold-rolled sample was covered with a simple, primarily chromium oxide layer approximately one micron thick. Interestingly, the D-9 material behaved more like the annealed than the more resistant cold-rolled material. In addition to these studies of 316/316L steel, other compositions of steel such as HT9 were also studied. These studies show the importance of surface preparation in resistance to corrosion by LBE.

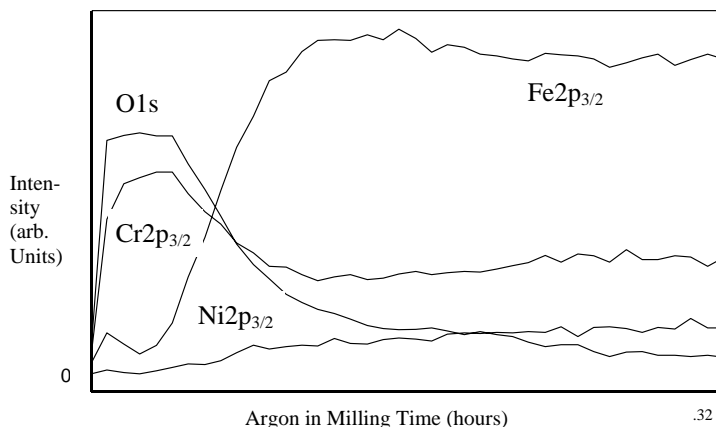
Another alloy studied in the Institute for Physics and Power Engineering in Obninsk, Russia series was EP823, an alloy similar to HT9 but with added silicon to improve corrosion resistance. A study of silicon in iron was undertaken to investigate the role of silicon in steels for LBE service. A series of silicon-containing iron samples were examined that were exposed to LBE at Idaho National Laboratory. Several unique features were observed: at low silicon concentrations in the starting alloy, the silicon was found as a silicate ( $\text{SiO}_3^{2-}$ ). As the concentration of silicon increased in the starting alloy, a layer containing silica ( $\text{SiO}_2$ ) was found also. Under the oxide layer, the silicon concentration in the metal was found to be decreased by approximately 30%. These were model systems, and the oxide layers that formed were not very protective. In all cases, pockets of LBE were found underneath the oxide layer, potentially corroding the steel.



*Professors Allen Johnson and John Farley next to an X-ray Photoelectron Spectrometer.*



*Sputter Depth Profile of annealed 316/316L stainless steel sample. Note iron oxide at the surface.*



*Sputter Depth Profile of cold-rolled 316/316L stainless steel sample. Note chromium oxide at the surface.*

### TASK 3 PROFILE

Start Date: June 2001

Completion Date: May 2004

(This work continued under Task 18, see pages 40-41.)

#### Thesis Generated:

Daniel Koury, M.S., Physics Department, "Investigation of the Corrosion of Steel by Lead-Bismuth Eutectic Using Scanning Electron Microscopy And X-ray Photoelectron Spectroscopy," December 2002.

#### Journal Article:

A.L. Johnson, D. Parsons, J. Manzerova, D.L. Perry, D. Koury, B. Hosterman, and J.W. Farley, "Spectroscopic and Microscopic Investigation of the Corrosion of 316/316L Stainless Steel by Lead-Bismuth Eutectic at Elevated Temperatures: Importance of Surface Preparation," *J. Nuclear Materials*, 328 (2004) 88-96.

#### Conference Proceedings:

"Mechanisms of Lead-Bismuth Eutectic Corrosion Chemistry involving Stainless Steels in Nuclear Reactor Cooling Systems," Annual Meeting of the American Chemical

Society, Anaheim, CA, March 29-31, 2004.

A. Johnson, D. Parsons, J. Manzerova, D. Koury, B. Hosterman, D.L. Perry, and J.W. Farley, "Surface Studies of the High Temperature Corrosion of Stainless Steel by Oxygen Controlled Lead-Bismuth Eutectic," American Vacuum Society, Baltimore, MD, Nov. 2-7, 2003.

"Chemical Species Involved in High Temperature Corrosion Resulting from the Interaction Between Stainless Steel and Lead-Bismuth Eutectic," 38th Western Regional Meeting of the American Chemical Society, Long Beach, CA, October 15-18, 2003.

A.L. Johnson, D. Parsons, J. Manzerova, D.L. Perry, D. Koury, B. Hosterman, and J.W. Farley, "Surface Studies of the Corrosion of Stainless Steel by Lead-Bismuth Eutectic: Surface Preparation Effects on 316 Stainless Steels," American Nuclear Society Summer Meeting, San Diego, CA, June 1-5, 2003.

D. Koury, A.L. Johnson, D.L. Perry, and J.W. Farley, "Investigation of Corrosion of Steel by Lead-Bismuth Eutectic," American Nuclear Society Topical Meeting on Accelerator Applications and International Meeting on Accelerator-Driven Transmutation Technologies and Applications, Reno, NV, November, 2001.

#### Research Staff

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Eric P. Loewen, Idaho National Laboratory



## Task 4

# Environment-Induced Degradation and Crack-Growth Studies of Candidate Target Materials

A.K. Roy

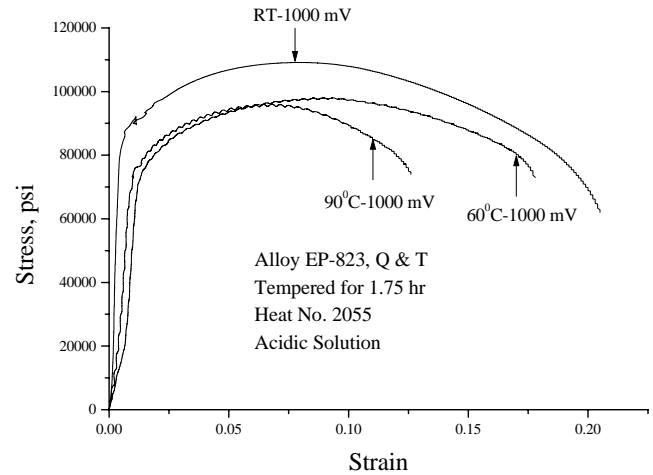
## BACKGROUND

The primary objective of this task was to evaluate the effects of environmental and mechanical parameters on environment-induced degradations of candidate target structural materials for applications in spallation-neutron-target systems. The materials selected for evaluation and characterization were martensitic stainless steels including Alloys HT-9, EP-823, and 422.

Accelerator-driven transmutation systems involve bombarding a target material such as molten lead-bismuth eutectic (LBE) by a proton beam, thereby producing neutrons. The molten LBE target will be contained in a subsystem structural container made of a suitable material such as Alloys HT-9, EP-823, and 422. During the transmutation process, the target structural material may become susceptible to different types of environment-induced degradations such as stress corrosion cracking (SCC), hydrogen embrittlement (HE), and localized (pitting and crevice) corrosion. While the performance of these candidate materials in the presence of a molten LBE is yet to be evaluated, substantial work has been performed in this task to evaluate the corrosion behavior of these alloys in aqueous environments of interest. These baseline data can eventually be utilized to compare them to those yet to be generated in the molten LBE environment.

## RESEARCH OBJECTIVES AND METHODS

This investigation was focused on the evaluation of the susceptibility of all three martensitic alloys to SCC, HE, and localized corrosion in neutral and acidic aqueous environments at ambient and elevated temperatures. State-of-the-art experimental techniques including constant-load (CL), slow-strain-rate (SSR), and cyclic potentiodynamic polarization were employed to evaluate these corrosion phenomena. The susceptibility of these alloys to HE was evaluated by applying cathodic potential while



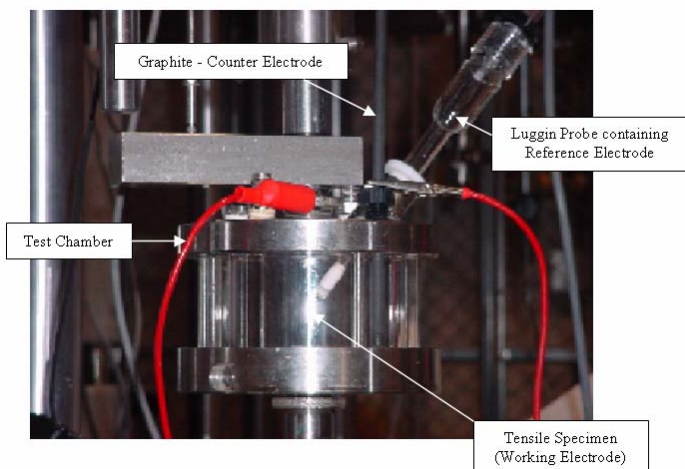
*Stress vs Strain under Controlled Potential.*

the test specimens were loaded in tension by the SSR method. Optical microscopy and scanning electron microscopy (SEM) were used to analyze the metallurgical microstructures and fractography, respectively of the tested specimens.

## RESEARCH ACCOMPLISHMENTS

The significant results derived from this task are summarized as follows:

- No failures were observed in smooth specimens of Alloys EP-823 and 422 in the neutral solution when tested at CL. However, Alloy HT-9 showed failure in the 90°C neutral solution at an applied stress ( $\sigma_a$ ) of 112 ksi.
- All three alloys exhibited failure in the 90°C acidic solution at 95% of their YS values. Alloys HT-9 and 422 also showed failures at  $\sigma_a$  of 90 and 85% of their YS values, but no failure was observed with Alloy EP-823 at stresses below 0.95 YS.
- The magnitudes of the threshold stress ( $\sigma_{th}$ ) for cracking for Alloys EP-823, HT-9 and 422 were 100, 95, and 98 ksi (689, 655, and 676 MPa), respectively based on CL testing in the 90 °C acidic solution. The presence of a notch in the test specimen reduced the  $\sigma_{th}$  values in all three alloys.
- The results of SSR testing in the acidic solution involving smooth specimens showed gradual reduction in ductility parameters (percent elongation - %El and percent reduction in area-%RA), time-to-failure (TTF), and true failure stress ( $\sigma_f$ ) with increasing temperature, indicating a synergistic effect of pH and temperature in enhancing the cracking susceptibility. The presence of a notch in the specimen produced enhanced SCC susceptibility due to the stress concentration. However, the  $\sigma_f$  value was increased due to plastic constraint resulting from triaxial stress field at the notch.
- The magnitude of %El, %RA, TTF, and  $\sigma_f$  was reduced under



*Controlled Potential Test Setup*

an applied potential of -1,000 mV (Ag/AgCl) compared to those obtained without an applied potential.

- The failure mode at the primary fracture face of the specimen tested in the neutral solution, determined by SEM, was characterized by dimpled microstructure, indicating ductile failures. However, intergranular and/or transgranular brittle failures were observed in the acidic environment.
- Secondary cracks with branching were observed by optical microscopy on all three tested materials along the gage section of the specimens tested in the acidic solution.

#### TASK 4 PROFILE

Start Date: June 2001

Completion Date: December 2004

##### Theses Generated:

- Ramprashad Prabhakaran, M.S., "Environment-Induced Degradations in a Target Structural Material for Transmutation Applications," August 2004.
- Sudheer Sama, M.S., "Embrittlement and Localized Corrosion in Alloy HT-9," August 2004.
- Phani P. Gudipati, M.S., "Stress Corrosion Cracking Resistance of Martensitic Stainless Steels for Transmutation Applications," December 2004.
- Mohammad K. Hossain, Ph.D., "Stress Corrosion Cracking and Hydrogen Embrittlement of Martensitic Alloy EP-823," December 2004.
- Venkataramakrishnan Selvaraj, M.S., "Environment Assisted Cracking of Target Structural Materials under Different Loading Conditions," December 2004.

##### Journal Articles:

- A.K. Roy and M.K. Hossain, "Cracking of Martensitic Alloy EP-823 under Controlled Potential," *Journal of Materials Engineering and Performance*, American Society of Metals International, Vol. 15, No. 3, June 2006, pp. 336-344.
- A.K. Roy, M.K. Hossain, R. Prabhakaran, and S. Sama, "Environment-Assisted Cracking of Structural Materials under Different Loading Conditions," *Corrosion*, National Association of Corrosion Engineers (NACE) International, April 2005, Vol. 61, No. 4, pp. 364-370.
- A.K. Roy, R. Prabhakaran, M.K. Hossain, and S. Sama, "Stress Corrosion Cracking of Nuclear Transmutation Structural Materials," *Materials Performance*, NACE International, September 2004, Vol. 43, No. 9, pp. 52-56.

##### Conference Proceedings:

- A.K. Roy, and M.K. Hossain, "Environment Induced Embrittlement of Martensitic Stainless Steel for Transmutation Applications," *Corrosion 2005*, NACE International, Houston, TX, April 2005.
- A.K. Roy, Phani P. Gudipati, Venkataramakrishnan Selvaraj, "Environment Degradation of Martensitic Stainless Steels for Transmutation Applications," *Materials Science and Technology (MS&T) 2004*, New Orleans, LA, September 26-29, 2004.
- A.K. Roy, R. Prabhakaran, "Stress Corrosion Cracking of Type 422 Stainless Steel for Transmutation Applications," *International Youth Nuclear Congress*, Toronto, Canada, May 9-13, 2004.
- R. Prabhakaran and A.K. Roy, "The Effect of Environmental and Mechanical Variables on Stress Corrosion Cracking of Martensitic Stainless Steels for Transmutation Applications," *International Conference on Nuclear Engineering, ICONE-12*, Student Paper Competition, Arlington, VA, April 25-29, 2004.
- A.K. Roy, M.K. Hossain, R. Prabhakaran, S. Sama, V. Selvaraj, P.P. Gudipati, "Stress Corrosion Cracking of Target Materials for Transmutation Applications," *Corrosion 2004*, NACE International, New Orleans, LA, March 28-April 1, 2004.
- A.K. Roy, R. Prabhakaran, "Characterization of Environment-Induced Degradation in Type 422 Stainless Steel," *Minerals, Metals and Materials Society*, Charlotte, NC, March 14-18, 2004.
- A.K. Roy, R. Prabhakaran, M.K. Hossain, S. Sama, V. Selvaraj, P.P. Gudipati, "Effect of Environmental Variables on Cracking of Martensitic Stainless Steels under Different Loading Conditions," *American Nuclear Society Meeting, Global 2003*, New Orleans, LA, November 16-20, 2003.
- A.K. Roy, R. Prabhakaran, M.K. Hossain, S. Sama, V. Selvaraj, P.P. Gudipati, "Environmental Effects on Materials For Nuclear Applications," *MS&T 2003*, Chicago, IL, November 9-12, 2003.
- A.K. Roy, S. Sama, R. Prabhakaran, M.K. Hossain, "Cracking of Martensitic Stainless Steels under Applied Electrochemical Potential," 204<sup>th</sup> Meeting of the Electrochemical Society, Abstract No. 1255, Orlando, FL, October 12-17, 2003.
- A.K. Roy, R. Prabhakaran, M.K. Hossain, S. Sama, B. J. O'Toole, "Environment-Induced Degradation of Spallation Target Materials," *American Nuclear Society Meeting, AccApp'03*, San Diego, CA, June 1-5, 2003.
- A.K. Roy, M.K. Hossain, B. J. O'Toole, "Stress Corrosion Cracking of Martensitic Stainless Steel For Transmutation Applications," *The 10<sup>th</sup> International High-Level Radioactive Waste Management Conference*, Las Vegas, NV, March 30-April 3, 2003.
- R. Prabhakaran, "Stress Corrosion Cracking of Type 422 Stainless Steel For Applications in Spallation-Neutron-Target Systems," *Spallation Neutron Source, Joint Institute for Neutron Sciences*, Neutrons in Solid-State Chemistry and the Earth Sciences Today and Tomorrow, Oak Ridge, TN, March 12, 2003.
- A.K. Roy, M.K. Hossain, and B.J. O'Toole, "Stress Corrosion Cracking of Martensitic Stainless Steel for Transmutation Applications," *International High-Level Radioactive Waste Management Conference*, Las Vegas, NV, Sept. 2002.

##### Research Staff

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Aaron Tippetts, Undergraduate Student, Mechanical Engineering Department

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Stuart A. Maloy, Ph.D., AFCI Materials Team Leader, Los Alamos National Laboratory

## Task 5

# Modeling Corrosion in Oxygen Controlled LBE Systems with Coupling of Chemical Kinetics and Hydrodynamics

S. Moujaes and Y. Chen

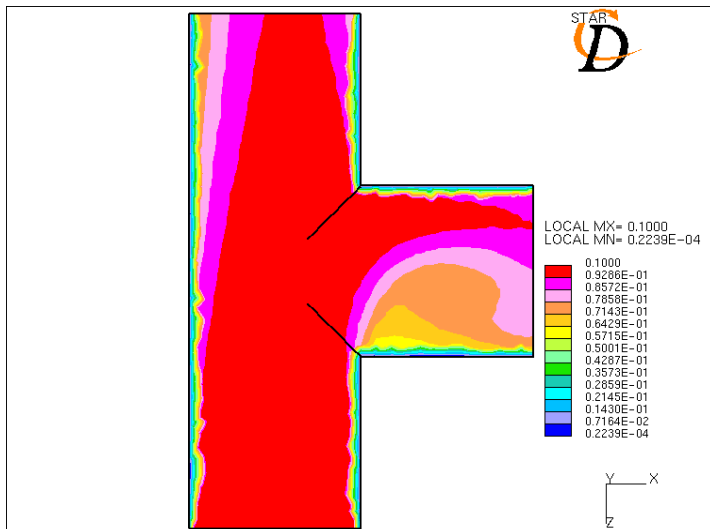
## BACKGROUND

The corrosion of structural materials is a major concern for the use of lead-bismuth eutectic (LBE) systems for nuclear applications such as in transmuter targets or fast reactors. Corrosion in liquid metal systems can occur through various processes, including, for example, dissolution, formation of inter-metallic compounds at the interface, and penetration of liquid metal along grain boundaries. Predicting the rate of these processes depends on numerous system operational factors: temperature, system geometry, thermal gradients, solid and liquid compositions, and velocity of the liquid metal, to name a few. Corrosion, along with mechanical and/or hydraulic factors, often contributes to component failure.

The goal of this project was to develop a corrosion model that combines the chemical kinetics and hydrodynamics in the system to predict corrosion rates. In this effort, these models were developed for the Delta test loop at Los Alamos National Laboratory (LANL) and a theoretical LBE accelerator target system. The resulting models are predictive tools that can be validated with corrosion test data and used to systematically design tests, interpret the results, and provide guidance for optimization in LBE system designs.

## RESEARCH OBJECTIVES AND METHODS

There were two subtasks to this research. The first subtask developed the necessary tools to predict the levels of oxygen and corrosion products close to the boundary layer using Computational Fluid Dynamics (CFD) modeling. The second subtask predicted the corrosion process kinetics between the LBE and structural materials by incorporating pertinent information from the first subtask.



Concentration profile for T-joint at  $Re = 200,000$ .

STAR-CD software was used to model the corrosion and precipitation rates in the LBE loop. This allowed researchers to compare the theoretical analysis with available experimental results. The surface corrosion analysis is being developed as a user supplied subroutine to STAR-CD. The information obtained from this analysis theoretically predicts likely locations for corrosion and precipitation along the axial lengths of the test loop.

The first subtask involved performing a series of parametric runs. Models prepared from the earlier work were used as guides for the parametric studies. Variables investigated included the average eutectic flow velocity, average mean bulk eutectic flow, inlet temperatures, and average inlet oxygen concentrations in the three geometries: a straight flow section, an elbow bend, and a tee section. The thermal-hydraulics study involved using a 3-D CFD code simulation to obtain averaged values of stream-wise velocity, temperatures, and oxygen and corrosion product concentrations at various axial locations close to the walls of several partial loop sections within the LBE loop. The oxygen and corrosion products inside the test loop were simulated to participate in chemical reactions with the eutectic fluid as it diffused towards the walls. Details of the geometry of these loops were obtained from scientists at LANL. These values acted as a set of starting boundary conditions for the second task.

The second subtask focused on the kinetics of the dissolution/deposition process as a function of temperature, flow velocities, dissolved metal concentrations, oxygen potentials of the system, the kinetics of film formations in the presence of oxygen, and the kinetics of metal transport through the oxidized surface film.

## RESEARCH ACCOMPLISHMENTS

Geometries and flow conditions similar to experimental results in the literature were set up and used to benchmark the models assembled using the STAR-CD software. Test case studies indicated that the outcome from STAR-CD was correct and that numerical modeling is applicable to the research in this problem.

Using these models, concentration flux profiles were obtained for both laminar and turbulent profiles in a straight pipe. This information was then used for the chemical kinetics analysis for corrosion on the inside walls of the LBE loop.

Several CFD runs were made to simulate flow in pipe fittings. These include sudden contraction, sudden expansion and a T-joint. Testing of a new turbulent model was also performed using the k- $\epsilon$  Chen model which works better with high Re number flows and predicts some of the peculiar flow features relevant to sudden expansions where eventually vortex generation is expected at the backward step.

The k- $\epsilon$  Chen model which works better with high Re number flows and predicts some of the peculiar flow features relevant to sudden expansions where eventually vortex generation is expected at the backward step.

A user subroutine was developed that simulated the corrosion/precipitation processes and predicted their maximum/minimum location in a typical LBE loop. A chemical reaction subroutine dealt with surface chemistry. The Arrhenius Equation was used to calculate the reactant reaction rate but some constants and coefficients used in calculating chemical reaction rate were updated using some empirical data found in chemical reaction research papers and textbooks.

The location in the loop with the highest concentration occurred in the baffle cell which is adjacent to the iron surface while the area with lowest concentration occurs around the central line of the pipe. It can be inferred that after  $\text{Fe}_3\text{O}_4$  is formed, it diffuses to the fluid area close to the central line of pipe. But, overall, the concentration value was very low.

Similar to the concentration gradient, the area with the highest temperature occurs in the baffle cell which is adjacent to iron surface while the area with lowest temperature occurs around the central line of the pipe. It is obvious, based on the model, that heat was transferred from inner wall to central area of the pipe due to the setting of constant heat flux boundary conditions in the baffle cells.

The chemical reaction model subroutine worked well and this simple CFD model roughly simulated the chemical reaction, diffusion, and heat transfer condition inside the LBE piping. Since

the subroutine works well, it can be used in much more complex modeling.

## TASK 5 PROFILE

Start Date: August 2001

Completion Date: August 2004

### Theses Generated:

Chao Wu, M.S., Mechanical Engineering, "Study of Geometry Effects on Local Corrosion Rates for LBE Loop," July 2003.

Kanthi Dasika, M.S., Mechanical Engineering, "Chemical Kinetics and Thermal Hydraulics of Lead Bismuth Flow Loops," December 2003.

Narain Armbya, M.S., Mechanical Engineering, "CFD Analysis of 3-D Thermal Hydraulics Flow Effects on Wall Concentration Gradient Profiles for LBE Loop Fittings," December 2004.

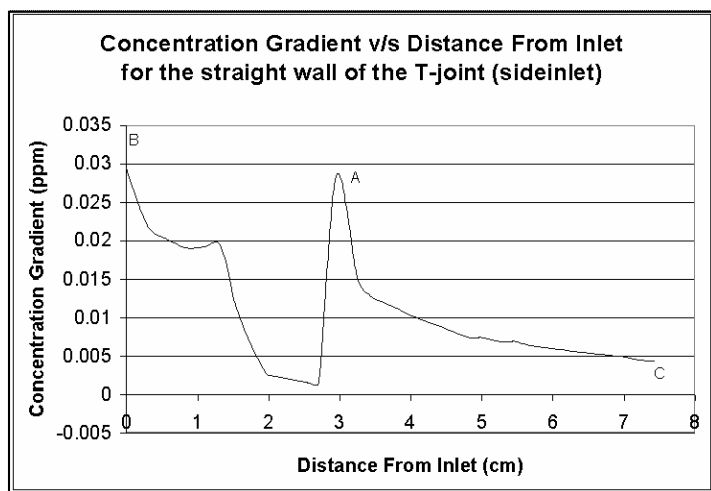
### Conference Proceedings:

C. Wu, K. Dasika, Y. Chen, S. Moujaes, J. Zhang and N. Li, "Study of Geometry Effects on Local Corrosion Rates for LBE Loop," American Nuclear Society Summer Meeting, San Diego, CA, June 1-5, 2003.

S. Moujaes, Y. Chen, K. Dasika, C. Wu, N. Li, and J. Zhang, "Simulation Considerations in Lead-Bismuth Transmutation Loops: Corrosion Concentration, velocity and Temperature Profiles of LBE Loops," 10th International Conference on Nuclear Reactor Thermal Hydraulics, South Korea, October 5-9, 2003.

K. Dasika, C. Wu, S. Moujaes, and Y. Chen, "Modeling of Oxygen Controlled Surface Reaction Kinetics and Hydrodynamics," International Youth Nuclear Congress, Seoul, South Korea, April 2002.

K. Dasika, C. Wu, S. Moujaes, and Y. Chen, "Numerical Modeling of Lead Oxidation in Controlled Lead Bismuth Eutectic Systems: Chemical Kinetics and Hydrodynamic Effects," International Congress on Advances in Nuclear Power Plants, American Nuclear Society, Hollywood, FL, June 2002.



*Concentration gradient versus distance from the inlet for the straight wall.*

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## Task 6

# Neutron Multiplicity Measurements of Target/Blanket Materials

D. Beller

## BACKGROUND

The U.S. Advanced Fuel Cycle Initiative (AFCI) is a program to develop economic and environmental methods to reduce the impact of waste from commercial nuclear fuel cycles. One concept for near-complete destruction of waste isotopes from used nuclear fuel is accelerator-driven transmutation. High-power accelerators would be used to produce high-energy charged particles, which then collide with heavy metal targets to create a cascade of neutrons. These neutrons then cause nuclear reactions in subcritical systems.

To design these systems, complex reactor physics computer codes and highly detailed data libraries are used to compute the reactivity of systems, reaction rates, destruction rates, and nuclear-induced damage rates to materials. In this project, a Russian-built detector system was used to make measurements of neutrons generated in a central target by a variety of accelerators.

## RESEARCH OBJECTIVES AND METHODS

A prototype modular Neutron Multiplicity Detector System (NMDS) with 64  $^3\text{He}$  gas counting tubes was developed to measure the neutron multiplicity of scaled lead accelerator targets. Its modularity allows it to be configured for a variety of experiments to measure neutron multiplicity from different sources: protons, electrons, high-energy neutrons, or even cosmic particles such as muons.

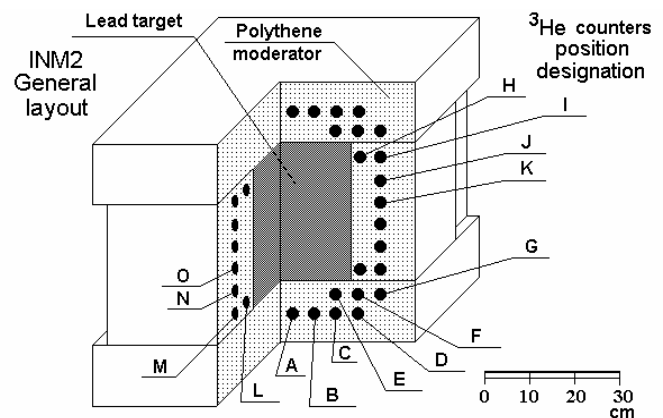
This system may be used to measure neutron production in a variety of configurations, on a variety of targets, with a variety of source particles, and over a range of energies (10 to 800 MeV) to produce a large database that may be used to validate neutron multiplicity predictions. This should enable the quantification of systematic errors in the latest version of MCNPX and its accompanying data libraries. Time-dependent measurements of neutron production in the NMDS should provide a systematic set of precise data that will enable direct comparison with code calculations.

Comparison of results from the NMDS may decrease uncertainties and allow the derivation of relative measurements in the few percent range at the 95 percent confidence level. In addition, discrepancies that are discovered with this system can contribute to the improvement of the codes and data libraries. Improved models of beam line experiments, accelerator targets, and detector designs will result from these code improvements.

## RESEARCH ACCOMPLISHMENTS

Initial work in this project included the development of geometric models of the target-detector assemblies for use with the MCNPX radiation transport code to optimize the design of the NMDS. Radiation transport calculations of neutron detection efficiency

were completed and interpreted prior to developing designs of the neutron detection systems needed to perform multiplicity measurements. Following completion of the modeling, a fabrication effort was initiated. A series of MCNPX models were developed at UNLV for a cylindrical target. Another generic model was created to examine response times, collection efficiencies, and escape probabilities. In addition to modeling at UNLV, colleagues at the V.G. Khlopin Radium Institute (KRI) completed preliminary radiation transport modeling using the CONTROL code developed by KRI researchers.



NMDS in the INM2 ("CUBE") geometry.

The 64-element  $^3\text{He}$ -detector-based NMDS was fabricated by KRI and shipped to UNLV. It was assembled at UNLV in the "CUBE" geometry (30 cm x 30 cm x 30 cm of lead inside and 8 to 12 detectors on each of the 6 sides of the cube. Detection efficiencies in  $^3\text{He}$  as well as fractional capture in Pb and polyethylene were calculated. A  $^{252}\text{Cf}$  source was used to calibrate the NMDS. Measured efficiencies were comparable to calculations and measurements were completed at KRI.

### ISU-IAC Experiments

To evaluate its usefulness for measurement of spallation neutrons, the NMDS was transported to the Idaho Accelerator Center at Idaho State University where it was used in conjunction with a linear accelerator to determine its performance.

An americium-beryllium (AmBe) source with a neutron production rate of  $2500 \text{ n/s} \pm 10\%$  was placed against the face of the Pb in all 5 configurations to measure the overall efficiency of the system. This weak source exceeded the counting capacity of the NMDS, such that its efficiency was reduced to 3.5% compared to earlier values at UNLV of 20-30% with source strength of  $\sim 600 \text{ n/s}$ . This was the first indication of a severe count-rate limitation of the NMDS.

To accommodate this limitation, the accelerator was "de-tuned" to reduce the neutron production rate within the boundaries of the

detectors. All results from the ISU-IAC accelerator-driven experiments were influenced by a count-rate limitation that is inherent in the NMDS hardware and software.

Accelerator-based testing commenced with the electron beam and several parameters and results were examined and compared to radiation transport predictions in these studies. These parameters include the neutron absorption time or lifetime, efficiencies of the systems and individual detectors, and multiplicity distributions.

#### NTS-RSL Experiments

In an effort to determine system contributions to dead-time, a dead-time measurement experiment was conducted at the Remote Sensing Laboratory (RSL) of the Nevada Test Site (NTS). Results indicated that the performance of individual detectors depends upon the number of detectors operating as well as the source strength. The individual detectors were determined to have a dead-time coefficient of a few ms, which would indicate a capability of the total system to count several thousand neutrons per second. However, the system has never counted more than 200 n/s, even with strong neutron sources. Each system component contributes to dead-time. In the final analysis, however, these experiments at ISU-IAC and NTS-RSL demonstrated that the performance of the system is critically limited by the Russian hardware and, as a consequence of these experiments, a modern data acquisition system was acquired that will support the maximum performance of each detector and all the detectors combined.



Graduate student Shruti Patil checks signals on one of the 8-detector control boxes of the NMDS.

## TASK 6 PROFILE

Start Date: August 2001

Completion Date: December 2005

#### Conference Proceedings:

- T. Beller, D. Curtis, D. Beller, A. Rimsky-Korsakov, and T. Ward, "The UNLV Neutron Multiplicity Detector System," *Proceedings of the Eighth Information Exchange Meeting on Actinide and Fission Product Partitioning & Transmutation*, Organization for Economic Cooperation and Development, Nuclear Energy Agency, Paris, France, pp 687-698, 2005.
- T. Ward, A. Rimski-Korsakov, N. Kudryashev and D. Beller, "Integral Neutron Multiplicity Measurements from Cosmic Ray Interactions in Lead," *Proceedings, XVII Particles and Nuclei International Conference*, Santa Fe, NM, October 24-28, 2005.
- D. Curtis, D. Beller, C. Hull, A. Rimsky-Korsakov, and T. Ward, "Modeling Neutron Multiplicities in a 60-element  $^3\text{He}$  Detector System," *Proceedings of the Sixth International Meeting on Nuclear Applications of Accelerator Technology*, American Nuclear Society, pp. 190-194, 2004.
- T. Beller, D. Curtis, D. Beller, A. Rimsky-Korsakov and T. Ward, "The UNLV Neutron Multiplicity Detector System," Eighth Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation, Organization for Economic Cooperation and Development, Nuclear Energy Agency, Las Vegas, NV, November 9-11, 2004.
- D. Curtis, D. Beller, C. Hull, A. Rimsky-Korsakov, and T. Ward, "Modeling Neutron Multiplicities in a 60-Element  $^3\text{He}$  Detector System," Sixth International Meeting on Nuclear Applications of Accelerator Technology (AccApp'03), American Nuclear Society, San Diego, CA, June 1-5, 2003. (Awarded Best Overall Poster for AccApp'03)
- T. Ward, A. Rimski-Korsakov, M. Todosow, G. Greene, M. Divadeenam, C.L. Snead, Jr., A. Hanson, E. Pitcher, D. Beller, C. Hull, W. Culbreth, A. Hechanova, and G. Cerefice, "Note on the Benchmark and Validation of the LAHET Code System," American Nuclear Society Winter Meeting, Reno, NV, November 11-15, 2001.

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# Task 7

## Development of Dose Coefficients for Radionuclides Produced in Spallation Targets

P.W. Patton and M.J. Rudin

### BACKGROUND

Ensuring the safety of workers at accelerator-driven nuclear facilities is paramount before these systems can be deployed for nuclear transmutation or any other mission. Spallation neutron sources produce as many as 660 rare radionuclides in either the target or blanket during the spallation process. No data exists for many of these radionuclides in the current radiation protection guidelines and standards. This research program seeks to address this problem through generating internal and external dose coefficients (DCs) for these “new” isotopes.

Dose coefficients permit simple determination of radiation dose associated with various exposure scenarios, and ultimately permit radiation safety personnel to assess the health risks to workers in a nuclear facility. Specifically, radiation safety personnel use dose coefficients to determine the radiation dose incurred to a tissue or organ system from a given exposure. These parameters are often expressed in terms of Annual Limits on Intake (ALIs) and Derived Air Concentrations (DACs).

### RESEARCH OBJECTIVES AND METHODS

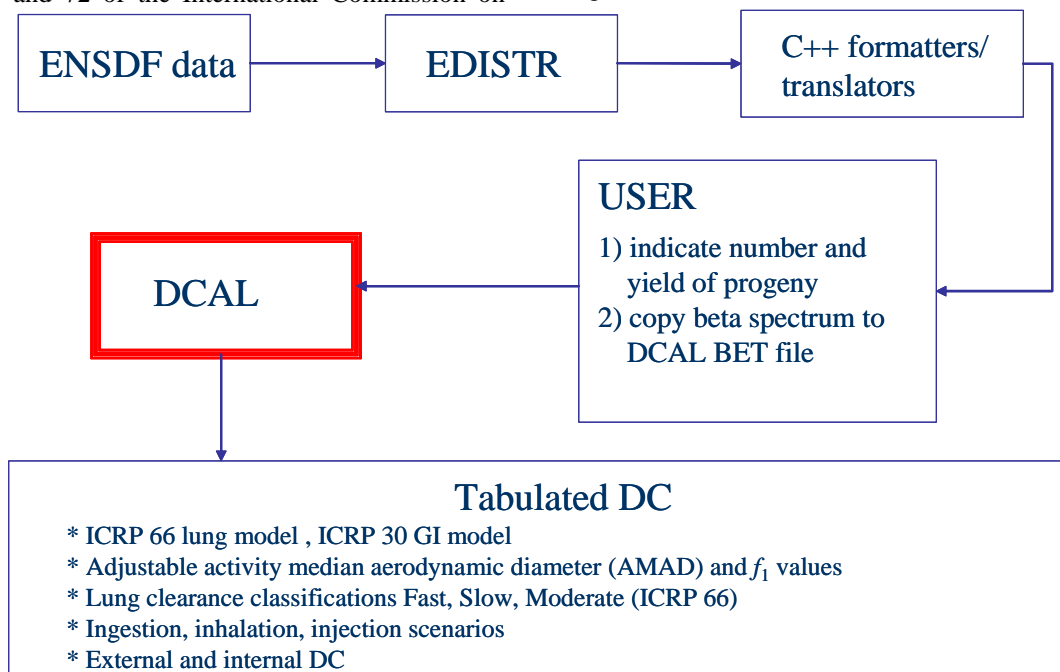
Results from this study will be used to produce ALIs and DACs for these rare radionuclides created by spallation target systems that are not included in Federal Guidance Report (FGR) No. 11. Additionally, DCs developed will augment the radiological data in Publications 68 and 72 of the International Commission on

Radiological Protection (ICRP), contributing to the safe operation of accelerator-driven nuclear systems.

A Dose Coefficient Working Group was established in 2001 (the first year of the project) to direct and oversee consortium activities. Representatives from the Dose Coefficient Working Group developed and verified a methodology to determine internal and external dose for select radionuclides. The first step involved obtaining radiological data from the ENSDF nuclear physics database developed at Brookhaven National Laboratory. Data collected included decay modes, decay energy levels, and radiation energies and intensities.

The DC working group prioritized a list of radionuclides projected to be released via air emissions or in the inventory of a mercury target following a lengthy irradiation period. Only radionuclides with a half-life greater than one minute were considered. These 81 radionuclides were then categorized into three distinct categories, based on half-life, available information, and other technical factors.

All Category 2 radionuclides were investigated to determine which database was most current. However, this task was not straight forward and thus both databases were used to calculate all radionuclides that had complete data. Dose coefficients were then generated for the Category 2 radionuclides using both ENSDF and NUBASE. The results were compared and showed good agreement. Metabolic models and data from ICRP publications



*Dose Coefficient Working Group Methodology Flow Sheet. The ENSDF code is used to obtain nuclear physics data. The EDISTR code prepares the data for input into the dose calculation code DCAL.*

(30 and 66) were applied in order to use the best technology available and to maintain consistency with current standards. In accordance with FGR No. 11, dose coefficients were evaluated for an adult male with the target tissues of gonads, breast, lung, red marrow, bone surface (endosteum), thyroid, remainder, and total committed effective dose equivalent (this considers total dose incurred to specific organs or tissues with respect to radiation type over a period of 50 years). Following determination of these variables, values of ALIs and DACs were then calculated for each radionuclide.

The consortium investigated the competing databases to determine the most appropriate one to use for dose coefficient calculations. However, conflicting data made it unclear which was better suited for this task, therefore the previously calculated coefficients were reported. Additionally, time was devoted to trying to acquire missing nuclear data for radionuclides in category three. The consortium believes large scale accelerator driven experiments are needed to accomplish this goal.

## RESEARCH ACCOMPLISHMENTS

The research consortium comprised of representatives from several universities and national laboratories has successfully generated internal and external dose conversion coefficients for twenty radionuclides produced in spallation neutron sources. These dose coefficients fill data gaps exist in Federal Guide Report No. 11 and in Publications 68 and 72 of the International Commission on Radiological Protection, and two articles containing the data have been accepted for publication in the *Journal of Health Physics*. Currently, more nuclear data is needed for the rare radionuclides produced from a mercury target. While attempting to develop a workable plan to acquire this missing data, Q-value discrepancies were investigated and reported. A detailed plan was developed to start a research effort at Idaho State University to produce rare radionuclides. This process will allow for the investigation of the missing nuclear data needed to complete dose coefficients.

## TASK PROFILE

Start Date: June 2002

Completion Date: April 2006

### Theses Generated:

John P. Shanahan, M.S., Health Physics Department, "Dose Coef-

ficients for Radionuclides Produced in a Spallation Neutron Source," August 2003.

Yayun Song, M.S., Health Physics Department, "Investigation and Calculations of Dose Coefficients for Radionuclides Produced in a Spallation Neutron Source Using the ENSDF and NUBASE Nuclear Databases," May 2004.

### Publications:

- J. Shanahan, K. Eckerman, A. Arndt, C. Gold, P. Patton, M. Rudin, R. Brey, T. Gesell, V. Rusetski, and S. Pagava, "Calculation of Dose Coefficients for Radionuclides Produced in a Spallation Neutron Source Utilizing NUBASE and the Evaluated Nuclear Structure Data File Databases." *Health Phys* 90:56-65, 2006.
- A. Arndt, J. Shanahan, C. Gold, R. Brey, T. Gesell, P. Patton, M. Rudin, K. Eckerman, V. Rusetski, and S. Pagava "Procedures and Quality Assurance for Calculating Dose Coefficients Using DCAL Software." *Health Phys* 90:74-80, 2006.
- J. Shanahan, K. Eckerman, A. Arndt, C. Gold, P. Patton, M. Rudin, R. Brey, T. Gesell, V. Rusetski, and S. Pagava, "Calculation of Dose Coefficients for Radionuclides Produced in a Spallation Neutron Source Utilizing NUBASE and the Evaluated Nuclear Structure Data File Databases," accepted August 16, 2005 for publication in the *Health Physics Journal*, *Health Phys.* 89(6), 2005.
- A. Arndt, J. Shanahan, C. Gold, R. Brey, T. Gesell, P. Patton, M. Rudin, K. Eckerman, V. Rusetski, and S. Pagava, "The Procedure for Determining and Quality Assurance Program for the Calculation of Dose Coefficients Using DCAL Software," accepted April 2005 for publication in the *Health Physics Journal*.
- J. Shanahan, K. Eckerman, A. Arndt, C. Gold, P. Patton, M. Rudin, R. Brey, T. Gesell, V. Rusetski, and S. Pagava, "An Interdatabase Comparison of Nuclear Decay and Structure Data Utilized in the Calculation of Dose Coefficients for Radionuclides Produced in a Spallation Neutron Source," accepted March 2005 for publication in the *Health Physics Journal*.
- J. Shanahan, A. Arndt, C. Campbell, R. Brey, M. Rudin, K. Eckerman, and P. Patton, "Calculation of Dose Coefficients for Radionuclides Produced in Spallation Neutron Sources," *Health Phys.* 84 (6S): S252 (2003).
- J. Shanahan, P. Patton, and M. Rudin, "Dose Coefficient Methodology Report," Health Physics Department, University of Nevada, Las Vegas, NV, Aug. 2002.

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Mark Rudin, Associate Professor, Department of Health Physics

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Rich Brey, Associate Professor, Idaho State University  
Adam Arndt and Chandra Gold, Graduate Students, Idaho State University  
Faculty and graduate students from Georgia Institute of Technology, University of Florida, Francis Marion University



## Task 8

# Development of a Systems Engineering Model of the Chemical Separations Process

Y. Chen, D.W. Pepper, and S. Hsieh

### BACKGROUND

The chemical processing of used nuclear fuel is an integral component of any strategy for the transmutation of nuclear waste. Due to the large volume of material that must be handled in this first step of the transmutation process, the efficiency of the separations process is a key factor in the potential economic viability of transmutation strategies. The ability to optimize the chemical separation systems is vital to ensure the feasibility of the transmutation program.

Systems analysis, or total systems modeling, is one of the strongest tools available to researchers for understanding and optimizing complex systems such as chemical separations processes. Systems analyses permit researchers to present decision-makers concise evaluations of system options and their characteristic features. The primary goal of this project was to develop a systems model that can be used to parameterize and optimize chemical separations processes.

### RESEARCH OBJECTIVES AND METHODS

This work includes reviewing and analyzing the Argonne Model for Universal Solvent Extraction (AMUSE) code structure, examining other possible implementations, defining software activities, developing a verification plan, and modifying and improving the software. This work also involves redefining the graphical user interface (GUI) to increase the utility of the AMUSE code suite as a stand-alone analytical package.

Developing a systems engineering model required discussions

with Argonne National Laboratory personnel to identify pertinent components of the chemical separations process. Each step required model development to establish its significance with regards to the overall process. Comprehensive model development involved defining the inputs and outputs from individual models and establishing how each connected to the other within in the chemical separations process.

### RESEARCH ACCOMPLISHMENTS

This project developed software for a general-purpose systems engineering model named Transmutation Research Program System Engineering Model Program (TRPSEMPro) that will be used to improve productivity in the design process. The system model also includes various numerical optimization technologies and "Design of Experiments" study technologies.

Object-Oriented Analysis and Design was used for developing and implementing the TRPSEMPro system. A graphical notation, Unified Modeling Language, was employed to express object-oriented designs. Microsoft.Net architecture was used for system development and Visual Basic.NET was the major programming language behind the system. XML (Extensible Markup Language) was used widely to describe data and sets of elements and attributes that can be defined by researchers. XML Schema was used for describing the structure of the system engineering model. XML Database was used to store all the run-time data for the AMUSE module. Since significant experimental data will be generated and require systematic analysis, MS SQL Server 2000 database was selected for housing all run-time parameters and simulation results.

The model is combined with commercial software packages MATLAB OPTIMIZATION toolbox and SIMULINK module from Mathworks.

The system model, TRPSEMPro, considers input simulation modules from multiple disciplines with inconsistent input/output handles. The package with the aid of middleware can communicate with various simulation modules developed by other research groups and create an XML-based model description file. The critical components for the system engineering modeling include System Manager, Model Integration, Study Plan, and Solution Viewer.

The introduction of the middleware design provides flexibility to interface to other simulation modules without significant program modification.

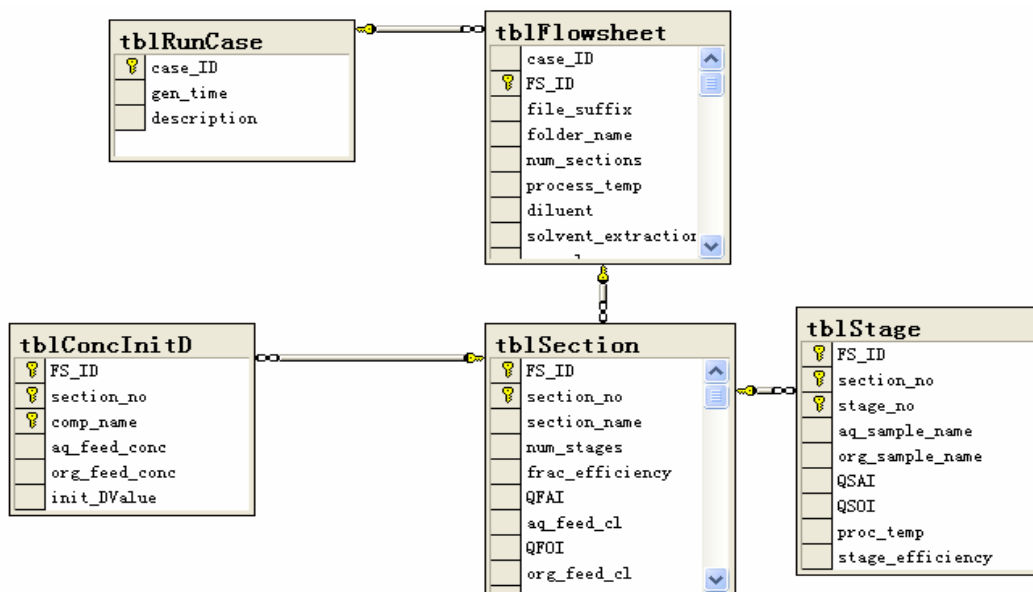


Diagram for the Structure of the Database Design.

The demonstration code from AMUSE macros is kept intact during all system development stages. AMUSESimulator, is the middleware software package which was designed and implemented to serve as a bridge between the AMUSE code, and the systems engineering model, TRPSEMPro. Such an approach can reduce the time-consuming modification on the system model side and keep flexibility on the simulation modules development side.

Further system enhancement allowed the user to select various process types. An interface for conducting multiple runs was created. The GUI included a list of variables, a range for those variables, all of which provide an envelope of end results.

## TASK 8 PROFILE

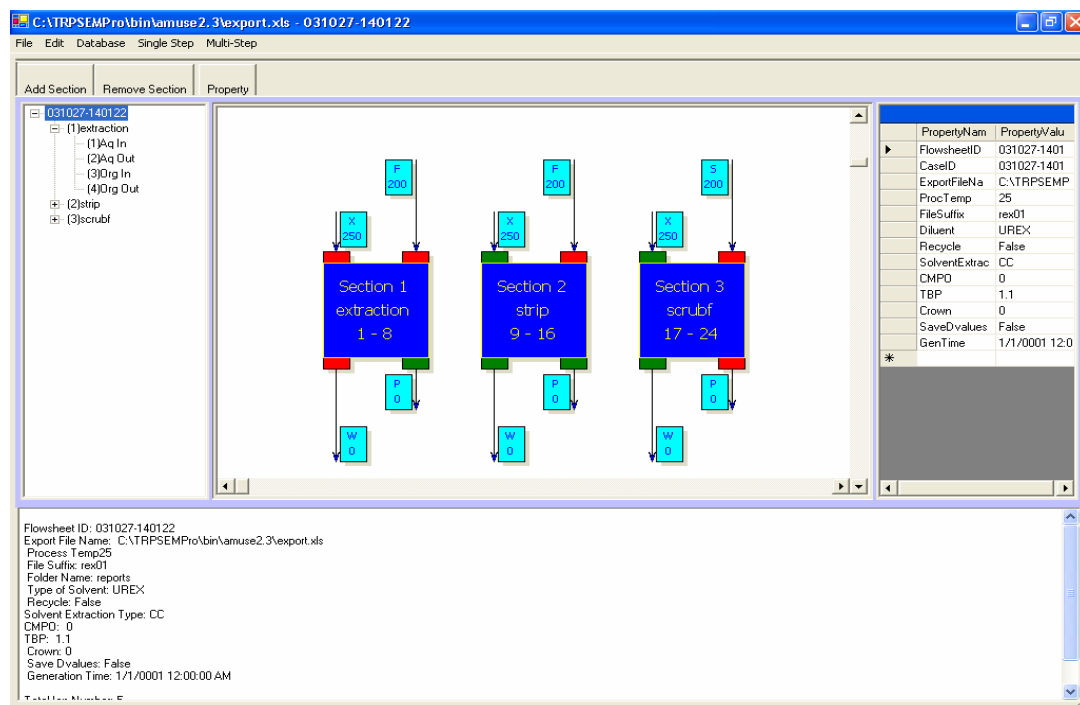
Start Date: August 2001

Completion Date: August 2004

(This work continued under Task 24, see pages 52-53.)

### Thesis Generated:

Lijian Sun, M.S., Mechanical Engineering, "Development of a Systems Engineering Model for Chemical Separation Process," December 2003.



L. Sun, Y. Chen, R. Clarksean, and J. Laidler, "The Development of a Systems Engineering Model for the DOE Advanced Accelerator Applications Program," International Congress on Advanced Nuclear Power Plants, Hollywood, FL, June 9-13, 2002.

*The main GUI for AMUSESimulator includes five parts as shown here. Menu and toolbar (Top Part) – where user can invoke all the available commands. Flowsheet contents displayed in tree view format (Left Part) – where user can select different section, stream. Flowsheet contents displayed in way of drawing blocks (Middle Part) – where user can select different sections, streams by clicking mouse at corresponding area.*

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# Task 9

## Design and Evaluation of Processes for Fuel Fabrication

G. Mauer

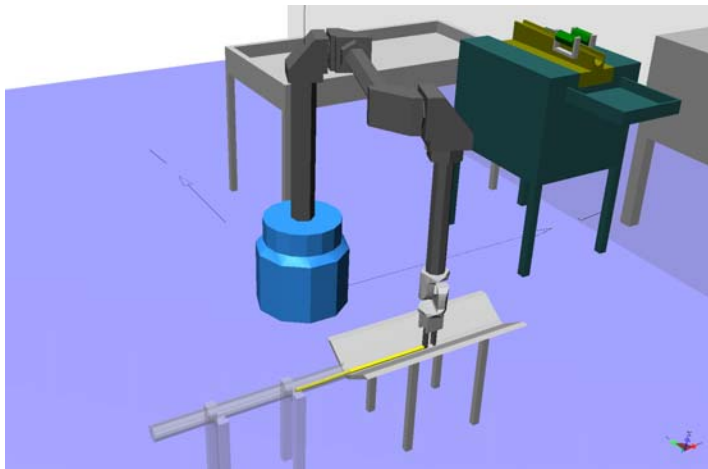
### BACKGROUND

The safe and effective manufacturing of actinide-bearing fuels for any transmutation strategy requires that the entire manufacturing process be contained within a shielded hot cell environment. To ensure that the fabrication process is feasible, the entire process must be designed for remote operation. The equipment must be reliable enough to perform over several decades, and also easy to maintain or repair remotely. The facility must also be designed to facilitate its own decontamination and decommissioning. In addition to these design factors, the potential viability of any fuel fabrication process will also be impacted by a number of variables, such as the current state of technology, potential problem areas, deployment scaling, facility safety, and cost.

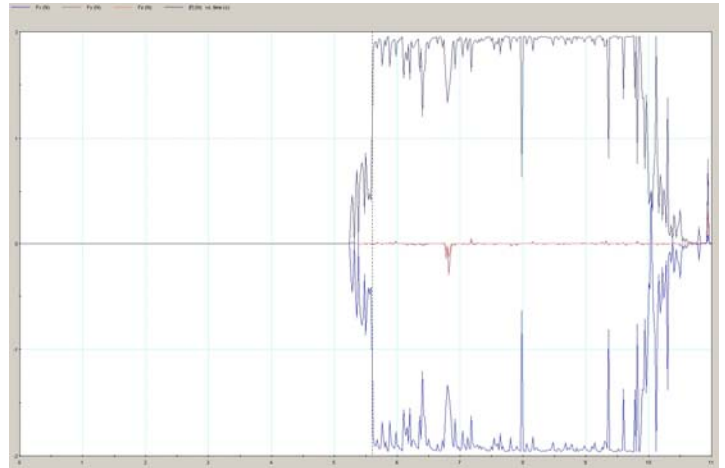
### RESEARCH OBJECTIVES AND METHODS

The goal of this research project was to provide technical support to process designers working on the development of the fuel cycles for transmutation applications. Detailed process models were developed to better define the impact of fuel choice on the transmuter fuel cycle, including relative process losses, waste generation, and plant capital cost. These process models provide insight regarding required plant size and number of plants needed to mesh with the fuel recycling line. They also determine requirements for automation.

Manufacturing models for large-scale production in a hot cell environment were also developed. Combined, these two models allow the assessment of plant layout, and provide the framework for estimation of plant capital and operating cost estimates, and for feasibility in general. The need for development in the areas of robotic and sensor technology was assessed. The manufacturing technology developed for hot cell applications was also applicable to other, more general uses, where occupational hazards



*The Waelischmiller robot inserts the fuel pins in the cladding tube.*



*Friction Force (N) between Second Pin and Cladding Tube vs. Time (sec) during Insertion.*

prevent human presence near processes.

The research work was divided into several tasks and subtasks:

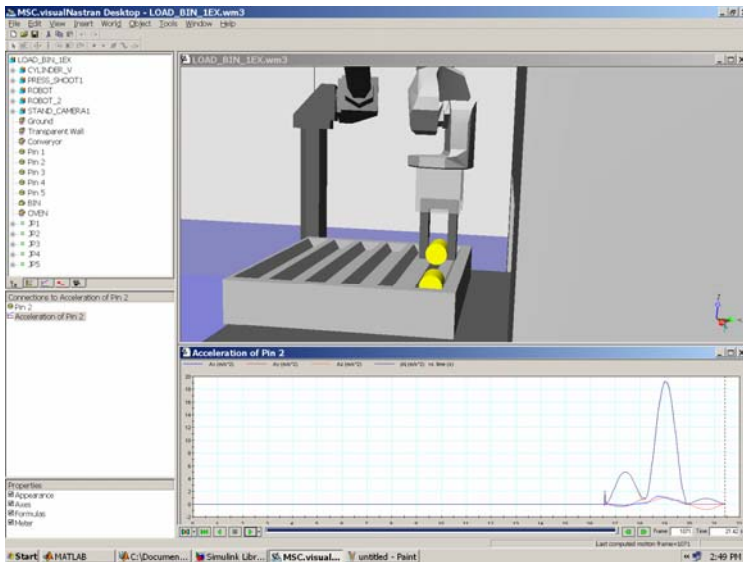
**Methods and Processes** – A literature survey and detailed analysis of the research and development pertaining to candidate processes for transmuter fuel manufacture was performed. Industry standards were used to refine equipment, instrumentation, and control specifications, and assessed the reliability and safety of operations.

**Simulations** – This task modeled manufacturing processes to generate a realistic assessment of plant layout, size, feasibility, and technology development required for large-scale remote fabrication of fuel. Modeling of the candidate fuel manufacturing processes was conducted using the MSC.visualNastran and ProEngineer simulation software tools. The modeling of powder-processed fuels was completed, and the modeling of other fuel types (metallic, TRISO etc.) was initiated.

**Process and Equipment for Autonomous Manufacturing** – This task developed an understanding of the cost and capability of current generation remotely operated equipment suitable for use in radiation environments. Monitoring of the market for equipment and components with regard to suitability for automated manufacturing under hot cell conditions was conducted.

**Sensors, Controls, and Operational Safety** – This task determined the adequacy of current technology and the need for suitable sensor technology development for deployment in hard radiation environments. A means to identify the precise location and spatial orientation of all parts in the robot's work envelope were implemented. The ability to position and handle materials along with trouble shooting techniques were evaluated. Radiation hardened vision systems appear to be promising technologies.





*Visual Nastran Analysis of Pellet accelerations. The simulation verified that pellet's acceleration did not exceed a specified maximum of 20 m/s<sup>2</sup>.*

**Cost, Feasibility, and Large Scale Deployment** – This task developed the database necessary to provide cost estimates and differential cost for various fuel manufacturing options. Efforts were initiated to tabulate and quantify estimates regarding projected cost, reliability, and plant life.

## RESEARCH ACCOMPLISHMENTS

A special simulation model with a Waelischmiller hot cell robot was developed and coupled with MatLab control software. Matlab provides the interface with the robot and is used to control the system. This renders a realistic simulation of the forces and torques present during robot motion. A 3-D manufacturing process simulation using computer aided design models and the Newtonian dynamics of the moving components was developed.

Results exist in the form of movies, data sets, and images. Simulations for several robot types were developed and their proper kinematic configuration was verified. The simulations permit the detailed analysis of forces and torques in any modeled part or component.

While the simulation process generally worked flawlessly, the simulation time rose considerably as more details were added to the simulation. The speed of the simulation has been increased about 100-fold by moving to fast dual-processor computers.

Efforts to develop a vision-based methodology for locating and identifying objects within the robot's workspace were conducted using the Artificial Intelligence algorithm for object identification.

Another accomplishment involved the development of algorithms for knowledge based pattern recognition using IF (a set of conditions is satisfied) THEN (a set of consequences can be executed) routines. Other simulation variables established included pattern matching using clustered indexing vectors containing information about an object and feature vector indexing, where a 3-D object is segmented into a set of simple geometric features. Each feature is stored with its vector segmentation and geometry information (magnitude, inner angle, etc.).

## TASK 9 PROFILE

Start Date: August 2001

Completion Date: August 2004

(This work continued under Task 22, see pages 48-49.)

### Thesis Generated:

Jae-Kyu Lee, Ph.D., Department of Mechanical Engineering, "Three Dimensional Pattern Recognition using Feature-based Indexing and Rule-based Search," December 2003.

### Conference Proceedings:

J.K. Lee and G. Mauer, "Feature-Based Pattern Recognition and Object Identification for Telerobotics," International Conference on Mechatronics, Institute of Electrical and Electronics Engineers, Seoul, South Korea, July 10-12, 2005.

G.F. Mauer and J. Renno, "Virtual Testing of Robotic Assembly Processes for Hot Cells," *Proceedings*, 10th International Conference on Robotics and Remote Systems for Hazardous Environments, March 2004.

G.F. Mauer and J. Renno, "Design and Analysis of Robotic Manufacturing Processes," *Proceedings*, American Nuclear Society Winter Annual Meeting, New Orleans, LA, November 2003.

G.F. Mauer, "Design and Evaluation of Processes for Transmuter Fuel Fabrication," *Proceedings*, American Nuclear Society Winter Annual Meeting, November 2002.

G.F. Mauer, "Object Recognition Over An Expanded Range Of Viewing Angles Using Indexing Methods," *Proceedings*, International Conference on Computer Applications in Industry and Engineering, San Diego, CA, November 2002.

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### Collaborators

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## Task 10

# Development of a Mechanistic Understanding of High-Temperature Deformation of Alloy EP-823

A. K. Roy and B.J. O'Toole

## BACKGROUND

During the transmutation process, a significant amount of heat can be generated in a molten lead-bismuth eutectic (LBE) target, which will be contained in a subsystem structural container made of a suitable martensitic iron-chromium-molybdenum (Fe-Cr-Mo) stainless steel such as Alloys EP-823, HT-9 and 422. These materials will be subjected to high tensile stresses while they are in contact with the molten LBE at temperatures ranging between 400 and 600°C. Therefore, a research program was conducted to evaluate the deformation characteristics of all three alloys in properly heat-treated conditions at temperatures relevant to the operating conditions.

## RESEARCH OBJECTIVES AND METHODS

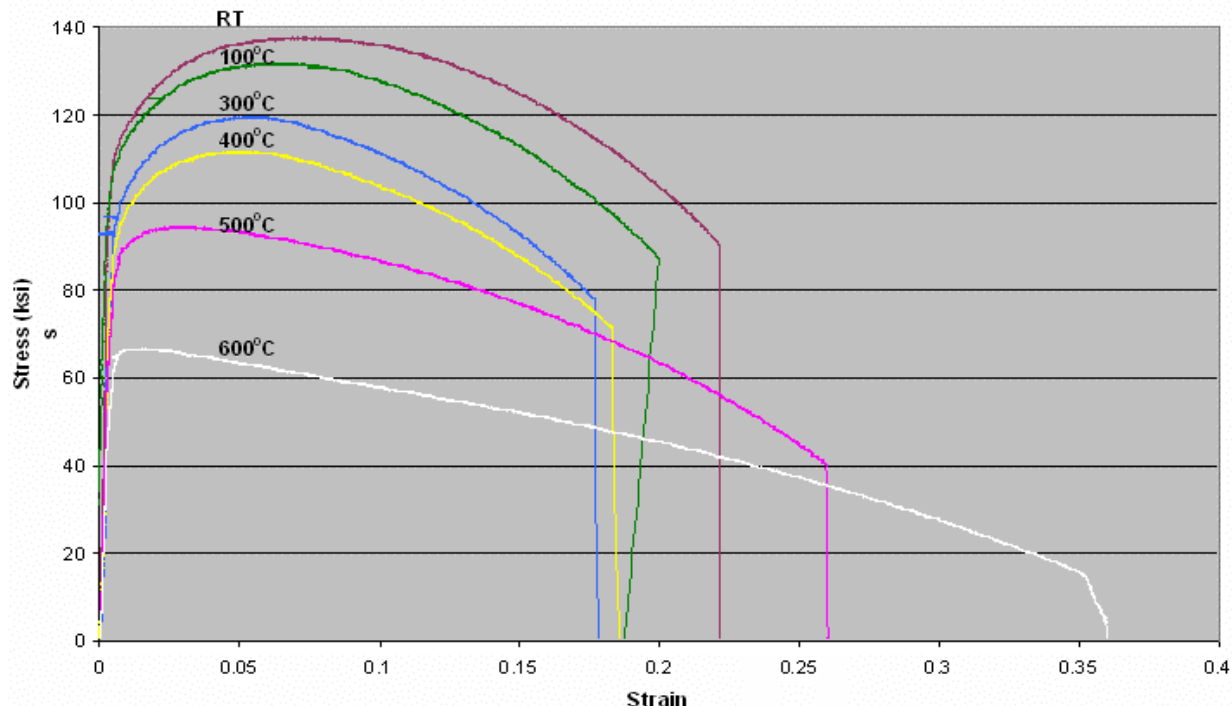
Experimental heats of Alloys EP-823, HT-9 and 422 were vacuum-induction-melted, followed by forging and hot rolling. The hot-rolled bars were subsequently thermally treated to produce a fully tempered and fine-grained martensitic microstructure without any retained austenite. They were austenitized at 1010°C, oil-quenched, and tempered at 621°C. The tempering operation was performed for 1.25, 1.75, and 2.25 hours, respectively, to study the effect of tempering time on the tensile properties. The hardness of all materials, before and after tempering, was measured using the Rockwell hardness scale. The tensile properties were determined at temperatures ranging from ambient to 600°C using smooth cylindrical specimens at a strain rate of  $10^{-3} \text{ sec}^{-1}$  accord-

ing to the American Society for Testing and Materials (ASTM) Designation E 8. A minimum of two specimens were tested under each condition, with the average value recorded. The metallurgical microstructures of the tested specimens were evaluated by optical microscopy. The primary fracture surface of the tensile specimens was analyzed by scanning electron microscopy (SEM) to determine the extent and morphology of failure. The resultant data include the percentage elongation (%El), percentage reduction in area (%RA), yield strength, and ultimate tensile strength as functions of the testing temperature and thermal-treatments. At least two specimens per material were tested under each of the three metallurgical conditions at the desired temperatures.

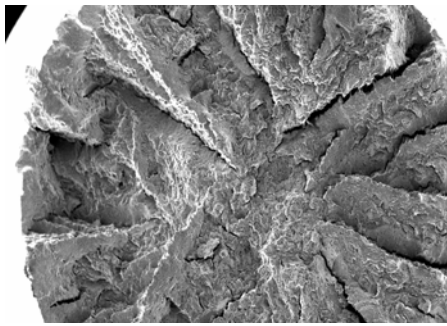
## RESEARCH ACCOMPLISHMENTS

The significant conclusions drawn from this investigation are summarized below:

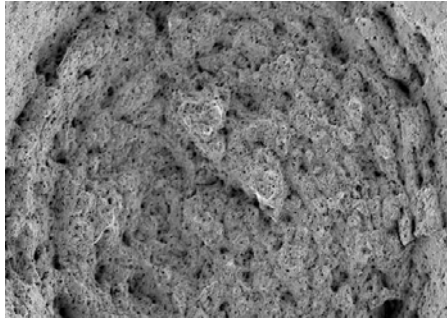
- The hardness of all three austenitized and quenched alloys were significantly reduced due to tempering, showing a gradual reduction with increasing tempering time.
- The magnitude of the yield, ultimate and failure stress were gradually reduced with increasing temperature, showing significant reductions at temperatures above 400°C.
- The extent of ductility in terms of %El and %RA was reduced to some extent in the temperature regime of ambient to 300°C due to strain hardening. However, beyond 300°C,



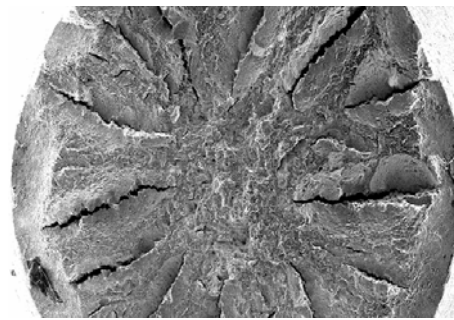
Stress-strain curves for Alloy HT-9 at different temperatures.



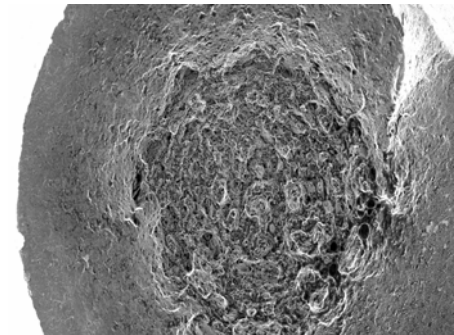
*Room Temperature (RT)*



*300°C*



*100°C*



*600°C*

*Scanning Electron Microscope micrographs of Alloy HT-9 at various temperatures (35X).*

the magnitude of these parameters was enhanced due to increased plastic flow.

- The morphology of failure was characterized by increased plastic deformation at elevated temperatures. Reduced cracking and dimpled microstructures were observed on the fracture surfaces indicating improved ductility at higher temperatures.
- The tempering time did not influence the metallurgical microstructure and the resultant tensile properties to any great extent irrespective of the testing temperature.

## TASK 10 PROFILE

Start Date: August 2001

Completion Date: August 2004

### Theses Generated:

Srinivasa R. Kukatla, M.S., Department of Mechanical Engineering, "Corrosion and High-Temperature Deformation Characteristics of a Target Structural Material for Transmutation Applications," June 2004.

Venkata Nagarjuna Potluri, M.S., Department of Mechanical Engineering, "Effect of Heat Treatment on Deformation and Corrosion Behavior of Type 422 Stainless Steel," August 2004.

Bhagath Yarlagadda, M.S., Department of Mechanical Engineering, "Elevated Temperature Mechanical Properties and Corrosion Characteristics Evaluation of Alloy HT-9," August 2004.

### Journal Article:

A.K. Roy, S. R. Kukatla, B. Yarlagadda, V. N. Potluri, M. Lewis, M. Jones and B. J. O'Toole, "Tensile Properties of Martensitic Stainless Steels at Elevated Temperatures," *Journal of Materials Engineering and Performance*, American Society of Metals International, April 2005, Vol. 14, No. 2, pp. 212-218.

### Conference Proceedings:

A.K. Roy, S.R. Kukatla, and B. Yarlagadda, "High Temperature Deformation Characteristics of Martensitic Stainless Steels," Society for the Advancement of Material and Process Engineering, International Technical Conference, Long Beach, CA, May 16-20, 2004.

M. Lewis, M. Jones, A.K. Roy, and B.J. O'Toole, "High-Temperature Deformation of Alloy EP-823 for Transmutation Applications," American Nuclear Society Conference, San Diego, CA, June 1-5, 2003 .

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## Task 11

# Nuclear Criticality, Shielding, and Thermal Analyses of Separations Processes for the Transmutation Fuel Cycle

W. Culbreth and D. Beller

## BACKGROUND

The first step in any transmutation strategy is the separation of radionuclides in used nuclear fuel. The current separation strategy supporting the Advanced Fuel Cycle Initiative (AFCI) program is based on the use of a solvent extraction separation process to separate the actinides, fission products, and uranium from used commercial nuclear fuel, and on the use of pyrochemical separation technologies to process used transmuter fuels. To separate the fission products and transuranic elements from the uranium in used fuel, the national program is developing a new solvent extraction process, the Uranium Extraction Plus, or UREX+, process based on the traditional solvent extraction reprocessing technologies.

Preparing fuel for possible burn up in light water reactors, fast reactors, or accelerator-driven systems involves various chemical processes to partition the transuranics (neptunium, americium, plutonium, and curium) from the fission products. This results in waste streams that are highly radioactive and require radiation shielding for safety. These transuranic elements pose varied criticality, thermal, and radiation risks during storage and handling. Additionally, the radioactive decay of strontium and cesium waste products of the UREX+ technique produce roughly half of the thermal products and gamma radiation emissions in spent fuel. These radioisotopes require storage for approximately 300 years before heat and radiation hazards decrease to a safe level.

As the volume of waste requiring treatment increases, a higher probability exists that fissionable isotopes of plutonium, neptunium, and curium can accumulate and form a critical mass. Criticality concerns warrant an assessment of the effective neutron multiplication factor, or  $k_{\text{eff}}$ , to prevent a possible sustained fission reaction. Maintaining  $k_{\text{eff}}$  below a safe level ( $<0.95$ ) prevents criticality events. This parameter can be computed for any combination of fuel and geometry using Monte Carlo neutron transport codes. Monte Carlo simulations establish the best means of examining the criticality safety of the proposed separation processes, and allow engineers to develop proper safety measures for the reprocessing and fabrication of actinide fuels.

Candidate storage containers also require analysis to assess the need for radiation shielding. Since minor actinides generate significant amounts of heat through radioactive decay, proposed containment measures must be designed to avoid excessive temperatures. Radioactive decay also generates heat that can lead to melting of the fuel during storage and handling.

## RESEARCH OBJECTIVES AND METHODS

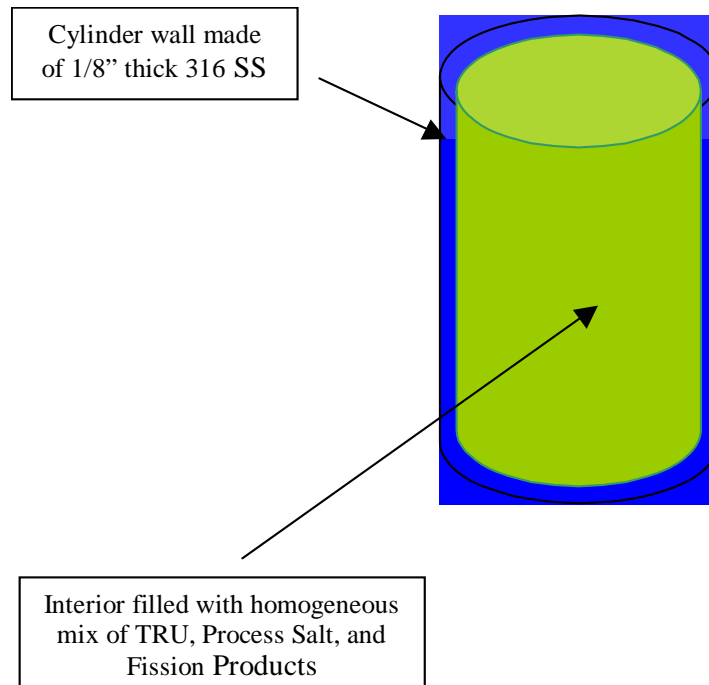
The primary goal of this research program was to provide the nuclear and thermal modeling support for the development of this new separation process. The assessments of nuclear criticality,

radiation for shielding, and thermal analyses of wastes in the Cs/Sr, Pu/Np, and Cm/Am waste streams will assist in designing the UREX+ process. This project was identified as a critical R&D need of the Chemical Technology Division (CTD) at the Argonne National Laboratory (ANL) as safety concerns associated with criticality, shielding, and heat buildup must be addressed prior to further development of the UREX+ process.

UNLV students used nuclear analysis codes to perform assessments of  $k_{\text{eff}}$  at different points in the separation processes that have been identified by the project collaborators at ANL-CTD. They also worked on problems to assess the need for radiation shielding and to develop software to assess the possibility of excessive temperatures due to radioactive decay in separated wastes. ANL-CTD has provided sample fuel process geometries and compositions for calculation of  $k_{\text{eff}}$  as a function of the relative concentrations of process salt, transuranics, and fission products.

## RESEARCH ACCOMPLISHMENTS

An investigation and analysis of criticality and thermal effects for the safe storage of curium was completed. The assessment involved determining  $k_{\text{eff}}$  as a function of fuel burnup, initial enrichment, and time since irradiation. Additionally, since curium generates a substantial quantity of decay heat, an analysis was completed to determine the mass of curium that will lead to temperatures high enough to melt the metal. A spherical geometry was



*Cylindrical problem with TRU, process salt, and fission products.*



used in the analysis. Heat removal from the sphere was assumed to be a combination of natural convection and radiation heat transfer. This heat transfer analysis was also modified and resulted in an analysis that utilized a more sophisticated and suitable cylindrical container. A report developed for Dr. Laidler at ANL described the in-depth investigation regarding the criticality and thermal properties of curium. The heat transfer spreadsheet was used for other combinations of minor actinides as indicated by ANL.

Investigators also investigated the properties of the other minor actinides, including plutonium and americium. A study was conducted on the values of  $k_{\text{eff}}$  and ultimate temperature for varying combinations of plutonium, americium, and the remaining minor actinides.

UNLV students used nuclear analysis codes SCALE 4.4 and/or MCNPX to perform assessments of  $k_{\text{eff}}$  at different points in separation processes that have been identified by ANL-CTD. They also worked on problems to assess the needs for radiation shielding and develop software to assess the possibility of excessive temperatures due to radioactive decay in separated wastes. ANL-CTD has provided sample fuel process geometry and composition for calculation of  $k_{\text{eff}}$  as a function of the relative concentrations of process salt, transuranic actinides (TRU), and fission products. The research team analyzed the cesium/strontium waste stream, the plutonium/neptunium waste stream, and the americium/curium waste stream.

Cm Metal Cylinder		Criticality		Heat Transfer	
		rad (cm)	mass (kg)	rad (cm)	mass (kg)
	bare	4.6	82.52	1.1	1.129
	water	2.7	16.69	3.3	30.48
Cm <sub>2</sub> O <sub>3</sub> Cylinder		Criticality		Heat Transfer	
		rad (cm)	mass (kg)	rad (cm)	mass (kg)
	bare	5.4	125.59	1.55	2.74
	water	3	21.53	2.25	8.37
Am <sub>2</sub> O <sub>3</sub> Cylinder		Criticality		Heat Transfer	
		rad (cm)	mass (kg)	rad (cm)	mass (kg)
	bare	11.2	1032.28	1.6	3.01
	water	10.5	850.58	1.9	5.04
Am <sub>2</sub> O <sub>3</sub> +Cm <sub>2</sub> O <sub>3</sub> Cylinder		Criticality		Heat Transfer	
		rad (cm)	mass (kg)	rad (cm)	mass (kg)
	bare	10	737.9	1.4	2.02
	water	9.3	593.54	2	5.88

*Recommendations for Cm and Am oxide inventories based on criticality and melting temperature.*

## TASK 11 PROFILE

Start Date: August 2001

Completion Date: August 2004

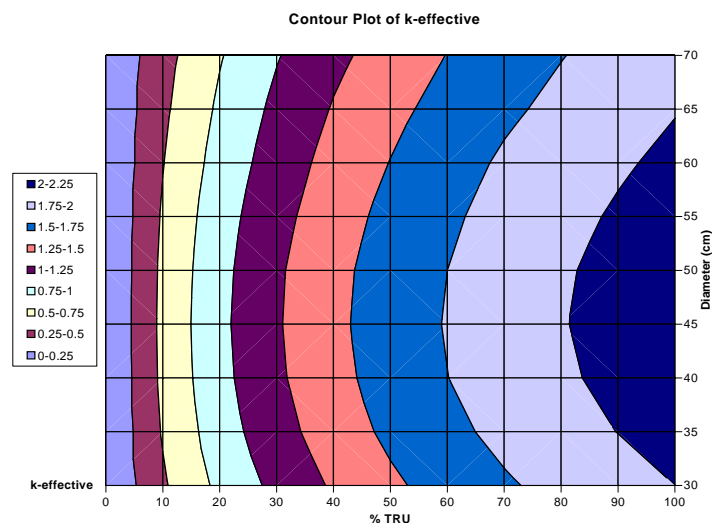
### Thesis Generated:

Elizabeth Bakker, M.S., Mechanical Engineering Department, "Criticality and Thermal Analysis of Separated Actinides in Transmutation," November 2003.

### Reports:

B. Culbreth, E. Bakker, and J. Viggato, "The Fission Properties of Curium Separated from Spent Nuclear Fuel," Department of Mechanical Engineering, University of Nevada, Las Vegas, April 2002.

B. Culbreth, D. Lowe, and J. Viggato, "Assessment of Criticality Safety for Cylindrical Containers to be Used In the Processing of Spent Fuel," Department of Mechanical Engineering, University of Nevada, Las Vegas, October 28, 2001.



*Contour Plot of the Effective Neutron Multiplication Factor as a function of cylinder diameter and % TRU in the mixture.*

### Research Staff

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## Task 12

# Radiation Transport Modeling using Parallel Computational Techniques

W. Culbreth and D. Beller

### BACKGROUND

One of the most significant tools available for the design and analysis of accelerator-driven systems, such as the systems proposed for transmutation, is the high-energy particle transport code MCNPX. The MCNPX code suite, developed by the national laboratories, allows researchers and engineers to model the complex interactions of high-energy particles with the target and related systems, including the spallation reaction and subsequent neutron multiplication expected in the accelerator targets.

The next stage in the development of the MCNPX code suite is to validate the code by comparing the theoretical predictions from the models with experimental observations. Additionally, the nuclear database, particularly the cross sections (i.e., reaction probabilities) for high-energy particle interactions, needs to be revisited to reduce the uncertainties associated with key nuclear properties.

The Department of Energy, through its national laboratories, has initiated several experiments geared towards removing uncertainties in the MCNPX libraries, with more in the planning stages. These experiments utilize the proton and neutron beam lines at the LANSCE proton accelerator at the Los Alamos National Laboratory (LANL) to irradiate a target, producing a pulse of neutrons which are observed by the experimenters. The results of these experiments are then compared against the predictions from the MCNPX models of the system. By comparing the predicted system behavior to the data acquired from the experiments, the experimenters will be able to validate the MCNPX code and its nuclear data libraries.

Through this project, UNLV researchers were involved in support of these experiments by developing the system models in MCNPX and benchmarking/validating the models against the experimental results. UNLV students were also involved in conducting experiments at LANL and in assisting researchers in designing new experiments.

### RESEARCH OBJECTIVES AND METHODS

This project involved modeling several aspects of the LANSCE beam experiments:

- Modeling targets of varying diameter in air, in a vacuum, and in the presence of humid air;
- Modeling various proton beam profiles;
- Modeling the effects of off-axis proton beam impingement on the target;
- Modeling the asymmetry introduced by the steel table below the target;
- Modeling the effect of varying ratios of Pb to Bi and the effect of impurities; and



*Robert O'Brien (left of center) and Daniel Lowe (far right) are both undergraduate Mechanical Engineering students working on the project.*

- Modeling the system, including other structures within the test room.

With the experience gained through modeling these systems, the UNLV researchers developed, with the assistance of their national laboratory collaborators, a benchmark program for the neutron leakage tests and other tests related to transmuter development. A comprehensive three-dimensional computer-aided design (CAD) image of the LANSCE experiments was prepared using ProEngineer to help benchmark the experiments and provide accurate geometric data for MCNPX modeling.

### RESEARCH ACCOMPLISHMENTS

Undergraduate student Daniel Lowe worked on neutron spallation tests at the LANSCE facility (Summer 2002). He performed MCNPX runs and worked on calculations for initial benchmarking data. His early MCNPX calculations helped the experimenters determine where foil packets should go and what types of neutron flux to expect from these foils. He also prepared foils to determine neutron flux from the experiment and assisted in radiation counting of the foils. Mr. Lowe completed Solid Works CAD models of the Blue Room at LANSCE and conducted MCNPX simulations of the summer experiments when he returned back to UNLV. His MCNPX runs included estimations of the effect of the proton beam striking the target at positions slightly off of the centerline. He also estimated the neutron energy spectra expected from the time-of-flight neutron detectors.

Through MCNPX simulations of the neutron leakage from lead-bismuth targets, the UNLV team was able to assist in the design of the experimental configurations for the LANSCE experiments.

These models were also used to predict the results for the experiments, and assist in positioning detectors for measuring the leaking. Similar computational support was also provided for proton activation experiments in sodium coolant.

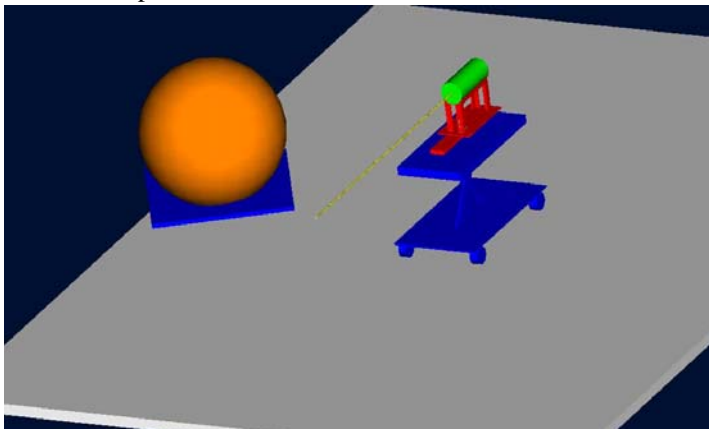
Extensive studies on how MCNPX performs with respect to MPI (Message Pass Interface) and PVM (Parallel Virtual Machine) have been run. PVM was no longer supported by the LANL team after 2005, hence more emphasis was placed on how MCNPX runs with MPI on a Beowulf system.

Parallelization of MCNPX for a Parallel Virtual Machine was completed. MPI bugs and compiling problems were resolved.

Analysis of linearization characteristics on a Beowulf cluster was completed. Work was then focused on characteristics of the Supercomputing Center and the linearization of criticality studies.

Benchmarking and optimization of MCNPX to run on multiple platforms was performed. This insured that the user will not be limited to a specific system type when running simulations. In addition, the MCNPX simulations of experiments was performed.

User guides were developed for future users. These will describe how to implement an optimized version of MCNPX on a heterogeneous cluster using a Message Passing Interface. Efforts to increase the speed of MCNPX on parallel clusters of computers was conducted and a preliminary graphical user interface (GUI) for MCNPX using open source code and tools was developed. The GUI interface is written in Visual Basic allowing easy integration into Excel codes that contain databases of results from criticality and heat transfer studies of waste storage containers. With the help of Trevor Wilcox, a doctoral student in mechanical



*Schematic of the experimental facility at LANSCE used for modeling.*

engineering, the MCNPX software was ported to a Beowulf cluster located in the Tiberti Laboratory at UNLV. The cluster has between 32 and 50 processors available to run a single MCNPX job.

## **TASK 12 PROFILE**

Start Date: August 2001

Completion Date: August 2004

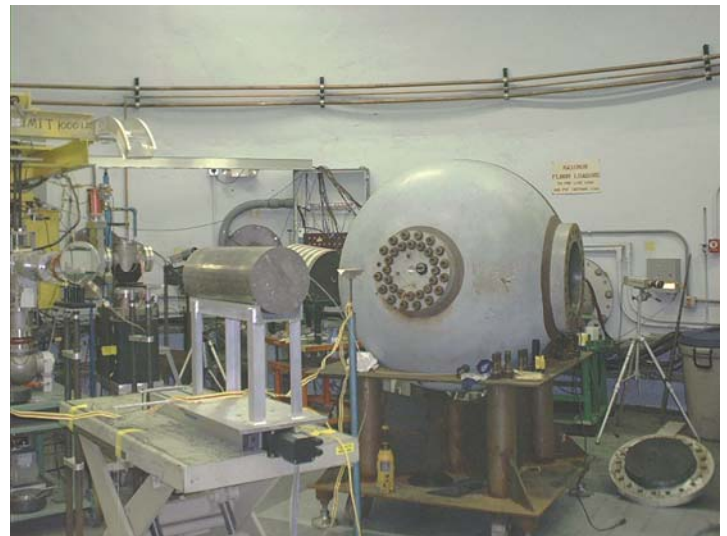
### Thesis Generated:

Suresh B. Sadineni, M.S., Mechanical Engineering Department, "Benchmarking Photoneutron Production of MCNPX Simulations with Experimental Results," December 2002.

### Conference Proceedings:

M.A. Reda, J.F. Harmon, and S.B. Sadineni, "Properties of Photo-Neutron Sources for Accelerator Driven Sub-Critical Systems," American Nuclear Society Conference, June 1-5, 2003, San Diego, CA.

M.R. James, R.T. Klann, G.L. Morgan, E.J. Pitcher, M.A. Paciotti, J.M. Oostens, J.E. Platte, and D.R. Lowe, "Measurements from Activation Foils of a Proton Irradiated Lead-Bismuth Target," American Nuclear Society Conference, June 1-5, 2003, San Diego, CA .



*Experimental facility at LANSCE, Los Alamos, NM.*

### **Research Staff**

William Culbreth, Principal Investigator, Associate Dean for Research, College of Engineering  
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### **Collaborators**

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Laurie S. Waters, Los Alamos National Laboratory



## Task 13

# Developing a Sensing System for the Measurement of Oxygen Concentration in Liquid Pb-Bi Eutectic

Y. Jiang and B. Fu

## BACKGROUND

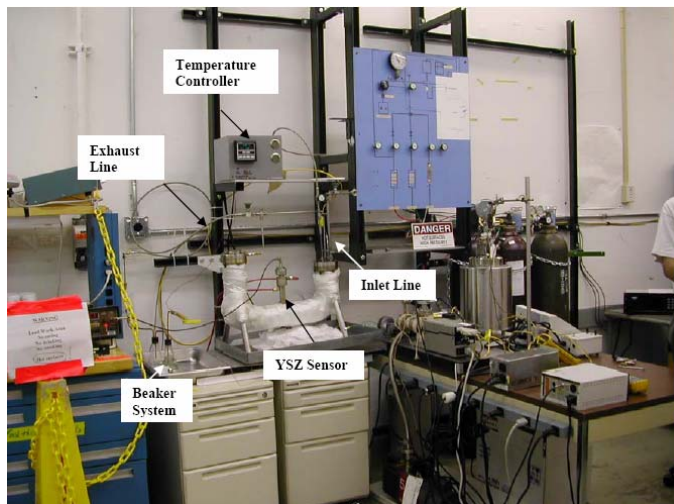
Although liquid lead-bismuth eutectic (LBE) is a good candidate for the coolant that can be employed in a subcritical transmutation blanket, it is known to be very corrosive to stainless steel, the material used in the containment structure. To mitigate this problem, trace levels of oxygen can be introduced into the system, causing the formation of a protective oxide layer at the interface between the LBE and steel. The proper formation of this oxide layer largely depends on the accurate measurement and subsequent control of the oxygen concentration in liquid LBE.

Yttria Stabilized Zirconia (YSZ) oxygen sensors, using molten bismuth saturated with oxygen as the reference, have been utilized to accurately measure the concentration of oxygen dissolved in LBE. By measuring the voltage difference across the YSZ sensor, the oxygen concentration in test solutions can be determined relative to that in the reference solutions (the potentiometric method). The theoretical model for calculating oxygen concentration based on voltage measurements from YSZ sensors in static conditions is well understood. The real world performance of these systems, however, is less predictable.

## RESEARCH OBJECTIVES AND METHODS

The research objectives of this project were as follows:

- To generate calibration curves of voltage versus oxygen concentration for the YSZ oxygen sensor system under various temperatures in liquid LBE.
- To determine the sensor characteristics of the YSZ sensor system.
- To determine oxygen dissolving rates in LBE under different temperatures in vitro.



The first sensor calibration experimental setup.

- To study the effects of unwanted electrical conductivity, contributed by the mobility of the electrons at high temperatures, for more accurate oxygen measurement.
- To study alternative and promising oxygen measuring methods.

## RESEARCH ACCOMPLISHMENTS

The first experimental set up consisted of a temperature controlled U-shape container, gas supplies and exhaust, a residual gas analyzer (RGA), a high-impedance electrometer, and a computer for data acquisition. The container is tightly sealed from the outside atmosphere using a conflat flange except for gas inlet and outlet, and openings for insertion of thermocouple or RGA signal wire. Flexible heating tapes around the container heated the liquid metal to the required temperature under the control of a temperature controller. Meanwhile, the thermally insulated container is placed on a rocker to provide fluid motion that promotes mixing and homogenization of oxygen concentration in LBE.

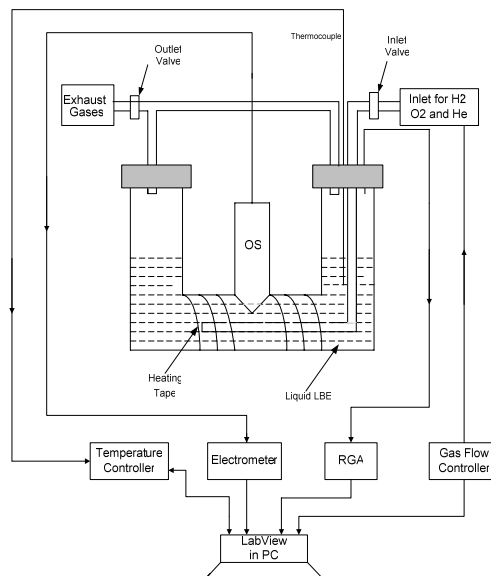
Although some calibration results were obtained using this setup, it had several shortcomings. For instance, it was impossible to heat the system to reach the desired high temperature (up to 750 °C). In addition, direct injection of O<sub>2</sub>/H<sub>2</sub> method adopted in this system is unlikely to produce a required extremely low oxygen level (ppm to tens of ppb) in liquid LBE. These problems in part were solved by developing a new apparatus. Some noticeable features of this apparatus were:

- Instead of using a steel tube, this apparatus incorporates a cylindrical crucible made of Magnesia Stabilized Zirconia (MSZ), and the liquid LBE is contained in this MSZ crucible. MSZ was chosen because of its desirable material properties.
- The MSZ crucible sits on a stainless steel beaker. The beaker acts as a pressure boundary, and it can distribute the weight

of the molten metal and crucible to the outer support. Back-up materials are used to fill the gap between the inner crucible and beaker.

- The crucible is tightly sealed with a metallic flange, with only a few openings left for gas inlets and outlets.

- A stirring unit is employed in order to mix the gases with the molten metal. The stirrer is made of Silicon Nitride (Si<sub>3</sub>N<sub>4</sub>) ceramic. Silicon Nitride has high temperature strength, creep resistance,



oxidation resistance, and it is not wetted by any molten metal. On top of those, compared to many other ceramic materials,  $\text{Si}_3\text{N}_4$  has good mechanical strength.

### Oxygen Sensor Calibration Results

Calibration curves were obtained from two oxygen sensors. After some initial transients, voltage-temperature curves first follow constant oxygen concentration lines according to the Nernst equation, and then turn to the concentration saturation line.

The slopes of experimental and theoretical curves are almost identical, ranging from 0.33 to 0.5. This indicates that the YSZ sensors are of high sensing quality. Overlapping of the calibration curves for the two sensors indicates consistency in the sensors of the same design.

Experimental results show that tantalum oxidizes at high temperature around  $480^\circ\text{C}$  after running for a certain amount of time. This directly causes tantalum wires to lose electrical conductivity, and consequently, the sensor fails to provide meaningful signal output. This effect was demonstrated. In the first trial experiment cycle, molybdenum, stainless steel (SS) and tungsten were tested for this purpose. When introducing hydrogen and helium mixture into the system to clean excessive oxygen in the LBE container, it was found that Mo responds a little faster than SS.

It had been suspected that different combinations of Bi or  $\text{Bi}_2\text{O}_3$  may have affected the sensor response. During Phase III of this project, several experiments were performed and it was determined that there are no evident effects on the sensor response. Experiment results further confirmed that even a small amount of residual oxygen inside sensor tubes will be sufficient for Bi to be

oxidized.

Commercial FEM (finite element method) software, FEMLAB was used to simulate the oxygen dissolving process and the distribution in liquid LBE for the new system under three different boundary conditions. Simulation results show that the oxygen concentration distributes evenly in the whole flow field due to the strong convection flow in LBE. These simulation results with the experimental measurements help to not only determine the oxygen dissolving rate and the diffusion coefficient under different temperatures, but also provide suggestions for better experimental design.

### **TASK 13 PROFILE**

Start Date: May 2002

Completion Date: May 2005

#### Theses Generated:

Ramkumar Sivaraman, M.S., Department of Electrical and Computer Engineering, "Calibration of YSZ Sensor for the Measurement of Oxygen Concentration in Liquid LBE," December 2003.

Xiaolong Wu, M.S., Department of Electrical and Computer Engineering, "Instrumentation of YSZ Oxygen Sensor Calibration in Lead-Bismuth Eutectic," December 2004.

#### Journal Article:

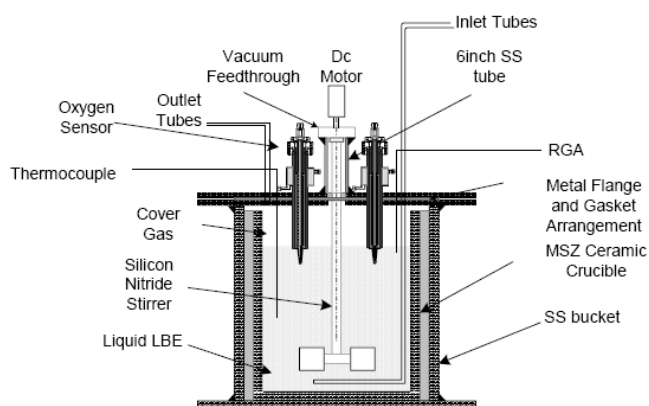
J. Ma, P. Guo, J. Zhang, N. Li, B. Fu, "Enhancement of Oxygen Transfer in Liquid Lead and Lead-Bismuth Eutectic by Natural Convection" *International Journal of Heat and Mass Transfer*, Vol. 48 (13), p. 2601-2612, January 2005.

#### Conference Proceedings:

X. Wu, J. Ma, Y. Jiang, B. M. Fu, W. Hang, J. S. Zhang, and N. Li, "Instrumentation of YSZ Oxygen Sensor Calibration in Liquid Lead-Bismuth Eutectic," *Proceedings of 2005 IEEE International Symposium on Circuits and Systems*, May, 2005.

X. Wu, R. Sivaraman, N. Li, W. Hang, T. W. Darling, Y. Jiang, W. Yim, B. M. Fu, "Design of an Oxygen Sensor Calibration/Measurement Apparatus for the Liquid Lead-Bismuth Eutectic System," *Proceedings of the 2003 Annual Meeting*, San Diego, CA, June 1-5, 2003.

X. Wu, R. Sivaraman, N. Li, W. Hang, T. W. Darling, Y. Jiang, W. Yim, B. M. Fu, "Calibration of YSZ Sensors for the Measurement of Oxygen Concentration in Liquid Pb-Bi Eutectic," *Proceedings of the 10th International High-Level Waste Management Conference*, Las Vegas, March 30-April 3, 2003.



*Schematic of the second sensor calibration experimental setup.*

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### **Collaborators**

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## Task 14

# Use of Positron Annihilation Spectroscopy for Stress-Strain Measurements

A. K. Roy

## BACKGROUND

Engineering metals and alloys, when subjected to tensile loading beyond a limiting value, undergo plastic deformation resulting in lattice defects such as voids and dislocations. These imperfections interact with the crystal lattice, producing a higher state of internal stress, also known as residual stress, which can be associated with reduced ductility. Residual stresses are also generated in welded structures due to rapid solidification and resultant dissimilar metallurgical microstructures between the weld and the base metals. Development of these internal stresses is often influenced by incompatible permanent strain resulting from thermal and mechanical operations associated with welding and plastic deformation. These types of operations can cause premature failures in structural materials unless these stresses are relieved by thermal treatments, which are commonly known as stress-relief operations.

During the past academic year, this project was focused on the characterization of residual stress in welded specimens consisting of austenitic and martensitic stainless steels using an activation technique based on the Positron Annihilation Spectroscopic (PAS) method. The extent of residual stress was expressed in terms of three line-shape parameters (S-, W- and T-). Further, efforts were made to characterize linear lattice defects such as dislocations in the vicinity of Fusion-Line (FL), Heat-Affected-Zone (HAZ), and the base material of the welded specimens using Transmission Electron Microscopy (TEM). The metallurgical microstructures at these three regions have also been evaluated by optical microscopy.

## RESEARCH OBJECTIVES AND METHODS

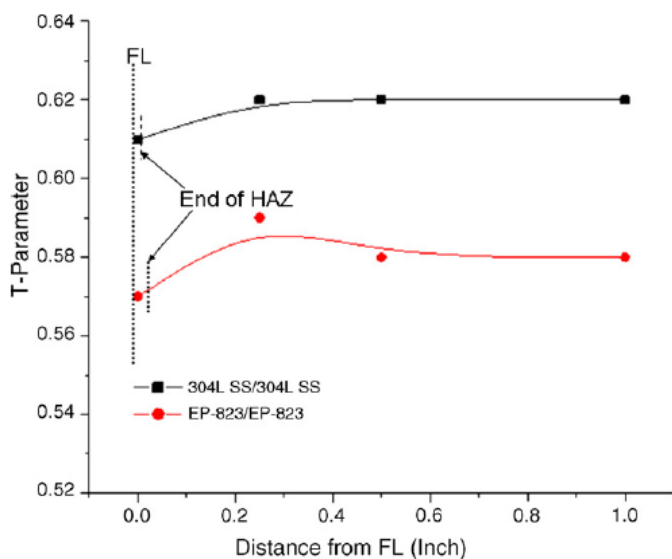
The primary objective of this task was to evaluate the feasibility of the characterization of residual stresses in plastically-deformed and welded structural materials using a new nondestructive technique based on PAS. The residual stresses measured by a modified PAS method have been compared to those measured by three other techniques, namely the Ring-Core (destructive), X-Ray Diffraction (non-destructive), and Neutron Diffraction (non-destructive).

All four techniques have been used to evaluate residual stresses in cold-worked, plastically deformed and welded specimens of austenitic Type 304L Stainless Steel (SS), and martensitic Alloys EP-823 and HT-9. Alloy EP-823 is a leading target structural material to contain the molten lead-bismuth eutectic nuclear coolant needed for fast spectrum operations of an Accelerator-Driven Transmutation System. Type 304L SS is a universally-known corrosion resistant low-carbon iron-nickel-chrome alloy having optimum formability and weldability. Alloy HT-9 is known for its superior high temperature tensile properties. The metallurgical microstructures and the nature of defects have been analyzed by optical microscopy, scanning electron microscopy, and TEM.

## RESEARCH ACCOMPLISHMENTS

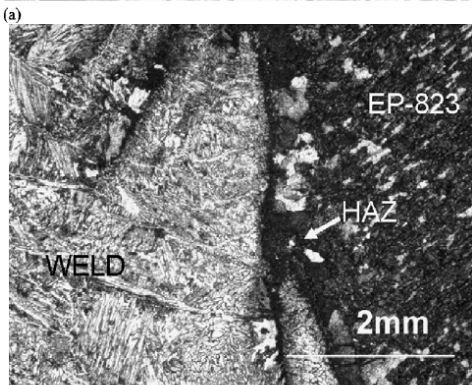
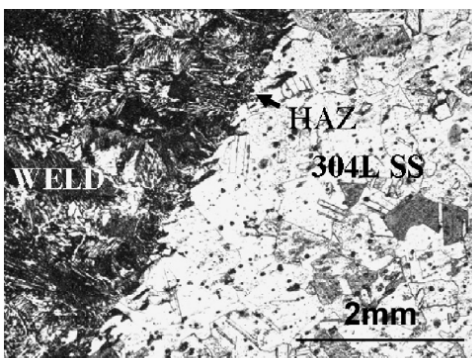
The significant results obtained from this investigation during the past academic year are summarized below.

- For welded specimens consisting of similar materials on both sides, the residual stress in terms of the S-, W-, and T-parameters was maximum at the FL. A gradual drop in residual stress was observed with these specimens at locations away from the FL.
- The extent of residual stress was higher in martensitic Alloy EP-823 compared to that of austenitic Type 304L SS, irrespective of the weld configuration.
- Compressive residual stresses were observed in Alloy EP-823, when welded to Type 304L SS.
- The magnitude of dislocation density ( $\rho$ ) was substantially higher at the HAZ compared to that of the base material of the welded specimens consisting of similar materials (Type 304L SS or Alloy EP-823) on both sides.
- In the case of the welded specimen of dissimilar materials (Type 304L SS and Alloy EP-823) on the opposite side, the concentration of dislocation in terms of  $\rho$  was greater at the HAZ on the Alloy EP-823 side of the weld.
- The enhanced value of  $\rho$  at the HAZ on the Alloy EP-823 side of the weld may be attributed to the faster rate of solidification of this alloy compared to that of the austenitic SS.
- The sizes of the HAZ on the Alloy EP-823 sides of the welded specimens were relatively larger, irrespective of the weld configuration.



*T-Parameter versus Distance from FL for Welded Specimens of Similar Materials*





Optical micrographs of welded specimens of similar materials. (a) Type 304L SS/Type 304L SS,  $\text{HNO}_3 + \text{CH}_3\text{COOH} + \text{C}_3\text{H}_5(\text{OH})_3$ ; (b) Alloy EP-823/Alloy EP-823, Fry's reagent.

## TASK 14 PROFILE

Start Date: May 2002

Completion Date: December 2006

### Theses Generated

Srinivas Chanda, M.S., Mechanical Engineering, "Characterization of Residual Stress and Defects in Welded Specimens," December 2006.

Silpa B. Suresh, M.S., Mechanical Engineering, "Use of Neutron Diffraction and Microscopy for Characterization of Residual Stresses and Defects," December 2005.

Subhra Bandyopadhyay, M.S., Mechanical Engineering, "Residual Stress Characterization and Defects Analyses by Microscopy," December 2005.

Anand Venkatesh, M.S., Mechanical Engineering, "Comparative Analyses of Residual Stresses in Target Sub-System Materials," August 2004.

Vikram Marthandam, M.S., Mechanical Engineering, "Metallurgical Characterization and Residual Stress Measurements of Target Structural Materials," August 2004.

Satish B. Dronavalli, M.S., Mechanical Engineering, "Residual Stress Measurements and Analyses by Destructive and Nondestructive Techniques," August 2004.

### Journal Articles

A.K. Roy, S. Chanda, A. Ghosh, P. Kumar, and L. Ma, "Defects Characterization of Welded Specimens by Transmission Electron Microscopy," *Materials Science and Engineering A*, Elsevier Science, Vol. 464/1-2, pp. 274-280, 2007.

A.K. Roy, S. Chanda, D.P. Wells, A. Ghosh, and C.K. Mukhopadhyay, "Residual Stress Characterization of Welded Specimens by Nondestructive Activation Technique," *Materials Science and Engineering A*, Elsevier Science, Vol. 464/1-2, pp. 281-287, 2007.

D.P. Wells, et al., "Gamma-induced Positron Annihilation Spectroscopy and Application to Radiation-damaged Alloys," *Nuclear Instruments and Methods in Physics Research A*, Elsevier Science, Vol. 562, pp. 688-691, 2006.

A.K. Roy, et al., "Comparison of Residual Stress in Martensitic Alloys by Nondestructive Techniques," *Materials Science and Engineering A*, Elsevier Science, Vol. 419, pp. 372-380, 2006.

A.K. Roy, et al., "Relationship of Residual Stress to Dislocation Density in Cold-Worked Martensitic Alloy," *Materials Science and Engineering A*, Elsevier Science, Vol. 416, pp. 134-138, 2006.

A.K. Roy, et al., "Residual Stress Measurements in Welded and Plastically Deformed Target Structural Materials," *Journal of ASTM International*, Vol. 2, No. 6, pp. 1-13, June 2005.

A.K. Roy, et al., "Residual Stress Characterization in Structural Materials by Destructive and Nondestructive Techniques," *Journal of Materials Engineering and Performance*, ASM International, Vol. 14, No. 2, pp. 203-211, April 2005.

F.A. Selim, et al., "Stress Analysis using Bremsstrahlung Radiation," *Advances in X-ray Analysis*, Joint Committee on Powder Diffraction Standards, Vol. 46, pp. 106-111, 2003.

### Conference Proceedings

Ten conference papers were also published. See TRP website at <http://aaa.nevada.edu> for more information.

Dislocation density ( $\rho$ ) in welded specimens of different configurations

Weld configuration	$\rho$ (no./m <sup>2</sup> )	
	Base material	HAZ
304L SS/304L SS	$5.1 \times 10^{13}$	$2.4 \times 10^{14}$
EP-823/EP-823	$7.6 \times 10^{13}$	$1.3 \times 10^{14}$
304L SS side of 304L SS/EP-823	$1.7 \times 10^{13}$	$3.2 \times 10^{13}$
EP-823 side of 304L SS/EP-823	$6.5 \times 10^{13}$	$2.2 \times 10^{14}$

### Research Staff

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### Students

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Farida Selim, Ph.D., Post Doctoral Researcher, Idaho Accelerator Center, Idaho State University



## Task 15

# Immobilization of Fission Iodine by Reaction with a Fullerene Containing Carbon Compound and Insoluble Natural Matrix

S.M. Steinberg, G.S. Cerefice, and D.W. Emerson

## BACKGROUND

The recovery of iodine released during the processing of used nuclear fuel poses a significant challenge to the transmutation of nuclear waste. Iodine-129, a long-lived fission product formed by both commercial nuclear power generation and nuclear weapons production, is released when reprocessing nuclear fuel. Since iodine can be concentrated in the human thyroid, any uncontrolled release of iodine may result in an increased rate of thyroid cancer in the exposed population. For this reason, recovery of iodine is important for implementing any nuclear transmutation strategy.

The first step in any transmutation strategy is the processing of the used nuclear fuel. This step involves separating the used fuel into its constituent elemental components, allowing the recovery of the uranium, transuranic actinides, long-lived fission products, and other components, depending on the strategy and processes involved.

When used fuel rods are dissolved in concentrated nitric acid in preparation for actinide recovery, iodine is released from the fuel. A significant fraction of the iodine is lost to the vapor phase during this process, where it may potentially become a fugitive emission and be released from the plant. To avoid this, specialized filtration systems are used to try to trap and sequester the released iodine (and other fission product gases).

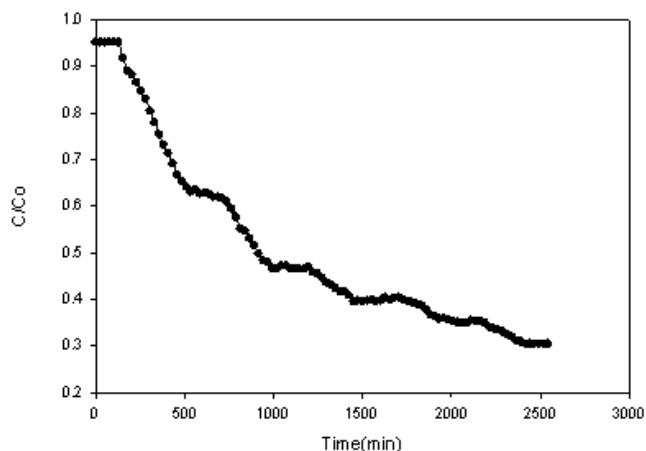
The primary goal of this research is to capture and immobilize the iodine released from these processes in a form that can easily be converted to a suitable target for neutron-induced transmutation. The investigators believe that iodine released during fuel reprocessing can be immobilized in a Fullerene Containing Carbon (FCC) compound or a Natural Organic Matter (NOM) matrix.

Natural organic matter (such as sphagnum moss, peat or brown coal) is an inexpensive and a renewable resource. Further processing of the trapped iodine using simple desorption or combustion processes should be able to produce iodine in a form suitable for transmutation. Furthermore, collaborators at the Khlopin Radium Institute (KRI) have proposed that the iodine-loaded FCC material, when combined with ceramics, is stable enough for use as a long-term storage form, and may be usable as a transmuter target matrix.

## RESEARCH OBJECTIVES AND METHODS

The stability of the association of iodine with FCC and NOM products were studied. Product distributions for the various matrices under various reaction conditions were examined in order to maximize the binding of iodine. The recovery of the iodine from the sequestration matrices was also examined, along with the conversion of the iodine to matrices more suitable for geological storage and/or use as transmutation targets.

Iodide Sequestration at pH 4  
Continuous Flow method



Sequestration of iodide ( $10^{-4}M$ ) in the presence of sphagnum peat and  $MnO_2$ . The solution was circulated through a column at 5 mL/min.

The following are the specific research objectives and goals:

- Develop bench-scale experimental set-up and procedures for simulating plutonium extraction process (PUREX) head-end vapor phase.
- Develop experimental procedures for evaluating iodine sequestering methods using bench-scale procedures.
- Develop FCC bearing material as potential iodine sequestration matrix.
- Determine binding of iodine to FCC and NOM.
- Examine alternate iodine sequestration matrices using techniques developed for FCC and NOM studies.
- Examine the effect of reaction conditions on binding.
- Elucidate the nature of the reaction products (volatile, hydrophobic, soluble, insoluble).
- Develop methodology and host matrix for converting sequestered iodine to solid matrix for evaluation as transmutation target and/or disposal matrix.
- Examine recovery of iodine from sequestration matrices.

The FCC compounds were developed and prepared by the KRI Research Industrial Enterprise (KIRSI). The KRI-KIRSI team researched the impacts of process parameters on sorption of iodine, and examined the material properties, such as how iodine attaches to the FCC compounds. The KRI-KIRSI team also examined the conversion of the iodine loaded FCC compound to a stabilized matrix (similar to ceramic) for potential use as a disposal form, acceptable transportation material, or potential target material.

## RESEARCH ACCOMPLISHMENTS

Observations related to the oxidation of iodide to iodine ( $I_2$ ) or hypiodic acid (HIO) by  $MnO_2$  were continued. During this study, a number of synthetic (nano-particle) manganese (III, IV) oxide preparations have been shown to be capable of oxidizing iodide to iodine (or IOH) at pH as high as 5. Various synthetic preparations of  $MnO_2$  were examined. These various nano-particle manganese oxides have been characterized by transmission electron microscopy, scanning electron microscopy, and atomic force microscopy. In addition, surface areas, average manganese oxidation states and the kinetics of iodide oxidation by these materials have been measured. The rate of iodide oxidation by various manganese oxide preparations varies significantly. The oxidation rate appears to have some relationship to the average oxidation state of the manganese.

The incorporation of iodine into NOM was demonstrated in batch mixtures of  $MnO_2$  and alkali lignin or sphagnum peat. The sequestration of iodine by NOM is illustrated to the left.

In another facet of this project, iodine distributions in salt impacted soils from the Virgin River, Nevada were examined. This study indicates that organic iodine was the most abundant form of iodine in the soil samples and that the content of organic iodine was correlated to total organic matter and to the lignin content (as measured by chemolysis) of the samples. These observations are consistent with the notion of the formation of organic iodine resulting from the cycling of iodine between iodide and iodate, with organic iodine resulting from the iodine or hypiodic acid ( $I_2$  and HIO) intermediate reacting with phenolic moieties in sedimentary and soil organic mater.

## ACADEMIC YEAR HIGHLIGHTS

- ◆ S.M. Steinberg and G. Kimble, "Immobilization of Fission Iodine By Reaction with Insoluble Natural Organic Matter," *Journal of Radioanalytical and Nuclear Chemistry*, (in press).
- ◆ S.M. Steinberg, G.M. Kimble, G.T. Schmett, and D.W. Emerson, "Abiotic Reaction of Iodate with Spahgnum Peat and Other Natural Organic Matter," *Journal of Radioanalytical and Nuclear Chemistry*, (in press).
- ◆ S.M. Steinberg, B. Buck, J. Morton, and J. Dorman, "Speciation of iodine in the salt-impacted Black Butte soil series along the Virgin River, NV," accepted, 234<sup>th</sup> American Chemical Society National Meeting, Boston, MA, August 19-23, 2007.
- ◆ S.M. Steinberg and N.R. Birkner, "Formation of organic iodine in soil and sediment by reaction of manganese oxide with iodide," accepted, 234<sup>th</sup> American Chemical Society National Meeting, Boston, MA, August 19-23, 2007.
- ◆ M.A. Cheney, N.R. Birkner, L. Ma, T. Hartmann, P.K. Bhowmik, V.F. Hodge, and S.M. Steinberg, "Synthesis and characterization of inorganic double helices of cryptomelane nanomaterials," *Colloids and Surfaces A: Physicochemical Engineering Aspects* 289, pp 185–192, 2006.

## FUTURE WORK

The oxidation of iodide with  $MnO_2$  will continue to be investigated using remaining funds under a no cost extension.  $MnO_2$  preparations will continue to be characterized. Presently, surface acidity of the various materials is being examined.

Combined Data							
	Depth	Org Iodide	Lignin	%C	% Clay	I	IO <sub>3</sub> <sup>-</sup>
Avg depth	1.000						
Org Iodide	0.458	1.000					
Lignin/mg	0.519	0.623	1.000				
%C	0.407	0.394	0.608	1.000			
% Clay	0.186	0.388	0.130	0.535	1.000		
I	0.339	0.303	0.030	0.023	0.084	1.000	
IO <sub>3</sub> <sup>-</sup>	0.260	0.223	-0.065	0.175	0.334	0.684	1.000

*Correlation analysis for Black Butte soils*

### Research Staff

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 David W. Emerson, Emeritus Professor, Chemistry Department

### Students

Ginger Kimble, Nancy Birkner and James Dorman, Graduate Students, Chemistry Department

### Collaborators

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 Michael Savopulo, V. G. Khlopin Radium Institute—Research-Industrial Enterprise, St. Petersburg, Russia  
 Boris E. Burakov, Head of Mineralogical Group, V.G. Khlopin Radium Institute—Research-Industrial Enterprise, St. Petersburg, Russia

## Task 16

# Evaluation of Fluorapatite as a Waste-Form Material

D.W. Lindle, O. Hemmers and D.L. Perry

## BACKGROUND

High Temperature Gas-Cooled Reactor (HTGR) systems are currently being designed and evaluated as part of the Advanced Fuel Cycle Initiative, both as a future nuclear reactor type (in the Generation IV reactor program) and as a potential system for burning plutonium in a dual-tier transmutation strategy. HTGR designs use a TRISO-coated fuel (a silicon-carbide and pyrocarbon composite coating) to provide much of the passive containment for radionuclides.

Although this fuel form is quite stable and comprises one of the key components in the safety performance of these reactor systems, TRISO-coated fuel is comparatively difficult to recycle. If HTGR systems are to be used as part of either the first tier of a transmutation strategy or as primary power reactors, the plutonium and other actinides in the used TRISO fuel must be processed to recycle plutonium and permit recovery of minor actinides and other fission products produced.

Argonne National Laboratory has proposed a new extraction procedure to handle TRISO-coated fuels, the Fluoride Extraction Process (FLEX). The FLEX process is designed to separate the uranium in the fuel from the actinides and most fission products by taking advantage of the unique properties of uranium hexafluoride ( $\text{UF}_6$ ). In the FLEX process, the used TRISO fuel is reacted with zirconium fluoride salt, forming  $\text{UF}_6$  and the fluoride salts of the actinides and fission products. At process temperatures, the  $\text{UF}_6$  volatilizes into a gas, and is released from the molten salt mixture. This leaves behind the actinides and most fission products in a fluoride salt, which is subsequently processed using pyrochemical techniques to recover the actinides and other long-lived fission products for transmutation. The  $\text{UF}_6$  is then cooled, causing it to sublime into solid form, which is then further processed for disposal or reuse.

The primary waste stream from the FLEX process is the fission products from the fuel, which are in a zirconium fluoride salt at the end of the process. Due to the fluorine in this waste stream, the fluoride salts are unsuitable for conversion into the traditional

borosilicate waste glass. Therefore, without a suitable disposal form, this process can not be deployed.

This research attempts to develop a waste form for disposing of the zirconium fluoride fission product waste stream. Fluorapatite, a naturally-occurring fluorinated calcium phosphate, has been identified as a potential matrix for the entombment of this waste stream. If the efficacy of fluorapatite-based waste-storage can be demonstrated, then new and potentially more efficient options for handling and separating high-level wastes, based on fluoride-salt extraction, will become feasible.

## RESEARCH OBJECTIVES AND METHODS

The following are the specific research objectives:

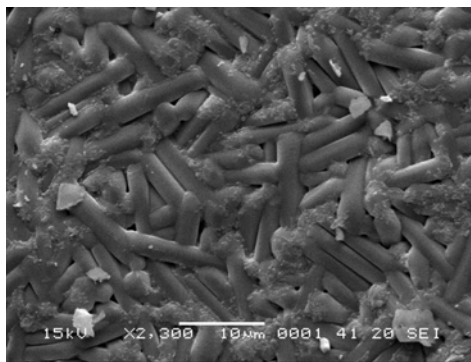
- To develop a waste matrix for the disposal of the fission product waste stream from the FLEX process;
- To develop a process to make synthetic fluorapatite that incorporates the FP-bearing  $\text{ZrF}_4$  salt;
- To develop a fundamental understanding of the chemistry of this new waste form in order to better predict its long term behavior in a repository environment;
- To develop a fundamental understanding of natural, fluoride-bearing mineral phases to use as natural analogs to bound the predicted behavior of the FLEX fission product waste stream.

Originally, the research effort had been divided along two parallel paths: the *Fabrication Path*, led by collaborators at the Khlopin Radium Institute (KRI) in St. Petersburg, Russia; and the *Characterization Path*, led by researchers from UNLV.

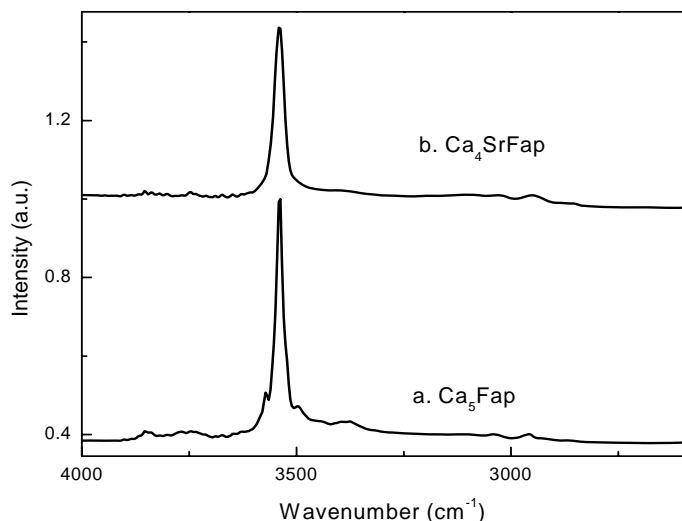
The Fabrication Path is focused on examining and evaluating various techniques for fabricating synthetic fluorapatite; synthesizing synthetic fluorapatite; and examining the impacts of waste loading and other fabrication process factors on the performance of the synthetic fluorapatite as a potential waste form.

The Characterization Path is focused on adapting and refining the X-ray spectroscopy techniques currently used to characterize borosilicate glass for use in examining the fluorapatite system. This path also encompassed the examination of the ceramic and synthetic mineral waste forms created at KRI, with subsequent examination of these techniques to develop a molecular-level understanding of natural fluorapatite and other fluorine-bearing natural phases as natural analogs for the waste form. These techniques will also be used to examine the changes in surface chemistry caused by environmental degradation of these materials.

Waste form development at KRI involves the formulation, synthesis, and examination of ceramic samples to investigate the impact of processing parameters and composition on material properties (e.g. homogeneity) and performance (via leach testing). The



SEM micrograph of  $\text{Ca}_4\text{SrFap}$  (annealed sample).



IR spectra of  $\text{Ca}_5\text{Fap}$  and  $\text{Ca}_4\text{SrFap}$  after annealing.

most promising fabrication process developed will be used to synthesize the ceramic in varying compositions to examine the impact of process parameters, ceramic formulation, and waste loading on the final ceramic phase. Based on these experiments, a baseline composition and fabrication process will be established. Finally, alternate fabrication processes, compositions, and potential alternate waste matrices will be examined and compared against the baseline composition.

Waste form characterization carried out at UNLV employs state of the art techniques that characterize the molecular structure of both natural fluorapatite and fluoride-bearing minerals and the fluorapatite-based ceramic waste form. Changes in the surface/interfacial chemistry of these materials as they undergo reactions with species in the environment will also be examined to help develop a basis for understanding the corrosion chemistry that the waste form and its natural analogs may experience under repository conditions. The UNLV researchers also synthesized several surrogate samples with help of the KRI collaborators in order to study their properties.

## RESEARCH ACCOMPLISHMENTS

Research highlights for the third year of the project can be summarized as follows:

- Applying x-ray spectroscopy and more-conventional characterization techniques (e.g., Fourier Transform Infrared Spec-

## ACADEMIC YEAR HIGHLIGHTS

- G. Silva presented a paper "Characterization of the Thermal Stability of Zinc Containing Fluorapatite" at the American Nuclear Society Student Conference, Columbus, OH, April 14-16, 2005.
- C. Rodrigo presented a paper "Characterization of Fluorapatite as a Waste Form Material" at the American Nuclear Society Student Conference, Columbus, OH, April 14-16, 2005.

troscopy, Scanning Electron Microscopy (SEM), X-ray Diffraction, and Raman Spectroscopy) to synthesized samples of apatite and fluorapatite doped with surrogates and compared those with baseline measurements of "pure" materials.

- Chemically prepared several samples in which some of the calcium in apatite materials is substituted by non radioactive actinide surrogates (Zn, Sr, Yt, Cs, Cu, Ni, Zr) or elements produced by decay of actinides.
- Chemically prepared apatite samples containing different Ca:Surrogate weight ratios and studying the physical properties of these apatites with different calcium to phosphorous molar ratios.
- Studied metal-containing apatites and fluorapatites with the same cadre of characterization techniques noted above to assess the degree of incorporation and any changes in the physical and chemical structure of the materials.

## FUTURE WORK

The work is completing its third and final year of the project with the two graduate students finishing their Masters degree. The Characterization Path, led by the UNLV team, has been performing baseline spectroscopic studies of natural and pristine (no artificially added impurities) apatite materials as well as of surrogate loaded samples. The studies found that it is possible to load surrogates successfully into apatites and that it is important to control the by-products such as metal phosphates and metal fluorites that weaken and/or destroying the crystal structure. The amounts of surrogates that can be loaded strongly depend on the type of surrogate and these amounts still need to be determined. The ultimate goal is to use these techniques to achieve a molecular-level understanding of fluorapatite and other fluorine-bearing phases as natural analogs for waste-form materials. These techniques will also be used to examine changes in surface chemistry caused by environmental degradation.

### Research Staff

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### Students

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## Task 17

# Interaction between Metal Fission Products and TRISO Coating Materials

C. Heske

## BACKGROUND

This project focuses on the chemical bonding and interface formation of metal fission products with the coating materials used in tri-isotropic (TRISO) fuel particles for gas-cooled reactors. By combining surface- and bulk-sensitive spectroscopic methods, intermediate chemical phases at the interface, intermixing/diffusion behavior, and the electronic interface structure as a function of material (metal and coating materials) and temperature are examined.

In detail, the project studies the interface formation of Pd, Cs, and Ag with SiC and pyrolytic carbon. Using SiC single crystals as substrates, interfaces are prepared under controlled conditions in an ultra-high vacuum environment and are studied with a combination of experimental methods, including Photoelectron Spectroscopy, Auger Electron Spectroscopy, Inverse Photoemission, X-Ray Emission Spectroscopy, and X-Ray Absorption Spectroscopy. Furthermore, microscopic techniques (Transmission Electron Microscopy, Scanning Tunneling Microscopy, Atomic Force Microscopy) and local scanning tunneling spectroscopy are being employed.

## RESEARCH OBJECTIVES AND METHODS

By combining results for the electronic and chemical structure of the fission product/TRISO layer interfaces, the research results give information about failure mechanisms of TRISO particles and fission product transport.

Furthermore, they can be used to derive strategies to tailor the interface properties for an optimization of TRISO particles in terms of, e.g., chemical and long-term stability.

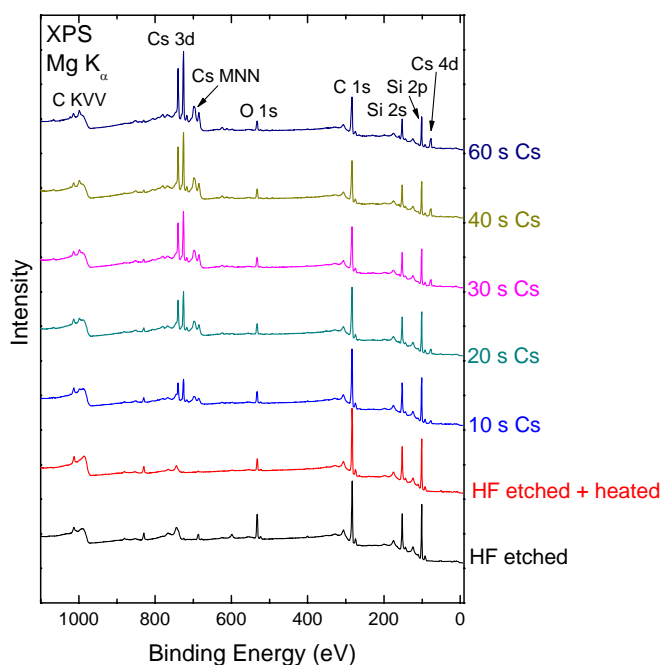
The experiments use two different experimental set-ups. First, a multi-chamber ultra-high vacuum system at UNLV (see photo in the 2005-2006 Annual Report) houses the majority of surface-sensitive methods. Second, the soft X-ray fluorescence (SXF) endstation at Beamline 8.0 at the Advanced Light Source, Lawrence Berkeley National Lab is used to perform X-ray absorption and emission spectroscopy. The apparatus at UNLV consists of a surface spectroscopy chamber, a preparation chamber, and an ultra-high vacuum scanning probe microscope. Samples can be introduced into the machine through a glove box with integrated load-lock and then transferred to each of the chambers via a distribution chamber. The analysis chamber is equipped with a state-of-the-art electron analyzer, an X-ray source, an ultraviolet (UV) source, and an inverse photoemission setup consisting of a low-energy high-flux electron gun and a UV detector. The preparation chamber is used for cleaning samples with an ion source and for the deposition of metal films with an evaporator.

## RESEARCH ACCOMPLISHMENTS

In the past year, emphasis was placed on a detailed analysis and description of the Cs/SiC interface formation process.

Great care was taken to prepare a clean SiC surface. It was found that the purchased SiC single crystals exhibit strong surface contaminations with oxygen. Based on an in-depth literature research, two different cleaning routes were investigated. The first route is an HF etch of the SiC surface, which is reported to result in a clean, C-terminated SiC surface. The second route is a sputter-cleaning of the surface with Ar<sup>+</sup> ions. It was found that it was not possible to entirely remove the O with either of the techniques, showing that the crystals were significantly oxidized into the bulk. As a consequence of this investigation, a new vendor was identified and new SiC crystals were ordered.

For the deposition of Cs films on the SiC substrate, a Cs evaporator was designed and constructed. Cs films of different thickness were deposited on SiC substrates (exhibiting some degree of surface oxidation, as discussed above). Exemplarily, the survey spectra of films with different Cs thicknesses are shown (left). These spectra illustrate the stepwise increase in Cs intensity after subse-



*XPS survey spectra of an HF-etched SiC single crystal surface, after heat treatment at approximately 400°C, and after various deposition steps of Cs (given is the deposition time in seconds).*

quent deposition steps, indicating an increase in the Cs film thickness. In parallel, the Si and C intensities decrease due to attenuation by the Cs film. A careful quantitative analysis shows that this attenuation is weaker than expected, suggesting either an inhomogeneous growth of the Cs film or an intermixing at the interface.

To gain further insight into this question, and to learn more about the detailed chemical environment at the Cs/SiC interface, detailed core level X-ray photoelectron spectroscopy (XPS) spectra were recorded. As an example, a series of C 1s core levels as a function of sample preparation and Cs deposition time (below right). As is evident in the figure, a second carbon species at higher binding energies emerges, which is directly indicative of the chemical interaction between Cs and SiC. Interestingly, no changes are observed in the Si core levels, suggesting that the chemical attack of SiC by Cs is initiated at the C sites.

The X-ray photoemission experiments were supplemented by UV photoemission data (not shown), which gives detailed information about the valence electrons. The students in the project have learned about the chemical and electronic information that can be exerted from such spectra, and a detailed analysis of the Cs/SiC dataset is currently ongoing. In the previously investigated case of Pd/SiC, similar data could be used to draw the picture of the formation of a Schottky barrier at the Pd/SiC interface.

Finally, selected Cs/SiC interfaces were also investigated at the Advanced Light Source using X-ray emission spectroscopy of the Si L<sub>2,3</sub> and the C K edge, giving additional insight into the intermixing behavior at the interface between Cs and SiC.

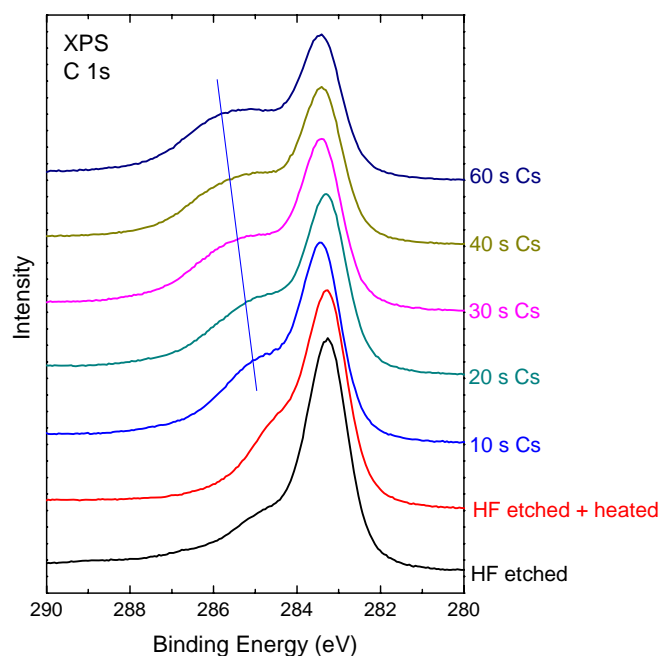
## FUTURE WORK

The experiments on Cs/SiC will be continued including the deposition on differently prepared substrates. In addition, the interaction between Cs and pyrolytic graphite surfaces will be studied. The focus will be on single crystalline surfaces and also on rough surfaces, which will be prepared by Ar<sup>+</sup> ion bombardment. This will allow an investigation of the influence of substrate roughness on the chemical Cs-SiC and Cs-C interactions.

Furthermore, the substrate temperature will be varied during deposition, up to approximately 1200 C. Both experiments will help to correlate the results to the real case of a TRISO particle with microscopically rough interfaces involving the SiC diffusion barrier and the pyrocarbon layers. In addition, the experiments will simulate the “natural” high temperature environment present in the nuclear reactor.

## ACADEMIC YEAR HIGHLIGHTS

- ◆ Participation of all graduate and undergraduate students in experimental campaigns at the Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA (October 2006 and March 2007).
- ◆ C. Heske, “How to reveal the chemical and electronic properties of interfaces, buried layers, and liquids with soft X-ray spectroscopy,” Physics Department, Boston University, December 8, 2006.
- ◆ C. Heske, “The surface and interface analysis ‘tool chest’ at UNLV,” Group seminar Prof. T. Moustakas, Boston University, November 17, 2006.
- ◆ C. Heske, “How to reveal the chemical and electronic properties of interfaces, buried layers, and liquids with soft X-ray spectroscopy,” Materials Science and Engineering Department, Stanford University, August 31, 2006.
- ◆ C. Heske, “Surface and Interface Analysis in Las Vegas,” Seminar Experimentelle Physik II, University of Würzburg, Germany, July 20, 2006.



*XPS detail spectra of the C 1s core level, indicating the presence of a second, reacted C species after deposition of the Cs films (indicated by the blue slanted line).*

### Research Staff

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Lothar Winhardt, Post-Doctoral Fellow, Department of Chemistry

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Alessio Luinetti, Sunil Subramanyam, and Kyle George, Undergraduate Students, Department of Chemistry

### Collaborators

David Williams, Oak Ridge National Laboratory

## Task 18

# Fundamental and Applied Experimental Investigations of Corrosion of Steel by LBE under Controlled Conditions: Kinetics, Chemistry Morphology, and Surface Preparation

J.W. Farley, A. L. Johnson, and D.L. Perry

## BACKGROUND

Advanced nuclear processes and facilities (e.g., transmutation of nuclear waste, fast reactors, and spallation neutron sources) impose special demands on materials, which must withstand high temperatures, high radiation fields, and chemical corrosion. Proposed schemes for transmuting nuclear waste require a non-moderating coolant such as lead-bismuth eutectic (LBE). While LBE corrodes most steels, small amounts of oxygen in the LBE greatly reduces the corrosion rate, and could ideally re-grow a damaged oxide layer in-situ. The protective oxide layer would thus be self-healing. However, the fundamental understanding of the role of oxygen and passivating oxide layers is presently incomplete.

## RESEARCH OBJECTIVES AND METHODS

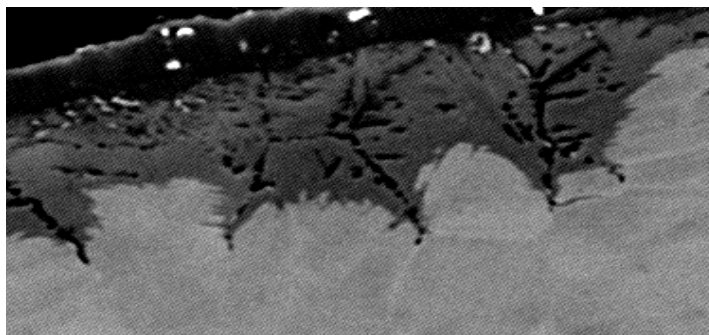
Steel samples have been characterized before and after exposure to LBE using different types of surface microscopy, including Scanning Electron Microscopy (SEM), Energy Dispersive X-ray analysis (EDX), Wavelength Dispersed X-ray, X-ray Photoelectron Spectrometry (XPS), and Sputter Depth Profiling. In past work, steel samples exposed to LBE at the Institute for Physics and Power Engineering in Obninsk, Russia, were examined using SEM and EDX. Samples with the same chemical composition but different surface treatments were compared, and cold-rolled samples were more corrosion resistant than annealed samples. Increased corrosion resistance was associated with changes in oxide layer thickness, morphology, and composition. These past results were published in the Journal of Nuclear Materials.

During the present reporting period, gas-phase experiments were conducted, in which steel samples were oxidized in glass capsules at elevated temperatures in a tube furnace. Corroded steel samples were analyzed from a variety of sources, including the Delta loop at LANL and samples corroded at UNLV in the gas phase experiments.

## RESEARCH ACCOMPLISHMENTS

An analysis of the role of silicon in conferring corrosion resistance was published during the present reporting period. Silicon and its various oxides were found in the oxides of silicon-containing steels after exposure to LBE, with  $\text{SiO}_2$  found near the oxide/metal interface, consistent with the formation of a layer between the metal and the oxide. Results were published in the Journal of Nuclear Materials.

A model was developed and presented at the AFCI materials working group March 2006 in Santa Fe. This model and supporting experimental results indicate that the conversion of the oxide



*Atom probe image of etched D-9. Note the high etch rate along grain boundaries and elsewhere. Also note the evidence of oxidation along the crystal planes in the metal.*

layer on the austenitic steels from an initial compact thin layer to a porous thick multilayer occurs at localized failures of the thin oxide, with the formation of diffusion channels in the thick oxide. At the May 2007 Heavy Liquid Metals (HLM) Workshop in Rome, Italy, other researchers supported this model. Currently, a paper is being prepared on the application of the defect generated diffusion channel model to austenitic and ferritic/martensitic steels for nuclear applications.

### Gas phase experimental results

The gas phase oxidation of steels has been examined at oxygen concentrations approximating those in LBE. This study determines the unique aspects of oxidation in LBE. For example, in the gas phase experiments on these steels, tin was sometimes observed at the surface. Tin has been implicated in temper embrittlement. In LBE, tin does not accumulate due to the solubility of tin in LBE. Conversely, nickel is depleted from the oxide layer that forms on the austenitic steels. In LBE, this nickel can dissolve. In the gas phase, Ni depletion was also observed, indicating that nickel must dissolve into the bulk metal in this case.

After 100 h of oxidation up to 10 microns of oxide is formed, which indicates a flux of oxygen onto the metal surface that is much higher than the oxygen control mechanism ( $\text{CuO}/\text{Cu}$  couple) would allow, suggesting that some other oxygen containing species is active. Of course water is a likely suspect, and experiments have been initiated to determine the role of water as an oxygen containing/transport agent in LBE. In summary, gas phase experiments have directed the project towards studies expected to give insight into the mechanisms of LBE corrosion of steel.

### Facility development

After the renovation of room 112C in the Chemistry building (CHE), the first experimental data came from an experiment in gas phase corrosion using a tube furnace. Steel samples were corroded by contact with controlled amounts of oxygen at elevated



temperatures. The gas phase facility has produced valuable data for comparison with corrosion of steel by liquid metal. A clean bench has been installed in CHE 112C for handling liquid lead safely. A small liquid metal experiment is being assembled, and the lower section is now finished.

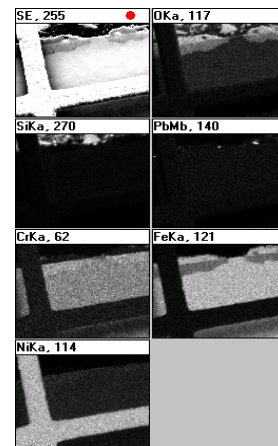
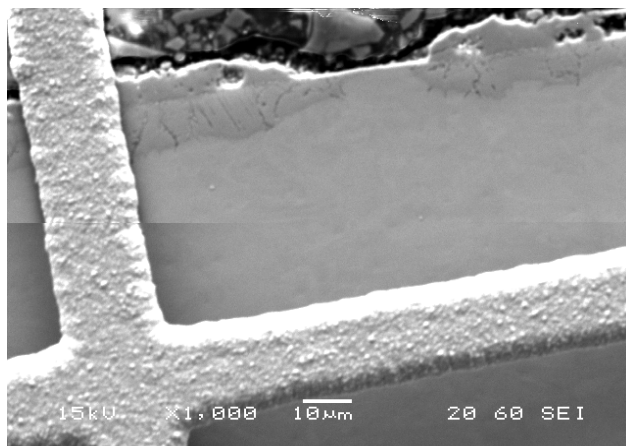
#### Analytical Techniques

In the last year, a laser Raman microscope was successfully developed, capable of performing Raman spectroscopy of sample surfaces with lateral resolution of a few microns, allowing detection of chemical species on the surface, whereas other analytical techniques (e.g., XPS or EDX) only provide elemental/oxidation state information. The laser Raman microscope can easily distinguish between the two oxides of iron, hematite ( $\text{Fe}_2\text{O}_3$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ), and was used in Hosterman's 2006 masters degree.

#### FUTURE WORK

Plans for Summer 2007 and later consist of continuation of work specified in previous work packages. The small liquid metal exposure facility will be completed, and physical, chemical, and corrosion LBE characterization will begin. Gas phase experiments will be continued with the use of the Oxygen Control System. These experiments are planned for completion in Fall 2007. They test the specifics of LBE corrosion versus standard gas corrosion of steel, and allow a clear indication of the differences induced by the LBE. Isotope labeling experiments turned out to be more difficult than planned.  $^{18}\text{O}$  labeling studies following the experiments of Martinelli et al. (recently mentioned at the HLM conference in Rome) will be done on D9 and 316, and training on the required TOF-SIMS technique at the National ECSA and Surface Analysis Center for Biomedical Problems workshop will happen in August 2007. A joint paper has been planned using task work as well as investigations by the LANL and French groups to expand the model to include a broad array of structure steel corrosion phenomena in LBE.

*D-9 shows failure of the thin oxide and formation of duplex oxide in localized patches. The iron moves outside the original metal surface to form  $\text{Fe}_3\text{O}_4$  (as shown by Raman Spectroscopy) and the chromium stays in place to form an iron/chromium oxide which undercuts the thin oxide.*



#### ACADEMIC YEAR HIGHLIGHTS

- ◆ Brian Hosterman, M.S. thesis, UNLV Physics Department, "Micro-Raman Spectroscopic Studies of Corrosion of Steel by Lead-Bismuth Eutectic," December 2006.
- ◆ A. L. Johnson, J. W. Farley, D. Koury, B. Hosterman, J. Welch, T. Ho, L. Ma, and U. Younas; "Protective Oxide Layers on Austenitic Stainless Steel (316L and D9) in Molten Lead Service: Formation and Reformation, Structure and Dynamics," poster, Annual Meeting of the American Vacuum Society, San Francisco, CA, November 12-17, 2006.
- ◆ A.L. Johnson, J.W. Farley, L. Ma, O. Tschauer, D. Koury, T. Ho, B. Hosterman, and J. Welch, "HLM efforts at UNLV, USA: LBE Corrosion of D9 and Other 316-Group Steels," oral presentation, IV Workshop on Materials for HLM Cooled Reactors and Related Technologies, Rome, Italy, May 21-23, 2007.
- ◆ A.L. Johnson, D. Koury, J. Welch, T. Ho, S. Sidle, C. Harland, B. Hosterman, U. Younas, L. Ma, and J.W. Farley, "Spectroscopic and microscopic investigation of the corrosion of D-9 stainless steel by lead-bismuth eutectic (LBE) at elevated temperatures: Initiation of duplex oxide formation," submitted, *Journal of Nuclear Materials*.
- ◆ T.D. Lane, C. Carr, J.W. Farley, A.L. Johnson, J.S. Welch, T. Ho, and D. Koury, "Formation of Oxide Layers in an Oxygen Controlled System," poster, Summer Undergraduate Research Experience, UNLV, Las Vegas, NV, August 11, 2006.
- ◆ P. Shafe, J. Farley, A. Johnson, D. Koury, and J. Welch, "Lead Bismuth Eutectic Corrosion Chamber Prototype," poster, Summer Undergraduate Research Experience, UNLV, Las Vegas, NV, August 11, 2006.

#### Faculty

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## Task 19

# Dissolution, Reactor, and Environmental Behavior of ZrO<sub>2</sub>-MgO Inert Fuel Matrix

K. Czerwinski

## BACKGROUND

There has been a recent resurgence of interest in different oxide fuel types (e.g., Th, inert matrix, and Pu fuels) as potential advanced fuels that can be operated to relatively high burnups at lower costs than current UO<sub>2</sub> fuels. These fuels can also be formed to incorporate transuranics elements in the matrix. Inert fuel matrices have the advantage of burning Pu and other transuranic elements from the fuel cycle without the production of other actinide elements. Of the possible materials for use in an inert matrix, ZrO<sub>2</sub> has been examined. The inclusion of ZrO<sub>2</sub> is expected to increase chemical stability and radiation resistance. The natural analogue of zirconia, baddeleyite ((Zr,M)O<sub>2</sub>), where M is a tetravalent ion such as hafnium), contains up to 3000 ppm U or Th. This supports the durability of inert matrix fuels using ZrO<sub>2</sub> in reactor conditions and repository conditions. However, fuels appropriate for the advanced fuel cycle applications should have desirable reprocessing properties, namely ease of dissolution for separations. An additional oxide which is somewhat soluble may need to be added to the ZrO<sub>2</sub> matrix to achieve desirable reprocessing properties. A candidate oxide is MgO.

## RESEARCH OBJECTIVES AND METHODS

This project will examine inert fuels containing ZrO<sub>2</sub> and MgO as the inert matrix. Ceramics with this inert matrix, Ce, U and eventually Pu will be synthesized and examined. While the Advanced Fuel Cycle Initiative focus is on inert fuels with Pu as the fissile component, this task will perform initial laboratory experiments with Ce and U. The initial work with Ce will be performed early in the project with results used as a basis for U studies. Reactor physics calculations will be used to examine suitable quantities of burnable poisons from the candidate elements Gd, Er, or Hf. Most fuels use Gd or Er, but the chemical properties of Hf lend themselves to formation of solid solutions with Zr and the tetravalent actinides and will therefore be investigated. This project will provide the necessary data for evaluating the performance, reprocessing, and waste behavior of the MgO-ZrO<sub>2</sub> fuels from a quantified, chemical perspective.

Reactor physics calculations are used to examine suitable quantities of burnable poisons from the candidate elements Gd, Er, or

Sample #	Zr %	Mg %	U %	Er %
1	92.5	0	5	2.5
2	87.5	5	5	2.5
3	82.5	10	5	2.5
4	77.5	15	5	2.5
5	72.5	20	5	2.5
6	62.5	30	5	2.5
7	47.5	45	5	2.5
8	32.5	60	5	2.5
9	17.5	75	5	2.5
10	0	92.5	5	2.5

*Metal Concentrations for Uranium Containing Ceramics*

Hf with reactor grade Pu providing the fissile component, with up to 10% of <sup>239</sup>Pu. Ceramics are synthesized and characterized based on the reactor physics results. The solubility of the fuel ceramics, in reactor conditions, reprocessing conditions, and repository conditions, are investigated in a manner to provide thermodynamic data necessary for modeling.

The research objectives of this project are as follows:

- To examine the neutronic behavior of MgO-ZrO<sub>2</sub> inert fuels. Variation of MgO and ZrO<sub>2</sub> composition ranges from 30% to 70% MgO in ZrO<sub>2</sub>. Analysis of Gd, Er, and Hf for reactivity control ranging from 5-10% lanthanides. Analysis of reactor grade Pu as fissile component ranging from 5-10% Pu. Results will be used as parameters for fuel composition.
- To synthesize and characterize MgO-ZrO<sub>2</sub> ceramics containing burnable poison and fissile composition. Synthesis is based on a precipitation method. Range of MgO in ZrO<sub>2</sub>, fissile component concentration, and burnable poison concentration based on results of neutronic calculations. Characterization of ceramics will include density, X-ray diffraction (XRD), surface area analysis, X-ray absorption fine structure, and chemical composition. Results will be applied to behavior in high temperature water, acid, and environmental conditions.
- To describe the chemical behavior of synthesized ceramics. Chemical thermodynamic and kinetic analysis will use equilibrium data, kinetic data, and surface area normalized dissolution. Different conditions will include reactor conditions (high temperature and high pressure water) and reprocessing conditions (nitric acid and elevated temperature). Environmental conditions will be near neutral solution conditions.
- To utilize project data in kinetic and thermodynamic modeling codes to evaluate the speciation of the elements in the ceramics under reactor, reprocessing, and repository conditions.

## RESEARCH ACCOMPLISHMENTS

### Development of X-ray fluorescence characterization method

A reliable method for X-ray fluorescence (XRF) was developed involving ashing the individual oxides, then preparing standards through the dry synthesis route. It was believed that the samples that showed heterogeneous Ce distribution were due to insufficient sintering times. Therefore, one such sample was removed from resin, resintered, and elemental mapping was performed a second time. This second mapping showed a homogenous distribution of cerium demonstrating the suitability of the method.

### Synthesis and characterization of U-containing ceramics

Ceramics were synthesized using MgO-ZrO<sub>2</sub> as the inert matrix and Er<sub>2</sub>O<sub>3</sub> as a burnable poison as in previous studies; however, UO<sub>2</sub> is now being used as a more accurate PuO<sub>2</sub> analog than the previous CeO<sub>2</sub> containing ceramics.

A soxhlet experiment was initiated to determine the corrosion resistance of the ceramics. The results demonstrated the corrosion resistance enhancement from the inclusion of  $\text{ZrO}_2$ . A thermogravimetry and differential scanning calorimetry scan was performed on the precipitated material to examine calcining and sintering behavior. The material appears to change from the oxyhydroxide precipitate to the oxide at the same temperature as the Ce-containing ceramics ( $260^\circ\text{C}$ ). The phase change also starts at the same temperature ( $510^\circ\text{C}$ ), but it does not proceed as quickly and therefore shows a broader peak.

XRD patterns were taken of all samples under investigation to qualitatively determine the phases present within the sintered sample. With no  $\text{MgO}$  present the  $\text{UO}_2$  and  $\text{Er}_2\text{O}_3$  only partially stabilizes the  $\text{ZrO}_2$  resulting in a mixture of monoclinic and tetragonal Zr oxide phases. With as little as 5% wt/wt  $\text{MgO}$ , the material fully stabilizes to form a pure cubic zirconium phase. Over 10%  $\text{MgO}$  results in a  $\text{MgO}$  phase, in addition to the cubic zirconia. This pure  $\text{MgO}$  phase increases with total  $\text{MgO}$  content. When there is no longer  $\text{ZrO}_2$  in the sample a  $\text{MgO}$  phase dominates, while there is a minor cubic uranium erbium oxide phase. Quantitative analysis will be performed once TOPAZ software is obtained.

Scanning Electron Microscopy and optical microscopy were used to image the material and identify the nature of the phase mixing within the sample. The  $\text{MgO}$  phase appears darker than the  $\text{ZrO}_2$  phase due to lower mass number. The color images show large areas of various colors, but higher magnification in greyscale shows a high degree of mixing the two phases. Microprobe was also used to sweep large areas of the sample to determine where each element is concentrated. This shows that Zr, Er, and U are all within the same area (phase), while Mg is contained within its own phase. This compliments the XRD findings well. In the U and Er map the brightness and contrast were enhanced because of the low concentrations of those elements.

Dissolution studies with nitric acid have shown a linear dissolution rate for U; however, improvements are needed for consistent kinetic constants. Also, U leaching in nitric acid is only possible at high Mg concentrations. This is due to the greater surface area of the exposed zirconia phase once the magnesia is dissolved, and the higher U concentration within the zirconia phase in these samples. Dissolution in supercritical water was extended to 3 weeks with the same results. Only Mg is found in solution.

#### Oxide waste forms based on project results

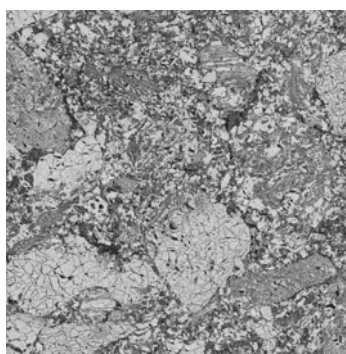
$\text{UY}_6\text{O}_{12}$  pellets were synthesized for Los Alamos National Laboratory for initial waste form studies complementary to the inert fuel research. Composition was confirmed to be delta phase by XRD.

## ACADEMIC YEAR HIGHLIGHTS

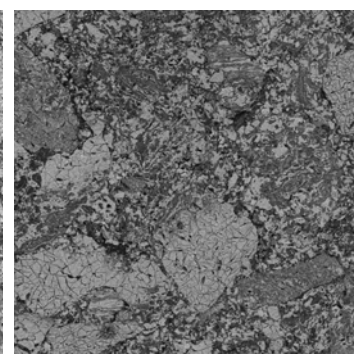
- ◆ K. Czerwinski was the U.S. delegate to the International Atomic Energy Agency Minor Actinide Inert Fuel Matrices working committee from May 2004 to present.
- ◆ K. Holliday, T. Hartmann, and K. Czerwinski, "Characterization of zirconium-magnesium ceramics for inert matrix fuel," *2006 Inert Matrix Fuel Workshop*, Park City, UT, October 2006.
- ◆ K. Holliday, T. Hartmann, and K. Czerwinski, "Characterization and dissolution of Zr-Mg ceramics for inert matrix fuel," *Advanced Fuel Cycle Topics*, American Chemical Society Regional Meeting, Boise, ID, June 2007.

## FUTURE WORK

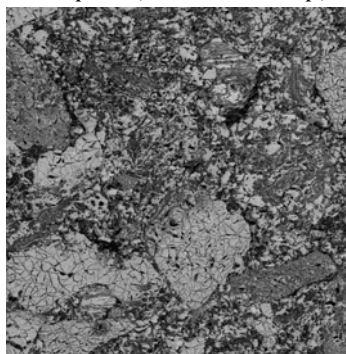
Further synthesis and characterization of  $\text{MgO-ZrO}_2$  ceramics will be performed with the use of Pu containing material obtained from Idaho National Laboratory. The project will be the basis of further fuel studies on the oxygen to metal ratio and research into the development of oxide waste forms for Tc.



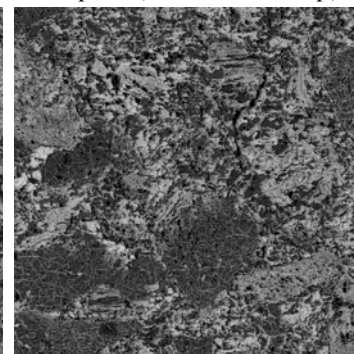
Sample 6 (3 x 3 mm U map)



Sample 6 (3 x 3 mm Er map)



Sample 6 (3 x 3 mm Zr map)



Sample 6 (3 x 3 mm Mg map)

Elemental Scanning by Microprobe

### Research Staff

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## Task 20

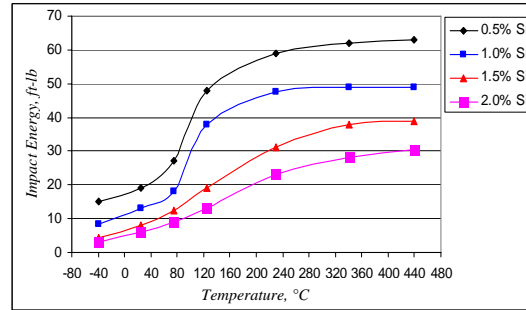
# Effect of Silicon Content on the Corrosion Resistance and Radiation-Induced Embrittlement of Materials for Advanced Heavy Liquid Metal Nuclear Systems

A.K. Roy

## BACKGROUND

This task is focused on the evaluation of the effects of silicon content on both the corrosion behavior and radiation-induced embrittlement of martensitic stainless steels having compositions similar to that of modified 9Cr-1Mo steel, also known as T91 grade steel. T91 grade steel was selected to be a candidate structural material to contain molten lead-bismuth eutectic (LBE), which can act both as a target material and a coolant during the spallation process. The operating temperature during this process may range from 420-550 °C. Thus, moderate tensile strength of the containment material (T91) is a major requirement.

The beneficial effects of Si on both the metallurgical and corrosion properties of chromium-molybdenum (Cr-Mo) steels have previously been demonstrated at UNLV. Therefore, additions of Si ranging from 0.5-2.0 weight percent (wt%) was attempted in this investigation to explore Si effect on both the high temperature tensile properties and corrosion behavior of T91 grade steel. Corrosion studies in the presence of molten LBE could not be performed due to a lack of proper experimental facilities at UNLV. Therefore, detailed corrosion studies involving Si-containing T91 grade steels were performed in an aggressive aqueous solution of acidic pH. Further, significant efforts have



Impact Energy (ft-lb) vs. Temperature (°C)

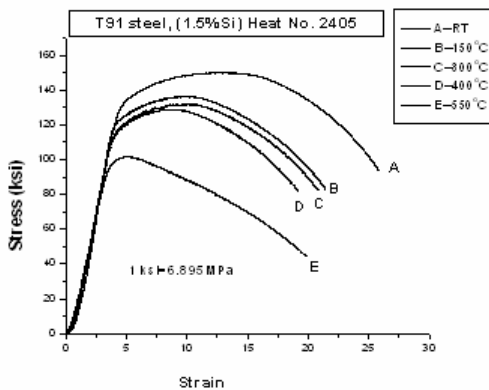
been made to determine both the impact and fracture toughness of the tested materials as a function of Si content.

## RESEARCH OBJECTIVES AND METHODS

Four heats of T91 grade steel having Si levels of 0.5, 1.0, 1.5 and 2.0 wt% were custom-melted by a vacuum-induction-melting practice. They were subsequently processed and thermally-treated to achieve fully-tempered martensitic microstructures. These materials were then machined to fabricate desired types of specimens for evaluation of tensile properties, impact toughness, fracture toughness, resistance to localized corrosion, stress corrosion cracking (SCC), and crack propagation behavior. Limited tensile testing was also performed on T91 grade steels under different levels of radiation. Numerous state-of-the-art experimental techniques were employed to evaluate the desired properties. The relevant experimental techniques have been described in previous annual reports. The significant results obtained during the past fiscal year are summarized below.

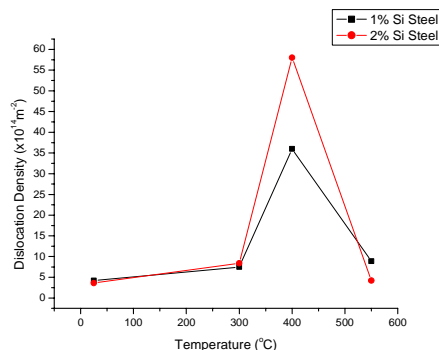
## RESEARCH ACCOMPLISHMENTS

- The results of tensile testing indicate that the magnitude of failure strain ( $\epsilon_f$ ) was gradually reduced with increasing temperature within a susceptible temperature range, irrespective of the Si content. Simultaneously, serrations were also noted in the engineering stress vs. strain diagrams.
- The reduced  $\epsilon_f$  values and the occurrence of serrations within a specific temperature regime can be attributed to a metallurgical phenomenon known as Dynamic Strain Ageing (DSA). Irrespective of the Si content, the susceptibility to DSA was predominant at temperatures ranging from ambient to 400°C.
- The DSA phenomenon, as seen in this investigation, is commonly associated with the diffusion of solute elements into the matrix of the material at elevated temperatures, thus impeding the movement of dislocations through the matrix and grain boundaries. Such reduction in dislocation mobilities can significantly impair the plastic deformation, which is manifested by reduced  $\epsilon_f$  values, as seen in this study.

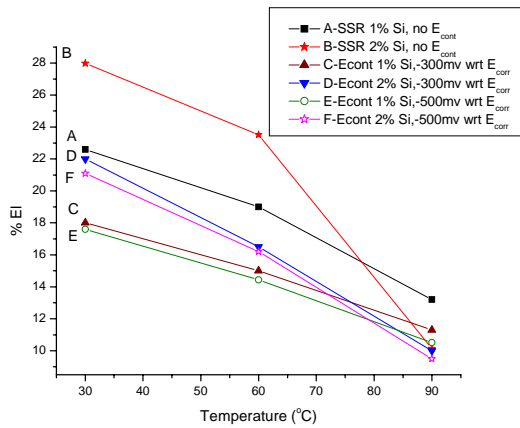


Stress-Strain Diagrams of T91 Steel with 1.5 wt% Si

Dislocation Density vs. Temperature (°C)







Variation of %EI with temperature for steels (1 and 2 wt% Si), with and without cathodic  $E_{cont}$ .

- A maximum dislocation density ( $\rho$ ), determined from the transmission electron micrographs, was seen at 400°C, irrespective of Si content.
- The work hardening index ( $n$ ) and activation energy for diffusion are two key parameters influencing the DSA behavior of engineering materials. Simultaneously, both temperature and strain rate can influence the DSA behavior. The variation of  $n$  with temperature at a strain rate of  $5 \times 10^{-4} \text{ sec}^{-1}$  is shown in the table below. A gradual increase in the  $n$  value was observed at temperatures up to 400°C, as expected.
- A longer activation time using an electron beam resulted in reduced ductility in terms of  $e_f$ .
- The presence of higher Si content in T91 grade steel resulted in reduced impact energy and higher ductile-brittle transition temperature, indicating reduced impact resistance.
- The susceptibility to SCC was enhanced at more cathodic (active) controlled potentials ( $E_{cont}$ ) and higher testing temperature, implying a synergistic effect of cathodic potential and temperature on SCC.
- The morphology of failure in double-cantilever-beam specimen used in SCC testing was characterized by a combination of striations (fatigue), SCC (intergranular/transgranular), and fast fracture (dimples).

Variation of  $n$  with Temperature (RT: Room Temperature)

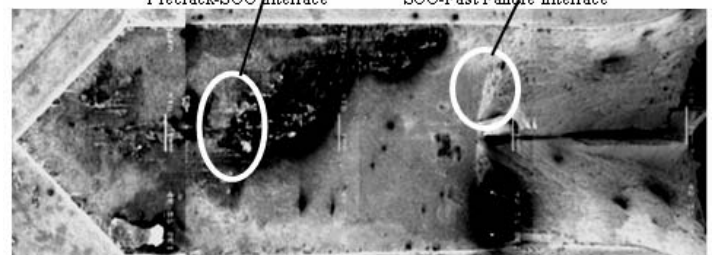
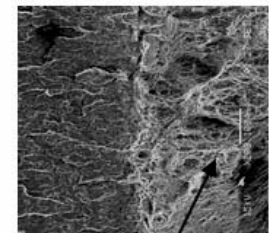
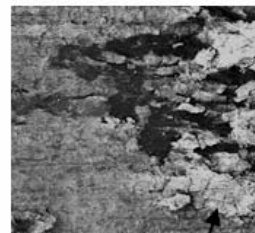
Heat no. / Temp (°C)	RT	150	300	400	550
2403 (0.5%Si)	0.1643	0.1698	0.1784	0.1984	0.1432
2404 (1.0%Si)	0.1716	0.1794	0.1945	0.2143	0.1564
2405 (1.5%Si)	0.1586	0.1702	0.1794	0.1802	0.1642
2406 (2.0%Si)	0.1669	0.1709	0.1772	0.1997	0.0994

## ACADEMIC YEAR HIGHLIGHTS

- ◆ S. Kohir, "Tensile Properties and Environmental Degradation of martensitic and Austenitic Stainless Steels," ISRS-2006, Madras, India, December 18-20, 2006.
- ◆ P. Kumar, D. Maitra, and A. Roy, "Temperature and Silicon Content Effects on Tensile deformation of T91 Grade Steel," Society for the Advancement of Materials and Process Engineering, Fall meeting, Dallas, TX, November 2006.
- ◆ D. Maitra, P. Kumar, and A. Roy, "The Role of Silicon Content on Tensile and Corrosion Properties of T91 Grade Steels," MS&T, Fall meeting, Cincinnati, OH, October 2006.
- ◆ D. Maitra, A. Roy, "Environmental Cracking and Localized Corrosion of T91 Grade Steel with Different Silicon Content," AMPT 2006, Las Vegas, NV, July 2006.
- ◆ P. Kumar, A. Roy, "Tensile Properties of T91 Grade Steel as a Function of Silicon Content," AMPT-2006, Advances in Materials and Processing Technology, Las Vegas, NV, July 2006.
- ◆ P. Kumar, D. Maitra, and A. Roy, "Metallurgical and Corrosion Studies of Modified T91 Grade Steel," *Materials Research Symposium Proceedings*, v 929, pp 149-154, 2006.

## FUTURE WORK

Stress corrosion cracking will be evaluated under anodic  $E_{cont}$ , dynamic strain ageing will be characterized by transmission electron microscopy, and fracture toughness will be evaluated.



Scanning electron microscope micrographs of double-cantilever beam specimens with 0.5 wt% Si subjected to SCC testing at 100°C in acidic solution for 30 days.

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Arindam Ghosh, Ph.D., Research Scholar, Mechanical Engineering Department

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Srinivas Kohir, M.S. Student, Mechanical Engineering Department

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Doug Wells, Ph.D., Associate Professor and Chair, Department of Physics, Idaho State University



## Task 21

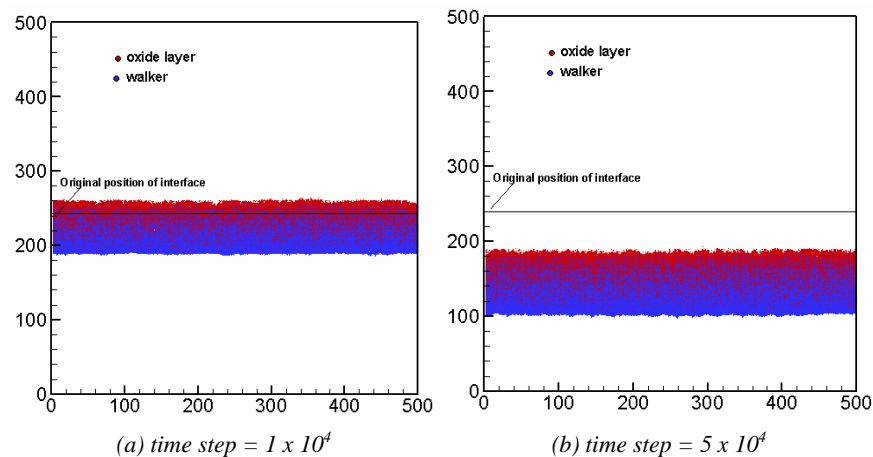
# Theoretical Modeling of Protective Oxide Layer Growth in Non-isothermal Lead Alloy Coolant Systems

Y. Chen, J. Zhang, H. Chen, J. Li

## BACKGROUND

In advanced nuclear energy systems, lead-alloys (e.g., lead, lead-bismuth eutectic) emerge as strong candidates for transmutation and advanced reactor systems as nuclear coolants and high-power spallation neutron targets. However, it is widely recognized that corrosion of materials caused by lead-alloys presents a critical barrier to their industrial use. A few experimental research and development projects have been set up by different groups such as LANL to study the corrosion phenomena in their test facilities and to develop mitigation techniques and materials. One of the central or main techniques in lead-alloys coolant technology under development is to use active control of oxygen thermodynamic activity (OTA) to provide protective oxide layers.

Setting OTA in flowing lead-alloys makes corrosion highly dependent upon the oxygen concentration and the oxidation processes at materials surfaces. The active oxygen control technique exploits the fact that lead and bismuth are chemically less active than the major components of steels, such as Fe, Ni, and Cr. By carefully controlling the oxygen concentration in LBE, it is possible to maintain an iron and chrome based oxide film on the surfaces of structural steels, while keeping lead and bismuth from excessive oxidization that can lead to precipitation contamination. Thermal analysis has given an ideal oxygen level range in a non-isothermal lead-alloy coolant system. However, in a practical coolant loop, the proper oxygen level depends not only on thermal factors but also on hydraulic factors (temperature profile, flow velocity, etc.). In addition, the oxygen distribution in a non-isothermal lead-alloy coolant system is still unclear. The optimal oxygen levels still need to be investigated.



*Snapshots of the simulated layer in the presence of corrosion with scale removal. They correspond to  $2.5 \times 10^4$  time step. The red dot is the oxide site; The blue dot is the walker site; The upper side of the layer is filled with solvent; The lower side of the oxide layer is pure metal. The corrosion probability of metal is taken as 0.5. The possibility of scale removal of the oxide site close to solvent is 0.004.*

The goal of the proposed research project is to provide basic understanding of the protective oxide layer behaviors and to develop oxide layer growth models of steels in non-isothermal lead-alloys (lead or lead-bismuth eutectic) coolant systems. Precise studies and simulations of all hydrodynamics with thermal conditions encountered in practical coolant loop systems by use of different flowing conditions in the laboratory are difficult and expensive, if not impossible. Therefore it is important and necessary to develop theoretical models to predict the protective oxide layer behaviors at the design stage of a practical lead-alloy coolant system, to properly interpret and apply experimental results from test loops, and to provide guidance for optimization in lead-alloy nuclear coolant systems. The research project, therefore, is aimed at understanding protective oxide layer growth and the optimal oxygen concentration level before lead-alloy nuclear coolants are ready for programmatic implementations and industrial applications.

## RESEARCH OBJECTIVES AND METHODS

- To elucidate the mechanism of the protective oxide layer growth of steels in static, non-isothermal flowing lead-alloy coolant systems with oxygen concentration level control.
- To elucidate the mechanism of mass transport of oxygen and corrosion products in the multi-phase system.
- To develop oxidation growth models of steels in lead-alloy coolant systems.
- To clarify the dependence of oxidation processes on thermal hydraulic factors (system operating temperature, temperature profile, flow velocity, etc.) and the oxygen concentration distribution and level.
- To clarify the optimal oxygen concentration levels in practical coolant system scales.
- To interpret the experimental results from test loops and to apply them to the design of practical nuclear coolant systems.

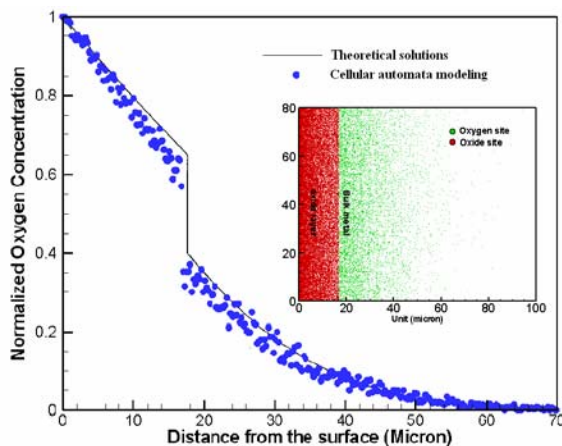
## RESEARCH ACCOMPLISHMENTS

Cellular automata modeling of oxide layer growth with scale removal: To simulate the scale removal effect on oxide layer growth, the previous cellular automata model of oxide layer growth has been improved to consider the scale removal effect. In this model, the scale removal rate was taken to be linear. It is assumed that the oxide layer sites which are close to the oxidant site have a probability to move away. The global random walker model is still used to simulate the solid state diffusion of the ionic metal site in the oxide layer. The phenomena of oxide growth which obeyed Tedmon theory was found.

Stochastic modeling with cellular automata method on the surface growth and internal oxidation: The quantitative cellular automata model on the inward oxidation mechanism was developed. The stochastic rule to the population of particles is based on the exclusion principle. Considering the exclusion principle, which permits at most one particle per site, a particle moves to its targeted site if this site is free and simply does not move if the site it targeted was already occupied. To avoid the confliction between particles competing for a single free site, the following rule was adopted. When more than one particle attempts to move to a single open site, only one of the competing particles, which will be chosen randomly from among them, is allowed to move to this open site and the others do not move. A benchmark with the theoretical solution was made, and a good agreement was obtained.

Numerical modeling on the diffusion controlling oxidation model with scale removal: A numerical diffusion-controlling oxidation model with scale removal was developed in oxygen-containing liquid flow. Scale removal effect was considered and the formation mechanism of duplex oxide layer structure was analyzed and employed in the model. The volume expansion effect caused by density difference during the oxidation is coupled with the consideration of increasing weight of reacted oxygen. To solve the diffusion equations with an advection term caused by the moving boundaries, a coordinate transform technique was employed. The governing equations were analogized with the Stefan problem in heat transfer with phase change in the enthalpy formulation and then solved numerically by finite difference method.

Cellular automaton model on the oxide growth coupled with inward oxygen diffusion: To simulate the oxide layer growth of steel in liquid lead alloy environment, a cellular automaton model



*Distribution of oxygen concentration at 0.5 hour. Application of quantitative cellular automata modeling of oxidation in metal matrix composite.*

## ACADEMIC YEAR HIGHLIGHTS

- ◆ Y. Chen, H. Chen, and J. Zhang. "Enhancement of oxygen transfer by forced convection in lead alloy system," *International Journal of Heat and Mass Transfer*, 2007, 50 (12): 2139-2147.
- ◆ H. Chen, Y. Chen, and H.T. Hsieh. "Stochastic modeling on oxide layer growth with scale removal effect in liquid metal environment," 15<sup>th</sup> International Conference on Nuclear Engineering (ICONE 15), April 22-26, 2007, Nagoya, Japan.
- ◆ H. Chen and Y. Chen, "Cellular automaton modeling on the corrosion/oxidation mechanism of steel in liquid metal environment," 2<sup>nd</sup> COE-INES International Symposium on Innovative Nuclear Energy Systems, November 26-30, 2006, Yokohama, Japan.
- ◆ X. Tan, Y. Chen, H. Chen, T. Tan, and H.T. Hsieh, "Numerical analysis of natural convection induced oxygen transport in liquid lead bismuth eutectic;" T. Tan, Y. Chen, H. Chen, and H.T. Hsieh, "Corrosion precipitation in non-isothermal lead alloy coolant systems;" and, H. Chen, Y. Chen, and H.T. Hsieh, "A stochastic model of oxidation mechanism on high temperature corrosion of stainless steel," 2006 ASME International Engineering Congress and Exposition, Chicago, IL, November 5-10, 2006.

was developed that considered inward oxygen diffusion. In this model, the lattice sites are occupied by metal, oxide, or lead alloy, while the interstitial sites are route ways for oxygen to occupy and diffuse. The benchmark of cellular automata model for pure oxygen diffusion has been made and a good agreement has been obtained.

## FUTURE WORK

The next phase of the project involves accomplishing the following tasks:

- Structure stability analysis on oxide layer under liquid metal environment for different operating conditions.
- Model the erosion-corrosion process mechanisms in oxygen-controlled lead-alloy systems.
- Identify the protective oxide layer growth under corrosion and oxidation mechanisms using stochastic methods.
- Clarify the dependence of the oxidation process on the hydraulics factors (system operating temperature, temperature profile, flow velocity, etc.) and the oxygen concentration distribution and level.
- Predict the optimal oxygen concentration levels in practical coolant system scales.

### Research Staff

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### Collaborators

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## Task 22

# Design Concepts and Process Analysis for Transmuter Fuel Manufacturing

G. Mauer

## BACKGROUND

The safe and effective manufacturing of actinide-bearing fuels for any transmutation strategy requires that the entire manufacturing process be contained within a shielded hot cell environment. To ensure that the fabrication process is feasible, the entire process must be designed for remote operation. The equipment must be reliable enough to perform over several decades, and also easy to maintain or repair remotely. The facility must also be designed to facilitate its own decontamination and decommissioning. In addition to these design factors, the potential viability of any fuel fabrication process will also be impacted by a number of variables, such as the current state of technology, potential problem areas, deployment scaling, facility safety, and cost.

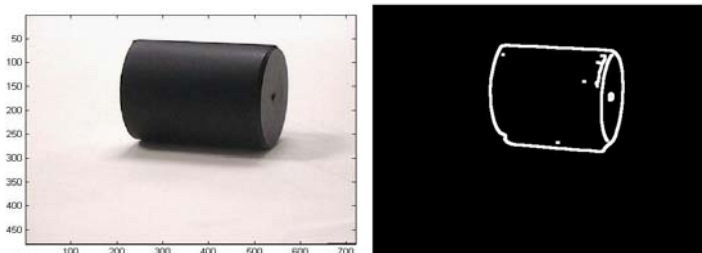
## RESEARCH OBJECTIVES AND METHODS

The goal of this research project is to provide technical support to process designers working on the development of the fuel cycles for transmutation applications. Detailed process models have been developed to better define the impact of fuel choice on the transmuter fuel cycle, including relative process losses, waste generation, and plant capital cost. These process models provide insight regarding required plant size and number of plants needed to mesh with the fuel recycling line. They also determine requirements for automation.

Manufacturing models for large-scale production in a hot cell environment have also been developed. Combined, these two models allow the assessment of plant layout, and provide the framework for estimation of plant capital and operating cost estimates, and for feasibility in general. The operations of robotic equipment and the sensor technology required for safe and reliable robot control have been evaluated through simulations in three-dimensional space. The manufacturing technology developed for hot cell applications is also applicable to other, more general uses, where occupational hazards prevent human presence near processes.

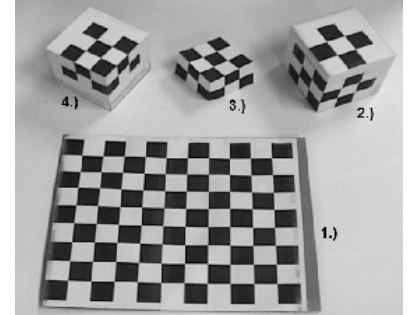
The research work performed during the reporting period was divided into several tasks:

**Simulations:** This task modeled manufacturing processes to generate a realistic assessment of plant layout, size, feasibility, and



CCD image (left), and Contour (right) of a cylinder

Calibration Objects



technology development required for large-scale remote fabrication of fuel. Modeling of the candidate fuel manufacturing processes was performed using the MSC.visualNastran and ProEngineer simulation software tools. To date, the modeling of dispersion and tri-isotropic (TRISO) fuels for gas-cooled reactors has been completed. A parametric study to determine the process reliability and possible reliability improvements for various fuel types and equipment configurations is in progress.

**Cost, Feasibility, and Large Scale Deployment:** This task will develop the database necessary to provide cost estimates and differential cost for various fuel manufacturing options. Cost estimates regarding projected capital cost, reliability, and plant life have been developed and are being refined as additional knowledge is developed.

**Automated Vision-Based Image Acquisition and Robot Control:** This task explores and demonstrates strategies for the reliable and flexible control of the material handling robots inside the hot cell by means of automated vision systems. Since the cameras can be positioned outside the hot cell, such systems would have significant advantages over sensors inside the hot cell, resulting in potentially reduced system maintenance and increased system reliability.

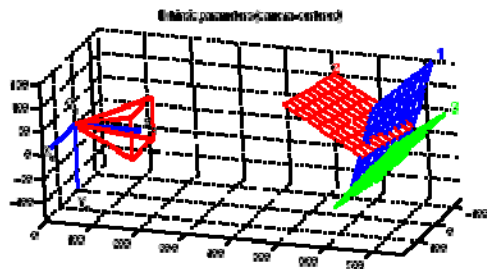
## RESEARCH ACCOMPLISHMENTS

Research during the past year focused on vision-based recognition and spatial location of fuel pellets inside a hot cell.

**Recognition of Cylindrical Fuel Pellets by the Charge-Coupled Device (CCD) Camera:** The images of cylinders that are captured by the camera have properties which make the recognition of the cylinder more difficult. The real time cylinder pictures contain shadows as well as reflections (specularity) caused by lighting conditions. This project seeks to detect the cylinders' contours in order to identify and classify it correctly. Changes of lighting conditions can make the correct identification difficult at times.

**Camera Calibration and Dimensional Measurements using the CCD Camera**

**Calibration objects:** Calibrating a camera requires several corre-



*Estimated 3D Structure of a calibration plane*

sponding 3D and 2D points. Calibration objects are mostly planes or cubes (two or three orthogonal planes) with special markings. Here, those markings are chess board patterns with equidistant corners distributed accurately over the object surface. The corners define the known points in the world coordinate system and can be easily identified in the image from edge detection algorithms. This step provides the opportunity to estimate the projection matrix. Another method of calibrating is self-calibration. This technique obtains correspondences from the camera movement in a static scene using image information alone.

*Estimation of the projection matrix:* The camera calibration algorithm was programmed in Matlab. The regions of interest were defined for every single image by selecting the 4 outmost corners of the chess pattern. The Matlab software identifies and saves the positions of the individual black square's corners for processing. The optimization method of Levenberg-Marquardt is applied which also includes the adaptive correction of the lens distortion.

*Two-View Triangulation:* Triangulation is the process of finding the position of a point in space given its position in a stereo image pair. This task is essential for vision-based robot pick and place operations. The Linear-Eigenmethod is the simple triangulation method that is used for extracting the 3D points.

*Optimal Triangulation:* Suppose there are two point correspondences  $x$  and  $x'$  from two images, and the goal is to reconstruct the 3D point  $X$ . If the correspondences are accurate (which cannot usually be expected) the rays of  $x$  and  $x'$  will lie in the same plane and thus will intersect in  $X$ . In the presence of noise, accurate point coordinates cannot be expected. It follows that  $x$  and  $x'$  may not lie in a plane, which means that there is no intersection. A method for correcting the existing point correspondences such that the corresponding rays will lie in the same plane consists in finding a global minimum of a cost function. For this approach, it is assumed that the fundamental matrix is well defined.

*Recognizing calibration cubes:* Until now a disadvantage of the calibration process has been the need to determine the point correspondences of the calibration object and a given 3D model manu-

## ACADEMIC YEAR HIGHLIGHTS

- ♦ G.F. Mauer, "Equipment Redundancy and Plant Reliability in Robotic Hot Cells for Fuel Fabrication," *Proceedings, American Nuclear Society Winter Annual Meeting*, November 2006.

ally. A desirable feature would be the automatic mapping from calibration cube points to the 3D locations of a 3 plane model. This would allow estimating the projective matrix automatically. For the experimental validation, several calibration objects were arranged on a paper grid in order to cover multiple points in the 3D space.

For the tests, 50 points were used to estimate the fundamental matrix. The same points have been reapplied as control points. The triangulation error was around 0.2 inches at a distance to the calibration points of 10 inches. In the proximity of the calibration points the error was below 0.1 inch. The errors are attributed by the following effects:

- Quality deficiencies of the camera device
- Inaccurate calibration objects (perpendicularity)
- Linearity of the algorithm

## FUTURE WORK

Vision-based control of hot cell robots: Images of scenes inside a hot cell, such as fuel pellets, will be acquired in real time under varying lighting conditions and in increasingly complex environments. The development of algorithms for reliable object identification, for validation and measurement of the object geometry, location, and orientation, and for camera calibration, will continue.

Vision-based robot servoing: Using a Fanuc M-16iB industrial robot, the stereo vision system will be installed in lab Thomas Beam Engineering Building (TBE) Room B-162, and the task will proceed to test the visual servoing algorithms under more realistic conditions.

Tests of the camera system in noisy environments will continue for the vision system's ability to discern fuel pellets from other objects present.

The conceptual design plant layout, and cost estimates for possible Transmuter Fuel fabrication plants will continue for various fuel types. (Simulations of oxide, metallic, and dispersion fuels have been completed.)

Capital and operations cost estimates will be developed for various fuel options. Target Plant capacity approximately 100 metric tons annually.

### Research Staff

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### Collaborators

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## Task 23

# Development of Nanostructure Based Corrosion-Barrier Coatings on Steel for Transmutation Applications

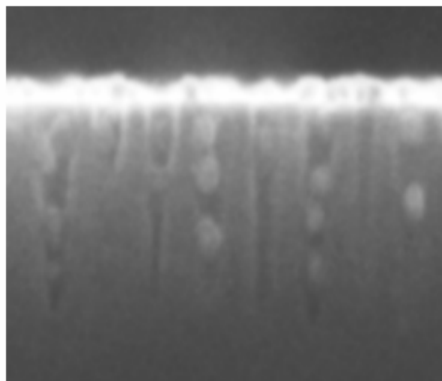
B.J. Das

## BACKGROUND

Advanced transmutation systems require structural materials that are able to withstand high neutron fluxes, high thermal cycling, and high resistance to chemical corrosion. The current candidate materials for such structures are ferritic and ferritic-martensitic steels due to their strong resistance to swelling, good microstructural stability under irradiation, and the retention of adequate ductility at typical reactor operating temperatures.

In parallel, lead-bismuth eutectic (LBE) has emerged as a potential spallation target material for efficient production of neutrons, as well as a coolant in the accelerator system. While LBE has excellent properties as a nuclear coolant, it is also highly corrosive to stainless steel. The corrosion is due to relatively high solubilities of the base and major alloying components of steel, such as Ni, Fe, Cr, etc. in LBE at elevated temperatures. Without some protection, the steel structures rapidly corrode in LBE through dissolution and leaching of these materials.

Thus, for long term reliability of the structures, it is necessary to provide some protection of the steel surface from corrosion, without affecting the bulk properties of the steel. One such technique that has been well investigated is the use of oxygen control at the surface of the steel, which maintains a coating of oxide layer that protects the steel surface. The protective layer forms due to the higher affinities of the steel alloying components to oxygen compared to lead and bismuth. However, once a continuous film of oxide is formed, a competing process takes place; the oxide layer interacts with the LBE causing reduction of the oxide layer at higher temperatures. It is thus critical to maintain an optimum flow of oxygen at the LBE/steel interface, which is made challenging by the non-uniform temperature distribution in the transmutation systems. In addition, while the oxygen control technique works effectively at lower temperatures, it is not appropriate for higher operational temperatures (500-600 °C), which is becoming increasingly important. Thus, it is necessary to develop alternative techniques for corrosion protection of steel that will perform reliably at elevated temperatures and under thermal cycling in LBE.



*Cross-sectional image of electro-phoretically deposited nanoparticles inside nanoporous alumina*

## RESEARCH OBJECTIVES AND METHODS

The objective of this project is to develop a novel nanostructure based coating technology that will provide significantly improved corrosion resistance for steel in LBE at elevated temperatures (500-600 °C), as well as provide long-term reliability under thermal cycling. The nanostructure based coatings will consist of a layer of nanoporous alumina with the pores filled with an oxidizing metal such as Cr, followed by a capping layer of alumina. Alumina, which is a robust anti-corrosion material, provides corrosion resistance at elevated temperatures. The Cr serves two purposes: (1) it acts as a solid filler material for the pores in the alumina, enhancing its mechanical and chemical integrity, and (2) it acts as a second layer of defense against corrosion by providing a replenishable source of Cr (for the formation of a chromium oxide protective layer) in case the alumina layer is compromised. The innovation of this project is the use of a nanoporous alumina layer for the coating, which is mechanically flexible and can expand and contract with the underneath steel surface. As a result, the mechanical integrity of the coating is preserved under thermal cycling. In addition to their usefulness at higher temperatures, the proposed coatings can also provide increased reliability at lower temperatures by complementing the oxygen control technique. The nanostructure based coatings developed in this project will significantly enhance the long-term reliability of steel structures in LBE at elevated temperatures and under thermal cycling.

Working with the national laboratory collaborator, the stainless steel alloys HT-9 and EP-823 were chosen as the candidate materials for investigation at this time. The above project objective will be achieved in three phases; each phase will be carried out over a one-year period.

Phase I will develop the fabrication technology for the coatings on steel, and study their structural integrity at elevated temperatures and under thermal cycling.

Phase II will perform corrosion studies of the structures in LBE at elevated temperatures.

Phase III will use the data from Phases I and II to develop an optimized coating technology for improved structural integrity under thermal cycling, and improved corrosion resistance in LBE at elevated temperatures. If necessary, multiple layers of such coating structures will be used for increased resistance to corrosion.

During Year 3 of the project (2006-2007), extensive investigation was carried out on the deposition of longer and improved quality metal nanowires inside the pores using a new technique as well as the establishment of the experimental setup for characterization of the coatings.

## RESEARCH ACCOMPLISHMENTS

As reported previously, during Phases I & II of the project, a significant problem was encountered with the synthesis of Cr nanowires inside the alumina pores, the uniformity of coverage was very poor. As a result, alternative metals to form nanowires were looked into and nickel was selected primarily due to its established electrochemical synthesis procedure.

A number of recipes were investigated for their suitability for synthesis inside nanoscale pores, and the process parameters were experimentally optimized for the synthesis of nanowires. The deposition of the Ni nanowire was performed in a two-electrode arrangement with a mixture of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{H}_3\text{BO}_3$  as the source of Ni. The wires were deposited at a potential difference of 1 V between the anode and the cathode and at ambient temperatures. The Ni nanowire samples were characterized by Field Emission Scanning Electron Microscopy (SEM), which showed excellent uniformity and coverage. However, while Ni can provide very good structural integrity to the porous alumina, one potential problem is its higher dissolution rate in LBE.

In addition, it was noted that the heights of the Ni nanowires were limited, and even with extended deposition times, the heights were limited to a few tenths of a micron. This limited height was believed to be arising due to the dynamics of fluid flow inside the nanoporous alumina.

To address the above issues, two different approaches were taken. A systematic study was continued during the past year to improve the deposition uniformity of the Cr nanowires, and some improvement was achieved. The uniformity of coverage showed improvement and experimental optimization of process parameters was continued for further improvement of the coverage uniformity. In addition, a new and promising approach was initiated for the deposition of metal nanowires inside the nanoporous alumina as described below.

During the past year, a new technique was initiated and investigated for the deposition of metal nanowires inside the nanoporous alumina. This technique involves the electro-phoretic deposition of nanoparticles inside the pores followed by recrystallization into nanowires. The major advantage of this technique is that the chemistry of nanoparticle synthesis is separated from the formation of nanowires, as a result it has the potential to eliminate the limitations encountered in nanowire synthesis. Nanowire deposition inside the alumina pores is made challenging by the nanoscale fluid flow and chemical reactions inside the nanoscale volume of nanoporous alumina pores. In this new technique, nanoparticles of the desired metal are first synthesized by an es-

## ACADEMIC YEAR HIGHLIGHTS

- ◆ B. Das, "Nonlithographic Nanoscale Devices," International Conference on MEMS and Semiconductor Nanotechnology, Kharagpur, India, December, 2006 (invited paper).

tablished technique in an emulsion form, which are then incorporated inside the nanoporous alumina pores. Since nanoparticles are relatively less complex to incorporate inside pores, it provides an excellent means for the synthesis of nanowires of good uniformity and desired heights. The nanoparticles can be synthesized using an established technique such as sol gel technique. The nanoparticles can be then annealed to form the nanowires or sonication can be used during electro-phoretic incorporation to form the nanowires.

Deposition of Cr nanowires on steel substrates will be achieved by using the following procedure. A new batch of steel samples will be coated with metallic aluminum which will be anodized using constant current anodization. Since it is not possible to obtain cross-sectional images of the structures on steel samples, the voltage-time characteristics will be measured to monitor the quality of the anodized alumina structures. A typical voltage-time characteristic obtained during the anodization of aluminum on steel samples, when compared to data from silicon samples, confirms the good quality of the nanoporous alumina. Cr nanoparticles will be synthesized using the sol-gel technique and will be then electro-phoretically incorporated inside the nanoporous alumina. Sonication will be used during deposition to fuse the nanoparticles to form nanowires. A sonication apparatus was obtained for this purpose. This will be followed by the deposition of a thick film of dense alumina, the process technology for which has already been developed during the previous phase of the research.

## FUTURE WORK

The next phase of the project is to characterize the samples fabricated using the new technique, including structural integrity of the coatings with Cr at elevated temperatures and under thermal cycling. The samples will then be characterized by SEM and also scratch tested to evaluate the structural integrity and adhesion properties of the coatings for thermal cycling at different temperatures. A programmable furnace had been acquired and a specialized sample holder fabricated to perform automated thermal cycling of the coatings developed on steel samples. However, the functions of the programmable furnace were delayed due to facility issues. To address this, a smaller furnace was acquired and installed for the characterization of the samples.

### Research Staff

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Nilanjan Halder, Post-Doctoral Researcher, Electrical and Computer Engineering  
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## Task 24

# Development of Integrated Process Simulation System Model for Spent Fuel Treatment Facility (SFTF) Design

Y. Chen and S. Hsieh

## BACKGROUND

The UNLV Transmutation Research Program is developing technology for the transmutation of nuclear waste to address long-term disposal issues. Integrating and enhancing the Argonne Model for Universal Solvent Extraction (AMUSE) code that contains a great part of chemical separations processing, is the major part of a previous 3-year project. Simulating the Light Water Reactor (LWR) Spent Fuel Treatment Facility (SFTF) processes is the major focus for this three-year project. The approach is to combine commercial process simulation software, ASPEN-Plus, with the chemical separation calculation from the AMUSE code. Based on the current Integrated System Optimization Program, ISOPro, developed by UNLV, the project objective is to create a system framework that interacts with both programs and provides analyzed results useful for SFTF design that provides the functionality of receiving, temporarily storing, and preparing spent nuclear fuel for leaching.

The spent fuel treatment facility has many individual processes that make up the overall separations processes. As illustrated in the overall process flow sheet below, each block represents a unique process that carries out an individual chemical separation. Each individual process block contains numerous operations that are responsible for the chemical separation. By removing the primary constituent, U, from spent fuel enables more waste to be stored at geologic repositories. The Uranium Extraction Process (UREX) is often the first removal process in the overall scheme of spent fuel recycling. After extracting U and Tc from the spent fuel, the washed and rinsed effluents (Cs/Sr raffinate) move on to the next separation process.

A key concept in the SFTF plant design is the recycling of nitric acid. The purpose of the nitric acid recycle system is to concentrate the spent nitric acid to a desired molarity that in turn can be recycled back into the process. The spent nitric acid streams from many processes are collected and sent to a distillation column where it is separated from the impurities collected in the various separation processes. The feed to the separation column contains acetic acid and water as well as the desired nitric acid.

## RESEARCH OBJECTIVES AND METHODS

The major objectives described below will lead to a creation of framework that combines all the strengths of AMUSE's complicated calculations, well-established commercial system process package and ISOPro's flexible parameter optimization modules. Development of the process simulation code can be done using the solvent extraction process at Argonne National Laboratory in collaboration with the research team from Mechanical

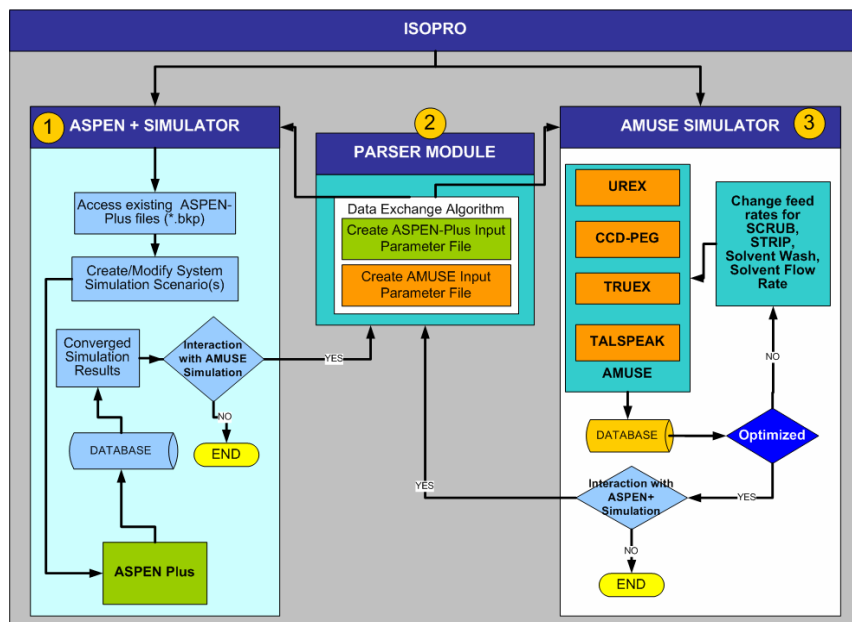
Engineering Department at UNLV. The objectives of this project are:

- To develop a framework for simulating the Spent Fuel Treatment Facility process using the AMUSE code, ASPEN-Plus commercial process package and ISOPro system engineering model.
- To develop middleware interfaces that can communicate between the AMUSE code and ASPEN-Plus packages.
- To extend the existing system engineering model for the optimization process that includes process simulation results.
- To include a scenario-based database system that efficiently reports required information as chart output using web-based programming, and Microsoft Visual Basic (MS VB).

## RESEARCH ACCOMPLISHMENTS

- Integrated the ASPEN-Plus process model with the ISOPro system engineering modeling package, developed by the UNLV team.
- Tested the simplified system process integration using the ISOPro package.
- Generated complete version of the ISOPro package user manual and tutorial.
- Made an interface to interact with ASPEN-Plus through the ISOPRO Package

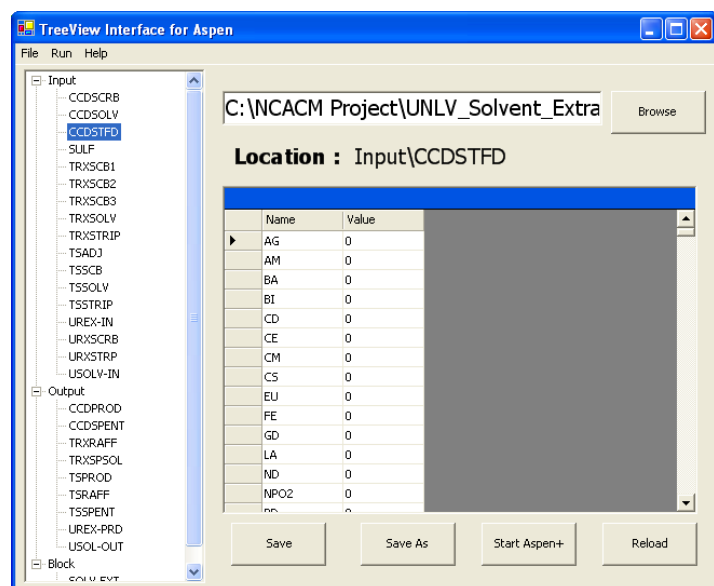
To interact with both the AMUSE and ISOPro packages, the middleware interface based on the ISOPro should provide the capability of interacting with external programs, converting input and



Modified TRPSEMPro system architecture

output data and managing process results. The major task for the year was to complete the interface to the ASPEN-Plus program through the developed ISOPro package. The data communication and result presentation from these two programs are valuable for the SFTF's process design task. The internal MS Access database was developed for storing intermediate and final simulation results from both programs. However, input and output data files originally generated from each individual program are kept intact and are used to populate the initial data sheet within each middle-ware interface. Although the program integration was completed, the final SFTF's system optimization work is not included in this report due the export control nature of the AMUSE code. The optimization can be completed by the ANL research team by plugging the full AMUSE program into the ISOPro package. The accomplishments for the year are summarized as follows:

- The framework design was revised to improve the performance of the system. It defines the data flow from ASPEN-plus to AMUSE with the data set "parser module" in the middle. Based on the discussion with ANL staff, the UREX+1a process simulation flow chart was updated based on the input and output natures defined in the database storage.
- The middleware for the ASPEN-Plus interacts with the ASPEN-Plus and populates data into a user friendly, tabulated format. It displays the information from streams and its elements. The user can modify the input values and directly run the simulation through the interface. There are sets of standard menu items listed to provide faster access. A "Tree"



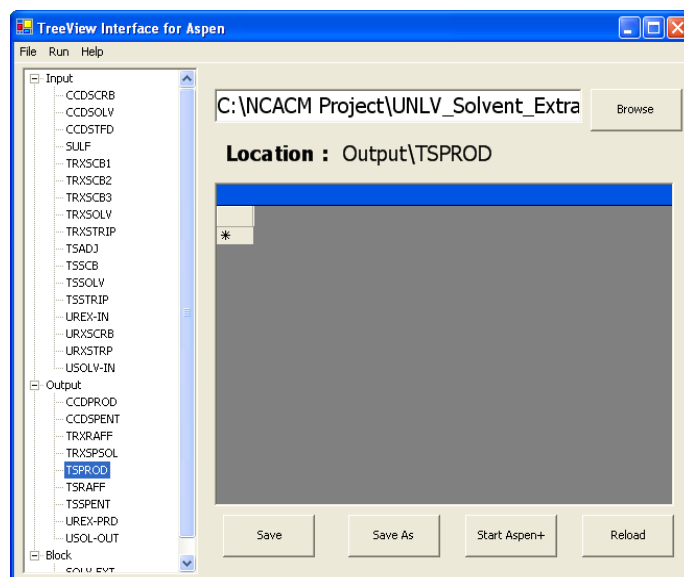
## ACADEMIC YEAR HIGHLIGHTS

- ♦ M. Cheng, M. Hodges, K. Kwan, H.T. Hsieh, and Y. Chen (UNLV); G. Vandegrift, J. Copple and J. Laidler (ANL), "An Object-oriented Systems Engineering Modeling Design for Integrating Spent Fuel Treatment Facility and Chemical Separation Processes," 2006 American Society of Mechanical Engineers, International Mechanical Engineering Congress, Chicago, IL, November 5–10, 2006.

view of the streams is organized into "Input" and "Output" based on the "Blocks" definition retrieved from the Aspen "bkp" file. After each simulation run from the ASPEN-plus, input/output information is updated into the interface. The selected programming algorithm can significantly impact the read/write efficiency of the code, especially loading a large and complicated "bkp" file. A "nested hash" programming technique was used. To accelerate data access, ASPEN-Plus information was stored in two hashes, one for Input streams and one for Output streams.

## FUTURE WORK

Future work will include optimization of the system and chemical separation processes using the ISOPro system engineering modeling package developed by the UNLV team.



Screenshots of the newly updated ISOPRO interface to the ASPEN-Plus; (left) input stream; (right) output stream.

### Research Staff

Yitong Chen, Principal Investigator, Associate Professor, Mechanical Engineering Department;  
Sean Hsieh, Research Assistant Professor, Mechanical Engineering Department; Nevada Center for Advanced Computational Methods

### Students

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### Collaborators

James J. Laidler, Senior Scientist, Chemical Technology Division, Argonne National Laboratory  
George F. Vandegrift, III, Senior Scientist, Chemical Technology Division, Argonne National Laboratory



## Task 25

# Electrochemical Separation of Curium and Americium

D.W. Hatchett and K. Czerwinski

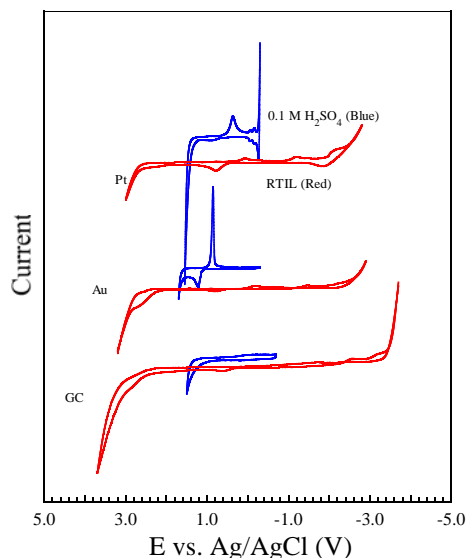
## BACKGROUND

In the Transmutation Research Program the separation of the trivalent actinides Am and Cm from the trivalent lanthanides, and even each other, has been identified as an area of particular interest. The removal of lanthanides from trivalent actinides is necessitated for the neutron economy of a fuel containing Am and Cm. Furthermore, a fuel containing only Am would ease the demands on a reactor for transmutation. The destruction rate of Cm isotopes in a reactor is comparable to their decay rate. Separation and storage of the Cm, and reintroduction into the fuel of the Pu daughters, is a transmutation option that can be explored if a suitable method for the separation of Cm from Am is obtained. Furthermore, removal of Cm would reduce difficulties in fuel fabrication.

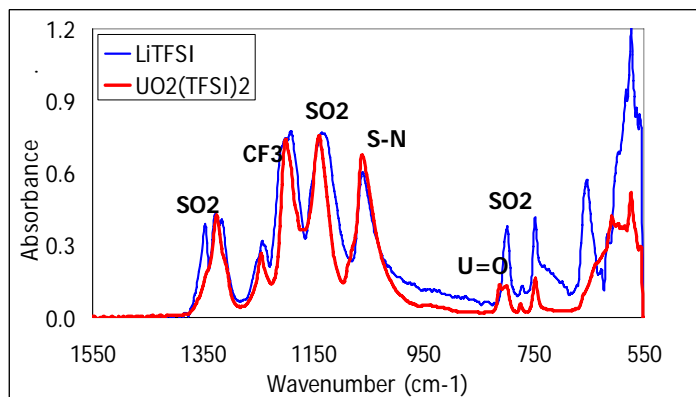
Electrochemical methods can be used to effectively separate actinide and lanthanide species from complex mixtures. This is based on the unique electrochemical properties of each specific target species. In studies it has been found that with the exception of Ce, aqueous solutions provide unsuitable electrochemical windows to effectively evaluate the thermodynamic properties that are useful for chemical separation. Therefore a more novel approach was examined which eliminated the aqueous solution with a Room Temperature Ionic Liquid (RTIL) solution. RTIL solutions do not suffer from the side reactions that are prominent in aqueous environments. In addition the potential window is much larger for the RTIL solutions. The RTIL solutions are a new starting point for the electrochemical separation of individual species from a mixture.

## RESEARCH OBJECTIVES AND METHODS

The objectives of this project are to use electrochemical tech-



Electrochemistry of GC, Au, and Pt electrodes in RTIL ([MeBu<sub>3</sub>N][NTf<sub>2</sub>]) (red) and 0.1 M H<sub>2</sub>SO<sub>4</sub> (blue).



The IR spectra show the typical RTIL anion Li(TFSI) (blue), and UO<sub>2</sub> complexed to TFSI (red). The shift of the SO<sub>2</sub> peak at 1350cm<sup>-1</sup> indicates TFSI complexation, and the peak around 810cm<sup>-1</sup> indicates the presence of a U=O bond.

niques to develop a thermodynamic understanding of actinide and lanthanide species in RTIL solution, and to use this data to effectively separate species with very similar chemical properties. In consultation with a national laboratory collaborator, electrochemical methods and materials will be evaluated and used to exploit the thermodynamic differences between similar chemical species, enhancing the ability to selectively target and sequester individual species from mixtures. This project is in its third year and has successfully completed phases 1 and 2. Phase 3 has been partially completed. The tasks have been expanded to include a fourth phase.

### Phase 1

Evaluate thermodynamic oxidation/reduction properties of Ce using electrochemical methods.

### Phase 2

Evaluate the thermodynamic properties of chelated Ce, Sm, and Eu at carbon, platinum and gold electrodes.

### Phase 3

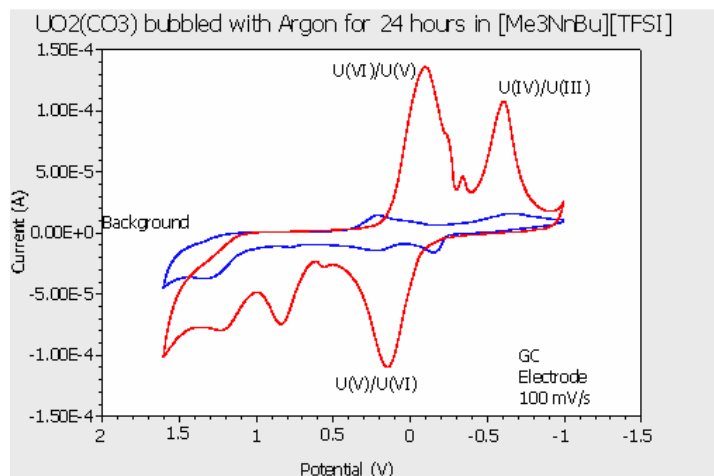
Examine the use of conductive polymer membranes for the uptake and expulsion of complexed and uncomplexed actinide and lanthanide species.

This phase still needs to examine the uptake, selective adsorption and separation of individual actinide and lanthanide species, including the isolation of Cm from Am, using conductive polymer/metal composite membranes containing bound chelates.

### Phase 4

Prepare and characterize RTIL solutions. Examine the electrochemical window and evaluate the electrochemical properties of lanthanide and actinide species in the non-aqueous ionic environment.

The following were specific goals for this year:



CV of  $\text{UO}_2\text{-TFSI}$  complex formed by added  $\text{UO}_2(\text{CO}_3)$  directly to the RTIL and using Argon to remove the carbonate from the system.

- To prepare RTIL solutions.
- To evaluate the potential window of RTIL solutions.
- To develop a fundamental understanding of the thermodynamic properties of actinide and lanthanide species (such as Cm, Am, Ce, Nd, Eu, and Sm) in RTIL solutions.

## RESEARCH ACCOMPLISHMENTS

The electrochemical window for RTIL systems is based primarily on the reduction of the cation and oxidation of the anion used to make the solution. The potential window is significantly larger for RTILs ranging from approximately 4.5 to 6 V when compared to aqueous environments. The figure to the left illustrates the potential windows obtained in aqueous solutions of 0.1 M  $\text{H}_2\text{SO}_4$  (blue line) and the RTIL, tri-*n*-butylmethylammonium bis(trifluoromethylsulfonyl)imide ( $[\text{MeBu}_3\text{N}][\text{NTf}_2]$ , red line) at GC, Au, and Pt electrodes. For each electrode the positive and negative potential limits provide an absolute potential window of approximately 4.5 V for Pt, 5.0 V for Au, and 6.0 V for GC.

The advantage to eliminating aqueous side reactions and expanding the potential window is that previously inaccessible electrochemical reactions may be observed. These systems provide a huge potential window for the observation of oxidation and reduction of lanthanides and actinides. In addition, the potential mediated deposition of f-elements is possible - indicating that the controlled separation of chemical species is thermodynamically feasible. For example, the reduction of  $\text{Pu}^{3+}$ ,  $\text{Am}^{2+}$ ,  $\text{Am}^{3+}$ ,  $\text{Cm}^{3+}$ , and  $\text{U}^{3+}$  all occur before  $E = -1.90$  V vs. Ag/AgCl, well within the negative potential limit for the RTIL at platinum (-2.6 V vs. Ag/AgCl), gold (-2.2 V vs. Ag/AgCl), and glassy carbon electrode (-3.4 V vs. Ag/AgCl) in the RTIL solutions shown in the before

## ACADEMIC YEAR HIGHLIGHTS

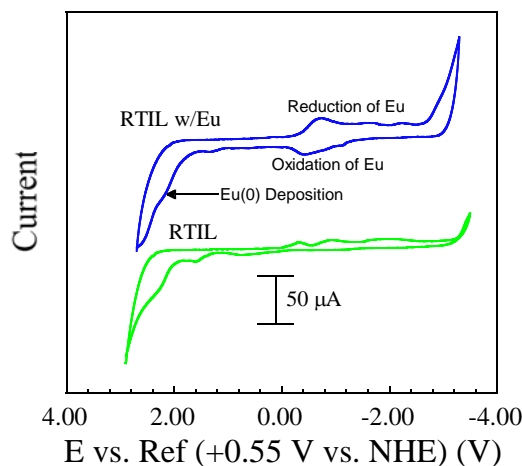
- ♦ Sandra Elkouz, M.S. thesis, UNLV Chemistry Department, "Complexation and Electrode Effects on the Electrochemical Behavior of the Cerium(IV)/Cerium(III) Redox Couple," April 2007.
- ♦ S. Elkouz, P. Houlihan, K. Czerwinski, and D.W. Hatchett, "The influence of electrode composition, pH, and ionic strength on the redox properties of Ce(IV)/Ce(III)," Submitted to *Electrochimica Acta*, April 2007 (Ms. Ref. No.: EA-S-07-00835).

mentioned figure. The preliminary electrochemical characterization of Eu in RTIL is shown in the figure below.

Through using infrared (IR) and ultraviolet-visible spectra, it was observed that the uranyl did complex to the anion of the RTIL. However, a more interesting way to complex the uranyl to the RTIL is by adding uranyl carbonate directly to the RTIL and then using Argon gas to remove the carbonate. The results yielded a soluble  $\text{UO}_2$ -bis(trifluoromethylsulfonyl)amide (TFSI) complex that produced reversible electrochemical reactions with Uranium including the U(VI)/U(V) couple. The Cyclic Voltammogram (CV) also yielded the U(IV)/U(III) couple. This method could prove to be very useful in observing the electrochemistry of any metal-carbonate species.

## FUTURE WORK

Future work will focus on the development of RTIL solutions suitable for the potential mediated oxidation/reduction and deposition of lanthanide and actinide species. The ultimate goal is to separate individual species using the electrochemical potential of species.



Electrochemistry of Eu at a Pt electrode in RTIL ( $[\text{MeBu}_3\text{N}][\text{NTf}_2]$ ).

### Research Staff

David W. Hatchett, Principal Investigator, Assistant Professor, Department of Chemistry  
Ken Czerwinski, Associate Professor, Department of Chemistry

### Students

Sandra Elkouz and Wendy Pemberton, Graduate Students, Department of Chemistry

### Collaborators

George F. Vandegrift, Associate Division Director for Nuclear Fuel Cycle Programs, Chemical Engineering Division, Argonne National Laboratory

## Task 26

# Fundamental Chemistry of U and Pu in the TBP-Dodecane-Nitric Acid System

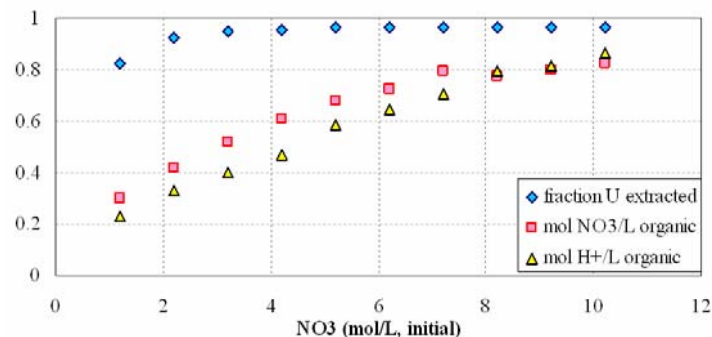
K. Czerwinski

## BACKGROUND

The extraction of tetravalent Pu and hexavalent uranyl in nitric acid solution by tributylphosphate (TBP), based on the formation of organic phase neutral complexes such as  $\text{Pu}(\text{NO}_3)_4 \cdot 2\text{TBP}$  and  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ , has been the foundation of actinide purification for a number of decades. Upon reduction of Pu(IV), Pu(III) is back extracted into an aqueous phase. However, the data needed for detailed modeling of Pu extraction is not available for all conditions of concern to the Advanced Fuel Cycle Research and Development program. This proposal was developed with Dr. George Vandegrift of Argonne National Laboratory to obtain the necessary data for Pu extraction modeling.

Understanding the role of nitrate in actinide speciation is important for determining the necessary data for extraction modeling. Difficulties in modeling Pu extraction under some nitrate conditions may be due to ill-defined constants of formation for the dinirate and trinitrate species of U and Pu. The influence of pertechnetate on the speciation of U and Pu in the TBP-dodecane-nitric acid system is still poorly understood. Since pertechnetate is capable of reoxidizing reduced Pu species, it may have a profound impact on the extraction of Pu.

In the uranium extraction process, acetohydroxamic acid (AHA) is expected to be used. AHA can complex and reduce Pu, decreasing its extraction into the organic phase; the effect of uranyl-



The measured concentrations of uranyl, nitrate, and acid in the organic phase extracted from 0.02 M U, 1.0 M HNO<sub>3</sub>, and varied initial nitrate.

AHA on U extraction has not been quantified. AHA can reduce pertechnetate as well, initiating a redox cycle with both U and Pu. In a solvent extraction system using AHA, it is necessary to determine the complexation kinetics, redox reactions, and thermodynamics of AHA interactions with these elements.

## RESEARCH OBJECTIVES AND METHODS

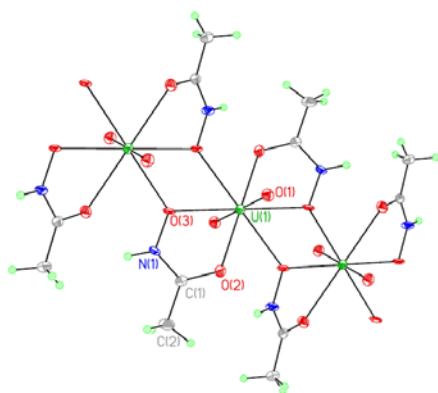
The research objective is to experimentally evaluate the fundamental speciation of Pu and U in the TBP-dodecane-nitric acid-AHA system and the effect of pertechnetate, specifically:

- To determine the influence of nitrate on the speciation of U and Pu in the TBP-dodecane-nitric acid system. The aqueous and organic speciation of U and Pu are examined as a function of the nitric acid concentration, nitrate concentration, actinide ion concentration, temperature, and time.
- To determine the speciation of U and Pu with AHA in the presence and absence of TBP-dodecane organic phase. The aqueous and organic speciation of U and Pu are evaluated as a function of AHA concentration, metal ion concentration, metal ion redox state, pH, and temperature.
- To determine the interaction of AHA with pertechnetate, and the effect on the interaction of AHA and pertechnetate with U and Pu.
- To incorporate thermodynamic and kinetic data into existing modeling codes.

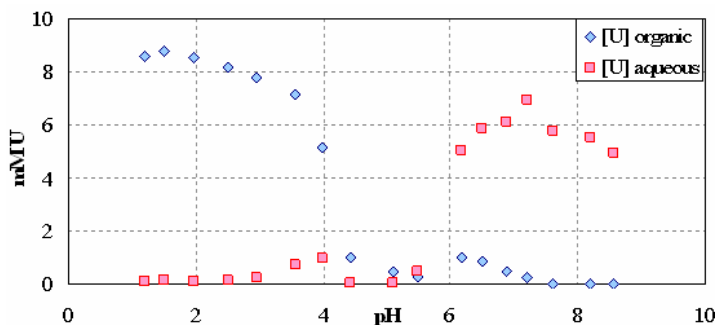
All of the initial experiments were performed with uranyl,  $\text{UO}_2^{2+}$ . The results obtained from U are the basis for further experiments with Pu. In extraction experiments, the aqueous and organic phases are contacted in equal volumes from 0.3 to 5.0 mL.

## RESEARCH ACCOMPLISHMENTS

**Uranyl Nitrate.** The complexation of uranyl (0.01 to 0.1 M) with nitrate was studied at 1 M HNO<sub>3</sub> with excess nitrate (from Li-NO<sub>3</sub>) varied from 0 to 10 M. It was found that at higher nitrate



Crystal Structure of Uranyl-AHA



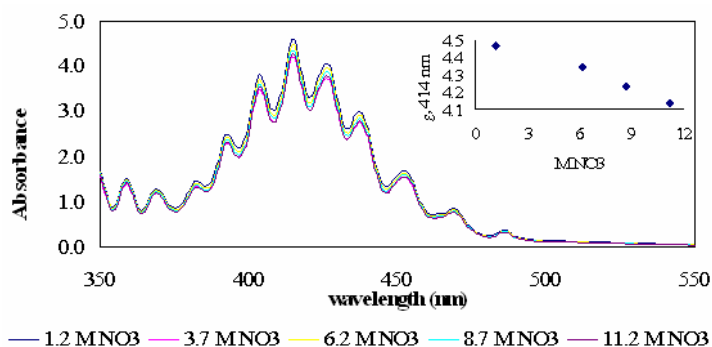
The measured concentrations in the organic and aqueous phases of 10 mM uranyl, 100 mM AHA extracted with TBP.

concentrations, more uranyl was present in the organic phase, and, in the absence of uranyl, more  $\text{HNO}_3$  extracted.

**Uranyl-AHA.** The complexation of uranyl with AHA and its effect on U extraction into TBP-dodecane was studied via ultraviolet-visible spectroscopy (UV-Vis), nuclear magnetic resonance (NMR), and Inductively Coupled Plasma-Atomic Emission Spectroscopy in perchlorate and nitrate media. The concentrations of uranyl (0.1 to 10 mM) and AHA (1 to 700 mM) and the pH (1 to 10) were systematically varied. It was determined via NMR that there are at least two species of uranyl-AHA, that the species formed is pH-dependent, and that there is little hydrolysis at 25 times or higher molar excess AHA. The low-pH species extracts from perchlorate media as well as free uranyl, and the high-pH species remains in aqueous solution. In nitrate media, the nitrate competes with and oxidizes the AHA under acidic conditions; the exact interactions remain to be explored.

In addition, methods for synthesis of the uranyl-AHA solid were developed; the solid was characterized by UV-Vis, Fourier Transform Infrared spectroscopy, NMR, laser fluorescence, melting point, and X-ray Absorption Fine-structure Spectroscopy (XAFS), and a crystal structure was obtained. The uranyl-AHA is present as a highly symmetrical polymer, in which each equatorial atom is exactly  $180^\circ$  from its opposite and the ligand planes are twisted within and between unit cells.

**Technetium-AHA.** Previous work failed to observe pertechnetate reduction by AHA; however, in the presence of catalytic acid (0.5 to 4 M  $\text{HNO}_3$  or  $\text{HClO}_4$ ) and a large excess of AHA (0.5 to 4 M), pertechnetate (0.1 to 20 mM) will be reduced to the  $\text{Tc}^{\text{II}}\text{NO}$  (AHA)<sub>2</sub> species in aqueous media. This species is highly water soluble and does not extract into 30% TBP. The presence of uranyl has no effect on the formation or extraction of this species, and up to hundredfold excess  $\text{UO}_2^{2+}$  does not affect the rate of formation. There is significant evidence that the reaction is in-



The UV-Vis spectrum of uranyl nitrate in 30% TBP varies with nitrate concentration.

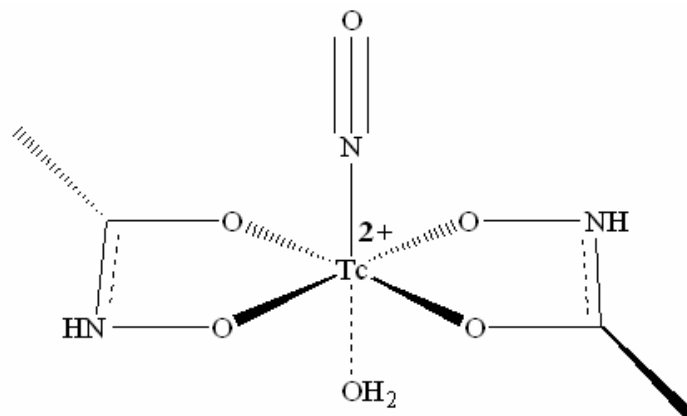
## ACADEMIC YEAR HIGHLIGHTS

- ◆ C. Gong, F. Poineau, and K. Czerwinski, "Synthesis and characterization of the solid uranium(VI) dioxo-diacetohydroxamate complex," *Radiochim. Acta* 95(8), 439-450 (2007).
- ◆ A. Wright and K. Czerwinski, "Nitrate effects on uranium and plutonium extractions," 233rd ACS National Meeting, Chicago, IL, March 2007.
- ◆ C. Gong, F. Poineau, and K. Czerwinski, "Synthesis and characterization of the solid uranyl-acetohydroxamic acid complex," 233rd ACS National Meeting, Chicago, IL, March 2007.
- ◆ K. Czerwinski, A. Wright, N. Smith, L. Wright, and G. Cereface, "Fundamental Chemistry of Uranium in Extraction for use in Enhanced Separations and Proliferation Resistance," MRS Scientific Basis for Nuclear Waste Management XXX, Boston, MA, November-December 2006.
- ◆ A. Wright, N. Smith, F. Poineau, and K. Czerwinski, "Nitrate effects on uranium and plutonium extractions in the tributylphosphate-dodecane system," 232nd ACS National Meeting, San Francisco, CA, September 2006

stantaneous and the change in the Tc-AHA UV-Vis spectrum is due to the increasing pH as AHA hydrolyzes to acetic acid. However, the mechanism of formation is yet to be elucidated.

## FUTURE WORK

The stability constants of the higher nitrado species of uranyl have yet to be determined; preliminary UV-Vis and laser fluorescence studies have been performed. The stability constant of the uranyl-AHA species is also unknown; UV-Vis and NMR studies are underway. The mechanism of Tc-AHA formation and its effect on Pu redox and extraction will be explored.



XAFS Structure of Technetium(II)-nitrosyl-AHA.

### Research Staff

Ken Czerwinski, Principal Investigator, Associate Professor, Department of Chemistry  
Cynthia Gong and Frederic Poineau, Post-Doctoral Researchers, Harry Reid Center

### Students

Amber Wright, Wendy Pemberton, and Jeanette Daniels, Graduate Students, Department of Chemistry (Radiochemistry Ph.D. Program)  
Jeremy Maute and Trent Ohman, Undergraduate Students, Department of Chemistry

### Collaborators

George Vandegrift, Argonne National Laboratory  
Thomas Albrecht-Schmitt, Auburn University



## Task 27

# Reactor Physics Studies for the AFCI Reactor-Accelerator Coupling Experiments Project

D. Beller

## BACKGROUND

In the Reactor-Accelerator Coupling Experiments (RACE) Project of the U.S. Advanced Fuel Cycle Initiative (AFCI), a series of accelerator-driven subcritical systems (ADSS) experiments have been conducted at the Idaho State University's Idaho Accelerator Center (ISU-IAC) and at the University of Texas (UT) at Austin. In these experiments, electron accelerators are used to induce Bremsstrahlung photon-neutron reactions in heavy-metal targets. They produce a neutron source of  $0.8$  to  $1.0 \times 10^{12}$  n/s per kW of electron beam, which will then initiate fission reactions in the subcritical systems. These subcritical systems include a compact, transportable assembly at ISU and a TRIGA reactor at UT-Austin. A variety of fuel and assembly geometries are being studied: at ISU 150 flat plates of 20%-enriched uranium-aluminum alloy plated with aluminum are used; and at UT-Austin 20%-enriched UZr-H fuel are used. A third phase at Texas A&M using 70%-enriched UZr-H "FLIP" fuel has been put on hold. The use of compact accelerators and a small target allow the target to be placed in various positions in or adjacent to these subcritical assemblies to "map" the coupling of driven neutron sources; measuring core coupling and mapping adjoint flux.

The RACE Project is an important intermediate step between the recent European program MUSE and a future near full-scale demo. For MUSE, which was conducted by the CEA at Cadarache, France, the driving neutron source was produced by D-D or D-T reactions which produced a nearly mono-energetic source of 2.45 or 14.1 MeV and a maximum strength of  $\sim 10^{10}$  n/s. For design of full scale ADSS, a complete knowledge of the effects of the driving neutron source is essential. This will ultimately require spectral, temporal, directional, and intensity fidelity in prototype experiments. In the absence of this fidelity, simulated sources should match some of the characteristics of projected driving sources to build confidence in the predicting performance of these systems, and codes and methods must be validated. The RACE Project will provide experience in a higher energy range (above 14.1 MeV) and with a stronger and more isotropic source than the MUSE experiments. In addition, a high-power RACE

phase could provide valuable information on thermal feedback effects in TRIGA reactors. This combination of attributes of the RACE Project will provide highly valuable information in advance of the prototype or demonstration programs.

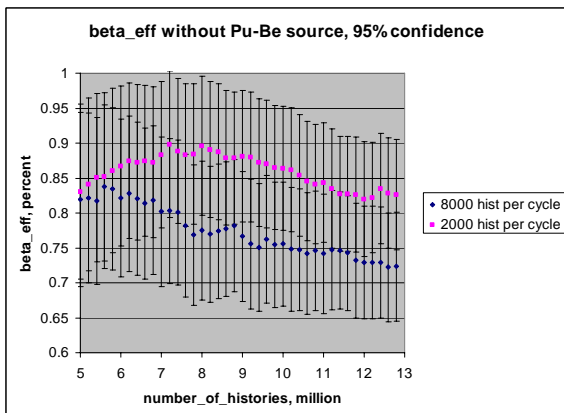
## RESEARCH OBJECTIVES AND METHODS

The specific research objective of this three-year project is to design and conduct accelerator driven experiments, which will help demonstrate in the U.S. the ability to design, compute, and conduct ADSS experiments and to predict and measure source importance, coupling efficiency, sub-critical reactor kinetics and source-driven transients. In addition, databases will be created for both steady state and transient ADSS experiments for the nuclear community to develop and test new computational codes and methods, and the importance of a driving neutron source in various regions of different subcritical assemblies will be mapped. Experiments will be conducted and compared to calculations with radiation transport and thermal-hydraulics codes such as MCNPX and RELAP.

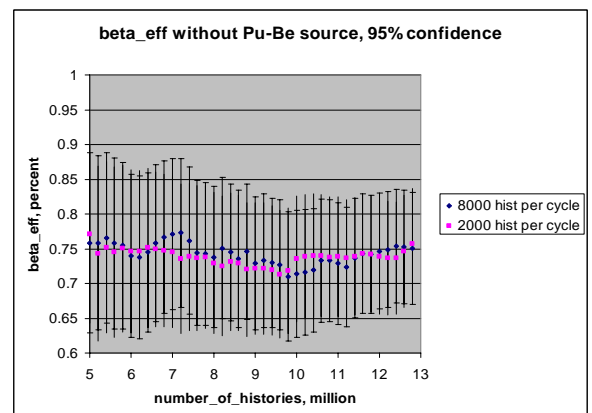
## RESEARCH ACCOMPLISHMENTS

ISU RACE Experiments: UNLV collaborated with ISU and CEA in a series of ADSS experiments at the Idaho Accelerator Center. This series of ADSS experiments was conducted with a low-power, 20-MeV electron accelerator coupled to the Subcritical Assembly (SCA) with a tungsten-copper neutron generating target. Dozens of individual experiments were conducted to measure a variety of parameters and ADSS responses, including break-point frequency, flux stability, a long-duration reference pulsed-neutron-source experiment, a beam trip experiment, and a variable criticality experiment, which was conducted by observing the neutron response while water was drained from the SCA. The last series of these experiments were completed in October, 2006.

Since the conclusion of the ISU RACE Project experiments, results were compared from ISU RACE experiments conducted at ISU in October with Monte Carlo radiation transport modeling to



*Calculated effective delayed neutron fraction for a subcritical (left side) versus a critical (right side); without a PuBe source.*





*UNLV graduate students Timothy Beller and Ryan LeCounte couple the UNLV High-Power RACE Target to a linear electron accelerator at the Idaho Accelerator Center.*

analyze effective delayed neutron fraction ( $\beta_{\text{eff}}$ ) in these far-subcritical, under-moderated systems using MCNP. The simplest approach based on 2 k-eigenvalue predictions with and without accounting for delayed neutrons gave unsatisfactory results due to the lack of convergence. Calculations have been completed with and without a plutonium-beryllium neutron source, which, although it was small, did affect the results. Two more-suitable techniques based on different weighting functions are currently under investigation.

The statistical behavior of calculated effective delayed neutron fraction based on two independent calculations (with and without delayed neutrons) for a critical system was more stable than for the subcritical case. Again, calculations have been completed with and without a plutonium-beryllium neutron source. Two more-suitable techniques based on different weighting functions are currently under investigation. The importance function is being used as an approximation of an adjoint weighting of the space- and velocity-dependent neutron population to calculate the effective neutron lifetime. Use of the value of a particle leaving a collision is being compared to that of a particle entering an event. Another computational approach that is based on a power iterations method (KCODE) to directly assess the efficiency of delayed neutrons is under development. The shape function for the steady-state problem, which will be used as a weighting function, was calculated and the relative efficiency of neutrons causing fission was determined.

**High-power Target Design:** The High-power RACE Target was transported to ISU's IAC in August 2006 for further tests to measure neutron generation and heat transfer while coupled to an electron linac. An accelerator-driven neutron production experiment was conducted and temperatures were recorded at several points. Since completing the experiments, experimental results are being evaluated. The Target is being modeled using Gambit and the CFD code FLUENT for comparison with experiments. During this reporting period, the potential complexity of the CFD modeling was upgraded with a parallel processing system. Refinement was continued of the MCNPX transport model to reduce

## ACADEMIC YEAR HIGHLIGHTS

- ◆ C.O. Maidana, A.W. Hunt, D. Beller, and K. Folkman, "Design, Modeling and Simulations in the RACE Project: First Study for the Development of a Transport Line," *Nuclear Instruments and Methods-A*, 562, 2, pp. 892–895 (2006).
- ◆ D. Beller, F. Harmon, E. Stankovskiy, T. Ward, and F. Goldner, "Reactor Accelerator Coupling Experiments (RACE) Project," poster, International Conference on Research Reactors in the 21st Century (RR-XXI), Moscow, Russia, June 20-23, 2006.
- ◆ D. Beller, "Update on the Reactor-Accelerator Coupling Experiments (RACE) Project;" T. Beller, R. LeCounte, and D. Beller, "Analysis of Neutron Production in the High-Powered RACE Target;" and, R. LeCounte, T. Beller, and D. Beller, "Thermal Analysis of Neutron Production in the High-Powered RACE Target," Winter Meeting of the American Nuclear Society, Albuquerque, NM, November 12-16, 2006.
- ◆ E. Stankovskiy, "The Experimental Results and Computational Analysis of the RACE-ISU," American Nuclear Society Student Conference, Corvallis, OR, March 29-31, 2007.

statistical uncertainty and to perform parametric studies to study impacts of accelerator performance and characteristics, such as beam spread in energy or position.

**RACE Project Management:** In his role as national RACE Project Director, the PI began to conclude the RACE Project with several universities and several European organizations. These organizations have contributed to several aspects of the RACE Project, including target design and analysis for High-Power RACE. Contracts supporting RACE Project work at the University of Michigan, Texas A&M University, and University of Texas at Austin ended during the summer, the Idaho participation was terminated in December, and the UNLV portion of the RACE Project will end summer 2007. EUROTRANS participants may continue to evaluate experimental data.

UNLV hosted, and students and faculty attended, an Advanced MCNPX Workshop at UNLV. As a result, the group was able to greatly improve statistical results of calculations of electron-photon-neutron transport.

## FUTURE WORK

During the summer of 2007, graduate student Evgeny Stankovskiy will complete his doctoral dissertation, which will be the final research within the RACE Project. In addition, the PI will be the General Chair of the Fifth Workshop on Accelerator-Driven Subcritical Systems Experiments will be conducted at the Idaho State University as part of the Eighth International Topical Meeting on Applications and Utilization of Accelerators (AccApp'07).

### Research Staff

Denis Beller, Principal Investigator, Research Professor, Department of Mechanical Engineering

### Students

Evgeny Stankovskiy, Graduate Student, Department of Mechanical Engineering

Timothy Beller, and Ryan LeCounte, Graduate Students, Department of Mechanical Engineering

### Collaborators

George Imel, Argonne National Laboratory; John Bennion and Alan Hunt, Idaho State University; William Charlton, Texas A&M University; Sean O'Kelly, University of Texas at Austin; and, John C. Lee, University of Michigan

## Task 28

# Impact of the Synthesis Process on Structure Properties for AFCI Fuel Candidates

K. Czerwinski

## BACKGROUND

Synthesis of actinium mononitrides using carbothermic reduction of the corresponding oxides has a few outstanding issues, including the formation of secondary phases such as oxides and carbides and low densities of the final product. Furthermore the requirement of a high process temperature at 1700°C, for more than 12 hours is also a drawback particularly for Americium-bearing samples. Therefore, it is important to explore the use of other possible routes to synthesize actinide mononitrides.

A low temperature process is used in this research to produce actinide mononitrides using a fluoride route in which the first step is to mix the actinide oxide with  $\text{NH}_4\text{HF}_2$ . The second step involves the heat-treatment of the resulting ammonium actinide fluoride salts in ammonia atmosphere. Using different analytical techniques available, the experimental conditions can be studied and optimized to synthesize the required materials with high phase purity. Such available techniques are X-ray Powder Diffraction (XRD), Thermogravimetry and Differential Scanning Calorimetry (TG/DSC), and microscopic techniques such as Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). Once the experimental conditions are studied and optimized, a number of actinide nitride systems (uranium, thorium, and neptunium) will be synthesized and characterized to provide knowledge on the chemistry of the systems. Characterization of these nitride systems will include chemical phase identification, lattice parameter refinements, morphological studies, microstructural verifications, thermal behavior, reaction mechanism, and reaction kinetics.

## RESEARCH OBJECTIVES AND METHODS

The research objectives are:

- To explore a low-temperature fluoride route to synthesize

actinide nitrides.

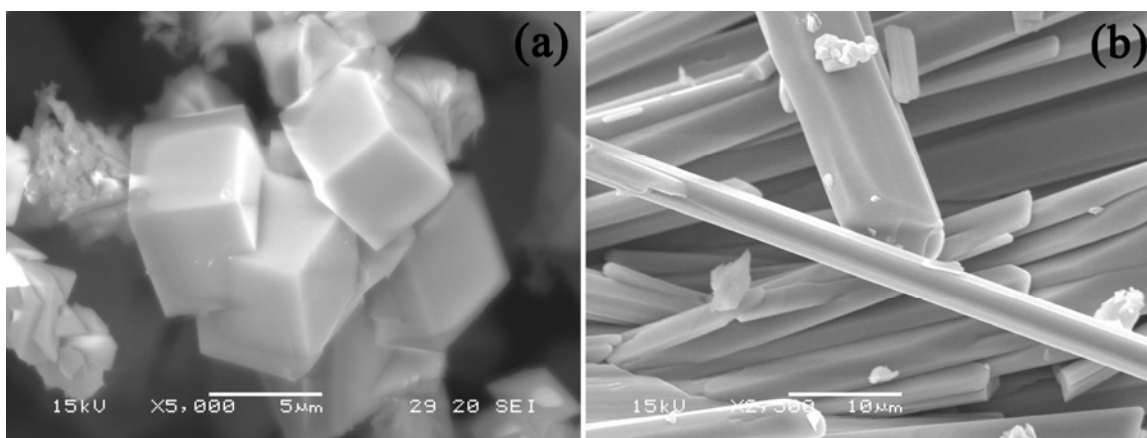
- To characterize actinide nitrides structurally and thermally.
- To use high resolution TEM techniques to explore the microstructure of the radioactive samples.

## RESEARCH ACCOMPLISHMENTS

### Uranium based nitride synthesis and characterization

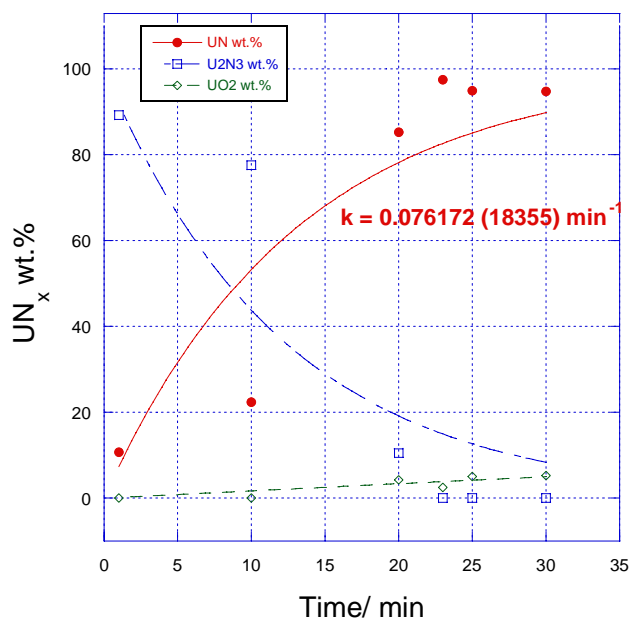
The fluoride route was successfully used to synthesize three uranium nitride samples with different stoichiometry ( $\text{UN}_2$ ,  $\text{U}_2\text{N}_3$ , and  $\text{UN}$ ). Experimental conditions were optimized to synthesize high phase purity  $\text{UN}$  (97 wt.%). Thermal decomposition of  $\text{UN}_2$  under different atmospheric conditions was also studied, and ultra high purity argon could successfully be used to reduce the sample completely to  $\text{UN}$  at 1100°C, see graph on the opposite page.  $\text{UN}_2$  and  $\text{U}_2\text{N}_3$  decomposition kinetics into  $\text{UN}$  were studied under argon at three different temperatures (1000, 1050, and 1100°C).

Optical microscopy and SEM were used to explore the morphology of uranium nitride samples. Bright Field Transmission Electron Microscopy was also used to confirm the morphological observations. Microstructural studies of the samples were carried out using high resolution (HR) TEM with the help of selected area diffraction (SAD) patterns. X-ray energy dispersive spectrometry of TEM was utilized to characterize the elemental distribution and to verify the phase purity of the samples. Powder XRD patterns of the as-synthesized uranium nitrides,  $\text{UN}_2$ ,  $\text{U}_2\text{N}_3$ , and  $\text{UN}$  were collected and analyzed. Optical microscopic studies showed that the particle sizes of these uranium nitride samples range from 100 to 5000 nm. The microstructure of the  $\text{UN}$  sample shows the presence of  $\text{UO}_2$  as a secondary phase on the surface of the sample. In this region, the lattice fringes correspond to the (222) interplanar  $d$ -spacing of  $\text{UO}_2$ . X-ray Energy Dispersive



Scanning Electron Microscopic images of the (a)  $7\text{NH}_4\text{F} \cdot 6\text{UF}_4$  and (b)  $(\text{NH}_4)_4\text{ThF}_8$  samples. (a)  $7\text{NH}_4\text{F} \cdot 6\text{UF}_4$  particles are well-crystallized (hexagonal unit cell with a rhomb-centered,  $a$  (b) = 15.40 Å and  $c$  = 10.49 Å and  $\text{UN}_2$  is cubic (fcc) with  $a$  = 5.310 Å) (b) Well-crystallized  $(\text{NH}_4)_4\text{ThF}_8$  acicular-shaped particles (triclinic unit cell with lattice parameters  $a$  = 8.477,  $b$  = 8.364, and  $c$  = 7.308 Å).



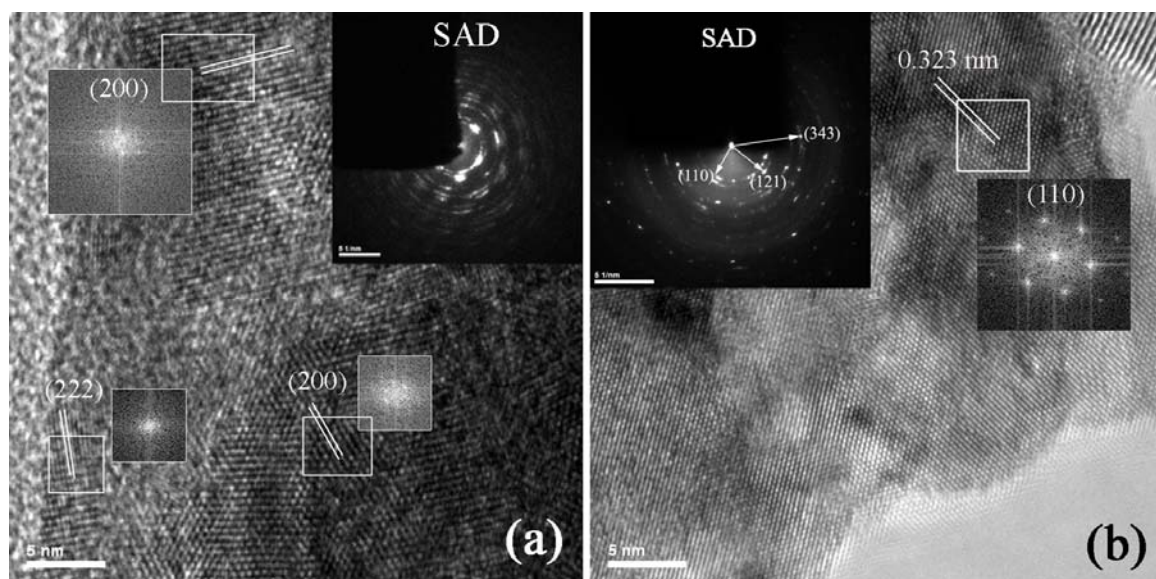


*Pseudo-first-order kinetics of UN<sub>2</sub> denitriding at 1100°C.*

Spectrometry (XEDS) demonstrated that U was prominent, but it is difficult to identify the presence of N due to overlaps with peaks from O and C. However, the magnified XEDS spectra verifies the presence of N in samples, and this figure also displays the presence of O only in the UN sample. Thus, the XEDS verifies the phase purity of the synthesized sample.

#### Thorium based nitride synthesis and characterization

Use of the fluoride route was successful only up to the formation of ThNF. The removal of fluorine, which should have lead to the formation of thorium nitrides was unsuccessful at different experimental conditions. However, the characterization of ammonium thorium fluoride and ThNF was done using the above mentioned techniques.



*High resolution TEM images of (a) UN and (b) ThNF samples. (a) Crystallography of UN was confirmed using the lattice fringes of HRTEM image, and the secondary oxide phase was only identified at the surface of the particle edge. (b) ThNF crystal structure which is determined using XRD was confirmed by the HRTEM and SAD pattern.*

## ACADEMIC YEAR HIGHLIGHTS

- ♦ G.W.C. Silva, T. Hartmann, and K. Czerwinski, "Nitridization of Zr-U-Er-Cxides," APCI Semi-Annual Meeting, Sept., 2006.
- ♦ G.W.C. Silva, C.B. Yeaman, G.S. Cerefice, and K. Czerwinski, "Reaction Mechanism of UN<sub>2</sub> conversion to UN," ACS 233<sup>rd</sup> National Meeting & Exposition, Chicago, IL, March 25-29, 2007.
- ♦ C.B. Yeaman, G.W.C. Silva, G.S. Cerefice, K.R. Czerwinski, T. Hartmann, A.K. Burrell, and A.P. Sattelberger, "Oxidative Ammonolysis of Uranium(IV) Fluorides to Uranium(VI) Nitride," *Journal of Nuclear Materials* (in press).

## FUTURE WORK

The next phase of the project involves accomplishing the following tasks:

- Explore other experimental conditions and chemicals to synthesize thorium nitrides.
- Study any reaction mechanism and kinetics involved in thorium nitride formations.
- Characterize thorium-based nitrides using the above mentioned techniques.
- Determine the ammonium bifluoride reaction with neptunium oxide.
- Explore the reaction route to synthesize Np-based nitrides.

### Research Staff

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## Task 29

# Investigation of Optical Spectroscopy Techniques for On-Line Materials Accountability in the Solvent Extraction Process

G. Cerefice and K. Czerwinski

## BACKGROUND

Increasing the proliferation resistance of the nuclear fuel cycle is one of the stated goals for the Global Nuclear Energy Partnership program. From a proliferation aspect, the greatest challenge to closing the nuclear fuel cycle is ensuring that nuclear material is not diverted during the recycling processes. As part of the safeguards-by-design concept, new separations facilities will incorporate integral systems capable of providing materials accountability for the actinide elements to minimize the potential for undetected diversion of material. The goal of this project is to evaluate technologies to meet this need. Optical spectroscopic techniques, such as Ultraviolet-Visible Spectroscopy (UV/Vis) and Laser Fluorescence Spectroscopy (LFS), are quantitative analytical techniques that have been used for measuring the concentration of the actinides under laboratory conditions.

In UV/Vis spectroscopy, the sample is illuminated by a continuous spectrum (from the UV through the Visible wavelengths). The transmitted light is measured, allowing the determination of the absorbance of the light as a function of wavelength. The wavelength of the absorbance is dependant on the electronic structure of the absorbing atom, and is proportional to the concentration of the absorbing element in the sample. For LFS, the sample is illuminated at a single wavelength, which is absorbed by the target atoms in the sample. The energy absorbed is re-emitted through fluorescence. The wavelength of the absorbance, and the fluorescence-response, is again dependant on the electronic structure of the absorbing atom, and is proportional to the concentration of the absorbing element in the sample.

Both techniques are strongly dependent on the chemical speciation of the elements to be measured, providing a tool for not only the determination

of material concentrations for mass balances, but also providing inspectors and plant operators with a tool to examine the process chemistry itself. As optical techniques, both of these methods can be adapted for fiber optics, allowing the instrumentation to be



*Laser induced fluorescence of a uranium sample in nitric acid*

placed in shielded areas of the plant to minimize the impact of the radiation fields on the detectors and increase the accessibility of the systems for maintenance and inspection.

## RESEARCH OBJECTIVES AND METHODS

The goal of this project is to evaluate the application of these analytical techniques to the on-line, real-time measurement of the actinide elements in the process streams of a solvent extraction process, with particular attention to the UREX+ and PUREX processes. Based on the experience gained through this effort, engineers will have the information necessary to decide if these technologies should be advanced to the prototype stage and tested at the pilot plant level. Through the experimental work planned as part of this effort, researchers will also develop a better understanding of the chemical interactions of the actinide elements, providing additional data for the development of first-principles based models of the solvent extraction process. The information gathered through these experiments will also add to the database on the UREX+ solvent extraction process, particularly in the off-normal operating regimes.

The research objectives are:

- To evaluate the potential for utilizing UV-Visible and laser fluorescence spectroscopy to determine actinide concentrations under process conditions, including the spectroscopic impact of acid concentration, solvent vs. aqueous product streams, ligand concentrations (TBP, AHA), and chromophoric agents (e.g. iron) from fission products or corrosion/degradation products.
- To examine what process chemistry information can be extracted from the spectroscopic signals along with the actinide metal concentrations.
- To examine the fundamental chemistry underlying the spectroscopic behavior under process conditions in support of process chemistry modeling activities.

## RESEARCH ACCOMPLISHMENTS

To evaluate the potential application of optical spectroscopy techniques for the determination of uranium in the aqueous process streams of the UREX process, the impact of process chemistry on the absorbance and fluorescence behavior of the uranyl ion was examined. For the UREX flowsheet, the potential areas for deployment of these techniques was divided into four categories, based on the chemical environment, each represented by a feed or product stream: the process feed, the raffinate (actinide/fission product) stream, the technetium product stream, and the uranium product stream. These process ranges also allowed researchers to examine the potential application of these technologies to a PUREX-based flow sheet as well.

## UV/Vis Spectroscopy

The UREX feed stream and uranium product will both have molar quantities of uranium present. The concentration of uranium in these streams is expected to exceed the linear range of detection for a 1 cm path length cell. To measure these high concentration streams by UV/Vis, plant designers would need to either insert a reduced path-length slip stream or add the capability for a fixed mass dilution in the slip stream. Either of these options, or more realistically the combination of the two, could reduce the absorbance in the system back to within the linear response range of the technique.

The raffinate and technetium streams are expected to have significantly lower concentrations of uranium. For the UREX process, the raffinate stream will also contain the AHA from the process. Based on the measured molar extinction coefficients for uranium under the chemical environments expected for these streams, the expected uranium concentrations will likely fall below the detection limits observed for a 1 cm optical path. While the limits of detection may be able to be extended with a longer path length, scattering and other phenomena would likely only limit this to an order of magnitude reduction in the detection limit. Even with these limitations, the technique could still be used to establish a threshold value for uranium, which may be useful in detecting changes in process chemistry. UV/Vis spectroscopy, combined with titration by a fixed mass of a caustic stream, can also be used to probe for the presence of AHA in the raffinate stream, allowing for independent confirmation that the plant is running the UREX flowsheet and has not switched to a plutonium extraction process (such as PUREX).

## Laser Fluorescence Spectroscopy

The primary focus of the year two work on the project was the evaluation of Time Resolved Laser-induced Fluorescence Spectroscopy (TRLFS) techniques for the determination of uranium under process conditions. The impact of process chemistry on the observed lifetime and fluorescence yield of uranium in the aqueous process streams was investigated. TRLFS was determined to be significantly more sensitive for the detection of uranium, so much so that the signals in the feed and uranium product streams would easily saturate the detection systems. This sensitivity, however, may make the technique ideal for observing streams where the uranium concentration is expected to be very low, such as the technetium product stream and the raffinate stream. The detection limits and linear response regimes for both these process streams have been examined.

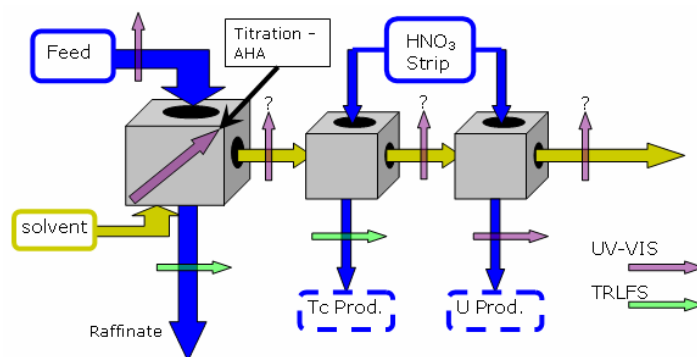
## FUTURE WORK

## ACADEMIC YEAR HIGHLIGHTS

- ◆ N.A. Smith, G.S. Cerefice, and K.R. Czerwinski, "Application of Optical Techniques for On-Line Materials Accountability in the UREX Solvent Extraction Process," *Proceedings, 47<sup>th</sup> Annual Institute for Nuclear Materials Management Annual Meeting*, Nashville, TN, July 16-20, 2006.
- ◆ N.A. Smith, G.S. Cerefice, and K.R. Czerwinski, "Use of UV-Vis spectroscopy and TRLFS for material accountability in solvent extraction processes," 233<sup>rd</sup> National Meeting of the American Chemical Society, Chicago, IL, March 27, 2007.

For the final project year, work will continue to apply the spectroscopy techniques to expand the fundamental understanding of the chemistry of uranium under process conditions, with the goal of providing the theoretical basis to allow a better interrogation of the observed spectra to confirm process chemistry conditions. Research will also examine the potential spectral interferences on the determination of uranium due to dissolved iron (and other corrosion products), fission products, and other actinide elements.

In parallel, the application of these techniques to the organic process streams will be examined. Initial TRLFS experiments on uranium samples extracted into the organic phase have showed no fluorescence under laser irradiation. The reason for this is being investigated, but the leading hypothesis is that the C-H oscillators of the organic matrix are acting as quenching agents in much the same way that O-H oscillators do in a water based system. As a result, it is unlikely that TRLFS will be useful for determination of uranium concentrations in the organic streams. Initial experiments suggest that UV-Visible spectroscopy, however, appears to be a viable alternative technique for these organic process streams.



Potential Application Locations for Optical Spectroscopy in the UREX Flowsheet

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## Task 30

# Combined Radiation Detection Methods for Assay of Higher Actinides in Separation Processes

D. Beller and W. Kernan

## BACKGROUND

Monitoring of transuranic actinides (TRU—includes neptunium, plutonium, americium, and curium) during the separation of used nuclear fuel has been identified as a critical research area in the U.S. Advanced Fuel Cycle Research and Development program (AFC R&D). Recycling of used fuel by chemically separating it into uranium, fission products, and TRU would be the first step in this new fuel cycle. Material Protection, Accounting, and Control (MPAC) is necessary for materials accounting, criticality monitoring, and assurance of proliferation resistance.

In the MPAC project, faculty and students are investigating the potential to use combined neutron and gamma-ray detector systems to measure quantities and isotopic constituents contained during separations and intermediate storage. This will require knowledge of the nuclear and decay characteristics of materials during processing, the development of conceptual designs of monitoring systems, radiation transport studies to develop an understanding of operational regimes, and experiments to confirm performance. In addition, both passive and active concepts will be investigated, including collaborations with the Idaho Accelerator Center at Idaho State University (ISU) to use electron linear accelerators for producing photoneutrons in situ, for photon activation of TRU, or for stimulating emissions processes (e.g. x-ray fluorescence).

## RESEARCH OBJECTIVES AND METHODS

The ultimate objective of this project is to develop technology to detect and accurately measure quantities of higher actinides in processing systems without taking frequent samples. These systems include used fuel receipt, separations batches, and pipelines. A variety of measurements may be combined to calculate flow rates of actinide elements with a to-be-determined precision. Nuclear and decay characteristics of materials during processing will be acquired, conceptual designs of monitoring systems will be developed, radiation transport studies will be conducted to develop an understanding of operational regimes, and experiments will be performed to confirm performance. Radiation transport and scoping studies will be conducted to investigate combined gamma-ray, neutron, and active and passive detection techniques to measure quantities and isotopic constituents contained during separations and intermediate storage. Scoping and design studies will first be performed using validated data sets (decay properties and reaction cross sections) and the radiation transport code MCNPX. Basic measurements will then be performed and compared to predictions. Experiments to be conducted in subsequent work are to be determined, but may include small quantities of radioactive actinides at UNLV in addition to accelerator-coupled experiments at ISU.

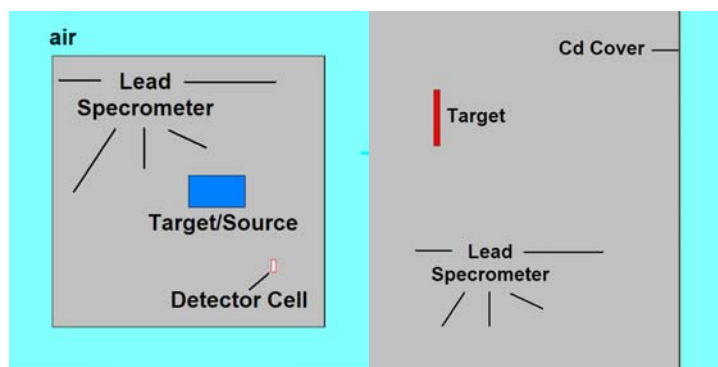
## RESEARCH ACCOMPLISHMENTS

Students continued to develop concepts and models for use of the  $^3\text{He}$  Neutron Multiplicity Detector System (NMDS, which was developed as part of Task 6) for MPAC. Technology for assaying fuel rods and/or complete assemblies, and the use of the NMDS and other techniques to assay dilute quantities of TRU in waste and other process streams were investigated.

### Lead and Carbon-based Slowing Down Spectrometers

Neutron slowing down spectrometers (SDSs) were modeled and plans were developed to conduct experiments at ISU with their carbon-based SDS. This work will be used to investigate technology for assaying fuel rods and/or complete assemblies. In preparation for these experiments, MCNPX was used to model neutron transport characteristics in lead and carbon-based SDSs. The energy of neutrons measured in a neutron detector with an SDS can be characterized by the equation  $E = K/(t+t_0)^2$ , where  $E$  is the energy of the neutron when it was created at the source (not its energy when detected),  $t$  is the time of the radiation detection (count) after a source event, and  $K$  and  $t_0$  are characteristics of the particular SDS. Thus, if an accelerator pulse is used to generate neutrons which then initiate fission, the time history of the spectrum can be de-convolved to yield the energy spectrum. In addition, the neutron multiplicity can simultaneously be measured by the NMDS.

However, the detector system must be able to resolve the time dependence of the neutron signal. Because  $^3\text{He}$  detectors, such as those contained in the NMDS, have a slow response, the SDS configurations must be studied before conducting experiments. Those studies are currently ongoing, beginning with benchmarking computational methods. A Los Alamos lead SDS was mod-



*Cross sections of the UNLV benchmark of the LANL lead SDS taken from MCNPX models. (Left) The overall geometry, (Right) A close-up of a cross section of the thin target. The response to neutrons of various energies (time constants) is influenced by the position and isotopic composition of the detector.*

eled to benchmark computational methods for determining energy-time correlation constants, and energy-time correlation constants are now close to those obtained in LANL experiments. The next step will be to use the MCNPX code to design an experiment using the ISU carbon-based SDS and electron linac, followed by experiments conducted at ISU in the next year. During this period, plans were developed to conduct experiments at ISU with the carbon-based SDS to develop technology for assaying fuel rods and/or assemblies.

#### MPAC for UREX+ Processes

Another application of NMDS to MPAC might utilize the measurement of both passive and active neutron multiplicity in very dilute concentrations of higher actinides, such as in a non-actinide waste stream. This is being investigated since it may be more feasible to monitor where actinides are not supposed to be than where they are. The NMDS will be used to assay actinides in pipes, tanks, etc. in a UREX+ fuel separations plant to measure quantities and isotopic constituents in such a stream. Sources and configurations were investigated to simulate a waste pipe that contains residual higher actinides from UREX-plus for use in upcoming experiments.

#### Neutron Multiplicity Detector System

Several programming and maintenance issues with the NMDS that were revealed during testing in December were repaired or resolved. New detector wiring that was installed on one detector group of NMDS significantly reduced background count rates (noise). As a result, all of the of standard cables were replaced with coaxial cables. In addition, as a result of differences in detector response between the original Russian data acquisition system and the new LabView-based system, detector response is being re-mapped with the data collection and analysis software. These improvements are expected to significantly improve the performance of the NMDS.

Isotope	Resonance energy (eV)	K (keV*μsec <sup>2</sup> ) LANL	K (keV*μsec <sup>2</sup> ) UNLV
In-115	1.5	164	
Ta-181	4.3	161	148
Au-197	4.9	158	194
Ag-109	5.2	161.5	191
Ta-181	10.4	162	153
Ag-107	16.3	162.5	166
Cd-111	27.5	163	167
Au-197	59	159	174

*Comparison of UNLV MCNPX computed time constants versus LANL's values for the LANL LSDS benchmark.*

### ACADEMIC YEAR HIGHLIGHTS

- ◆ D. Beller, W. Kernan, M. Schanfein, T. Ward, A. Rimsky-Korsakov, F. Harmon, Q. Newell, L. Lakeotes, P. Attur, T. Beller, and R. LeCounte, "Combined Radiation Detection Methods for AFCI MPAC Project," *Proceedings, 47th Annual Meeting of the Institute of Nuclear Materials Management*, Nashville, TN, July 16-20, 2006.
- ◆ A collaboration with the V. G. Khlopin Radium Institute was developed for an upgrade to and maintenance on the Neutron Multiplicity Detector System.



*Neutron Multiplicity Detector System configured in a cubic geometry for background and source counting.*

### FUTURE WORK

In the final year of this project modeling will be completed, the NMDS will be tested further, and it will be employed in two separate experiments. One is with a carbon-based neutron slowing down spectrometer to develop lead-based SDS technology to assay fuel assemblies upon receipt for separations, and the other is to assay a process pipe containing dilute concentrations of separated higher actinides. The carbon-based SDS has been constructed at the Idaho Accelerator Center. Actinides for the pipe assay experiments are available at UNLV, how they will be used in these studies is yet to be determined.

#### Research Staff

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#### Students

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#### Collaborators

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Thomas Ward, UNLV Science Adviser for Russian Collaborations, TechSource, Inc.



## Task 31

# Decoupling and Disturbance Rejection Control for Target Circulation

J. Ma, J. Lee, W. Yim

## BACKGROUND

In 1998, the Institute of Physics and Power Engineering (IPPE) and Experimental and Development Organization “Gidropress” in Russia, began the design and construction of a prototype lead-bismuth eutectic (LBE) accelerator target, the Target Complex 1 (TC-1), under the International Science and Technology Center (ISTC) project #559 (“Pilot Flow Lead-Bismuth Target of 1 MW Power for Accelerator Driven Systems”) in support of the international efforts to develop accelerator-driven spallation systems for nuclear transmutation and other applications.

Liquid LBE is employed as a spallation target as well as a coolant in the TC-1. The TC-1 design, fabrication, and initial testing were completed at IPPE in Obninsk, Russia, in mid-2001. The system was then prepared for transport and shipped to UNLV, arriving in May 2002, where it was to become a viable testing facility in the U.S. to support research in heavy liquid metal coolant technology for the nuclear industry.

During the thermal and engineering test of the TC-1 in 2005 at UNLV, it was observed that the existing control algorithm led to a very slow convergence to the target temperature setting and also showed unstable oscillatory behavior. The original algorithm was not robust enough to handle the complicated heating system of the TC-1, where nine heating zones (elements) are compacted in one tight container. This interaction and coupling between each heating zone, as well as a heat disturbance from a low efficiency electromagnetic (EM) pump caused the overall temperature control system to be complex and nonlinear.

The objective of the proposed research was to study the coupling effect between each heating zone, and to improve the overall temperature control system of the TC-1 loop. In addition to the temperature control algorithm modification, a 24-hour automatic monitoring system of the EM pump was developed for robust and safe operation of the loop.

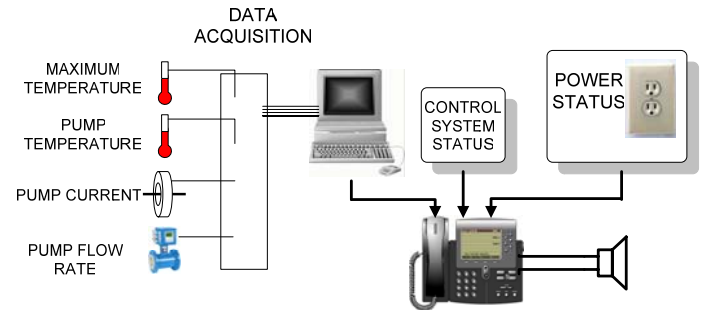


Diagram of the alarm and dial-out system.

## RESEARCH OBJECTIVES AND METHODS

The Primary objective of this task was to modify the existing control algorithm to achieve precise temperature control to the desired setting range. Safety issues, such as an alarm system and user-friendly design, were secondary objectives.

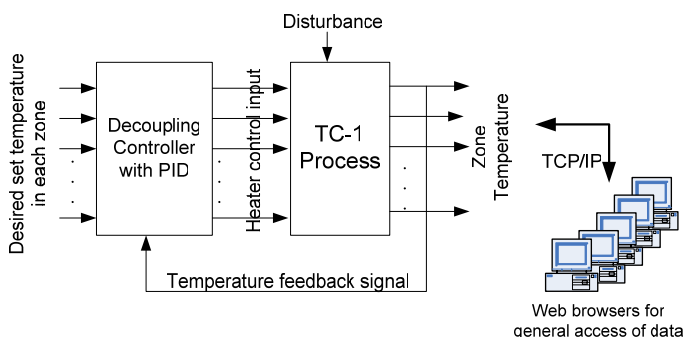
The TC-1 system has more than a single input and a single output, and it exhibits a nonlinear interactive property between the heater inputs and temperature outputs. For the effective control of the temperature in multiple locations of the TC-1 system, these nonlinear interaction terms must be eliminated or decoupled in the control loop. Eliminating these interaction terms requires the identification of these interacting, or coupling, terms. After successful elimination of the coupling terms, the closed loop control algorithm can be designed to achieve the precise tracking of the temperature on multiple locations of the TC-1 under external temperature disturbance from the EM pump. One example of such algorithms is a Proportional-Integral-Derivative control law that can be easily implemented for the existing LabVIEW codes of the Monitoring and Controlling and Scram Protection System.

In addition, the electromagnetic pump used for molten LBE circulation becomes a large heat source, particularly due to its low efficiency. A disturbance-observer-based control method was used to compensate modeling uncertainties as well as external disturbance. The disturbance observer regards the difference between the actual output and the output of the nominal model as an equivalent disturbance applied to the nominal model. The disturbance-observer-based control algorithm can achieve a precise tracking of set temperatures despite the highly coupled thermal disturbance existing in the loop.

Furthermore, the alarm system and a 24-hour monitoring and dial-out system was designed.

## RESEARCH ACCOMPLISHMENTS

The performance of the TC-1 loop in 2001 at Obninsk, Russia and 2005 at UNLV was evaluated using available raw data. The proc-



Overall control block diagram of the TC-1 system.

esses of heating-up, cooling-down, non-circulation and circulation while running the EM pump were studied. The temperatures of different zones were not regulated well at the desired levels. The temperature of all zones should be controlled within the range of 190-200°C, however the temperature difference for all heating zones was approximately 80°C. This exceeds the safety range and has a high risk to cause thermal inhomogeneity.

The interacting terms between heater inputs and target temperature outputs in each zone were identified experimentally. These identified terms were expressed in a discrete transfer function matrix. The system identification was carried out by heating up one zone from room temperature to 50°C, while keeping others off. This temperature was selected to avoid a large difference between others. The transfer functions, which are used to describe dynamic response between individual inputs and outputs, were identified. A non-interacting, or decoupling, control algorithm based on the identified model was developed to reduce the influences from each zone.

Significant improvement in the controller performance was achieved by upgrading the existing controller. The heaters of all heating zones were well controlled to maintain the temperature of all zones within the desired range. The temperature difference is approximately 5°C.

A 24-hour monitor device was installed and wired to the main program. It can automatically dial out when the temperature is too high, or when an abnormal current passes through the EM pump. The current transformers were assembled to detect actual

## ACADEMIC YEAR HIGHLIGHTS

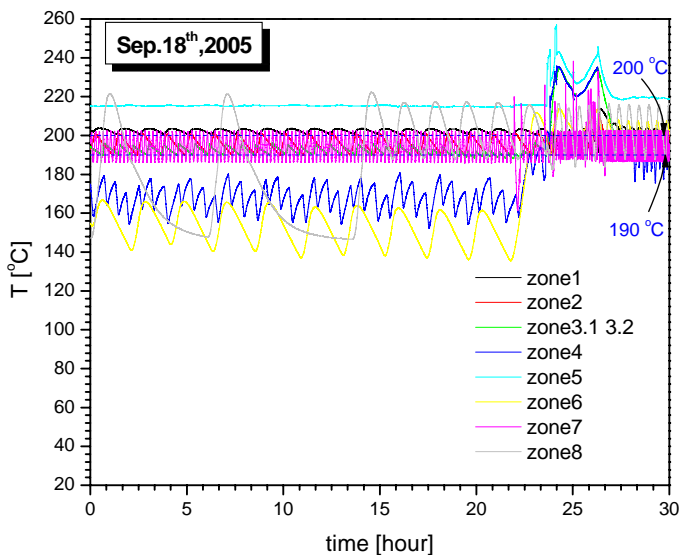
- ◆ X. Tan, J.S. Lee, J. Ma, and W. Yim, "Disturbance Observer based Thermal Hydraulic Control of the Lead Bismuth Eutectic Loop," paper submitted, Eighth International Topical Meeting on Nuclear Application and Utilization of Accelerators (AccApp 07), Pocatello, ID, July 30-August 2, 2007.

heater on/off statuses. Signals from these current transformers were regulated and recorded by the data acquisition system for further investigation.

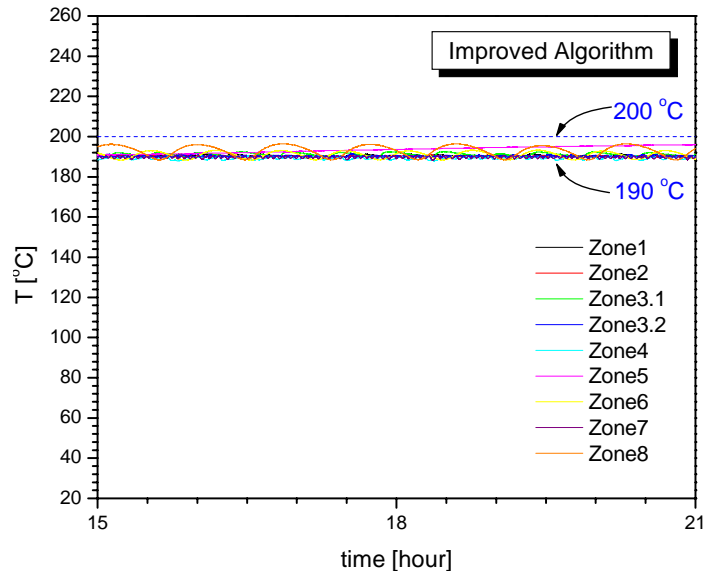
One fatal defect of the watch-dog device was found that will need to be corrected. This significant defect will lead to a continuous heating up without control.

## FUTURE WORK

A by-pass system was designed and is under construction to modify the TC-1 loop as a testing loop for material and thermal hydraulic studies. The control program will consider the new heating components for the bypass system, which will be connected to the TC-1. Control improvement of the EM pump, variable voltage transformer, variable frequency driver, heat indication, etc. will make this main control system more user-friendly and easily manipulated.



*Temperature profiles of nine heating zones before algorithm improvement*



*Temperature response of nine heating zones obtained by the new algorithm*

### Research Staff

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 Dr. Woosoon Yim, Professor, Mechanical Engineering Department

### Students

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# Task 32

## Modeling and Design Algorithms for Electromagnetic Pumps

D.P. Cook

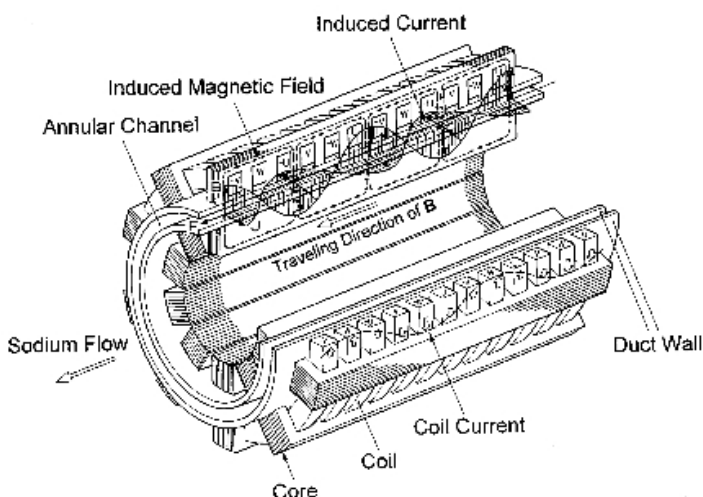
### BACKGROUND

Electromagnetic (EM) induction pumps are used in a number of nuclear energy related applications, such as circulation of molten lead-bismuth eutectic alloys in neutron targets, and circulation of liquid sodium metal in Gen IV Sodium-cooled Fast Reactors (SFR). Because EM pumps have no moving parts which can fail, they are considerably more reliable than conventional mechanical pumps for molten metal usage, and thus EM pumps are favored over mechanical pumps even though their pumping efficiency is lower and their initial cost is higher when compared to mechanical pumps of similar flow rates.

The figure below shows a cut-away picture of an annular, linear induction pump (ALIP), such as has been used in prototype SFRs and the Target Complex 1 (TC-1) loop at UNLV. These ALIPs consist of three main parts:

- an inner cylindrical core fabricated from a ferromagnetic material,
- an annular channel through which the liquid sodium flows, and
- an outer ferromagnetic core in which a set of inductor coils are embedded.

During operation, a 3-phase, alternating current travels through the inductor coils. This current produces a magnetic field which, in turn, induces a current in the liquid sodium in the pump annulus and inner core. Pumping forces develop in the liquid sodium due to the interaction of the magnetic field and the induced current, causing the liquid sodium to flow down the length of the annulus. The magnitude of these pumping forces, and hence the operational efficiency of the pump, is dependent on a large number of design parameters, including coil current and position, ma-



*Cut-away picture of an annular, linear induction pump (ALIP)*

terial selection for the inner and outer cores, and size of the annular gap.

Research on the design of EM pumps has been conducted by a number of researchers in Korea, Germany, Japan and Russia. No major papers on the topic have been published by researchers in the U.S. in the past 10 years. If the U.S. is to continue to maintain a research presence in nuclear power research and development, it is imperative that a solid foundation in EM pump design be developed by researchers within this country. The development of this foundation is the primary aim of this research task.

### RESEARCH OBJECTIVES AND METHODS

The research objectives of this task are:

- A literature review of topics pertinent to EM pump design. These topics include the equations governing the physical phenomena occurring in EM pumps and mathematical algorithms used in modeling these physical phenomena, different EM pump configurations, and the effects of materials properties on pump performance.
- Development of computational models of the TC-1 loop at UNLV.
- Evaluation of the computational models through comparison with experimental data taken on the TC-1 loop.
- A parametric study of the TC-1 loop investigating the pumping efficiency as a function of operating conditions, materials properties, and geometric parameters.

### RESEARCH ACCOMPLISHMENTS

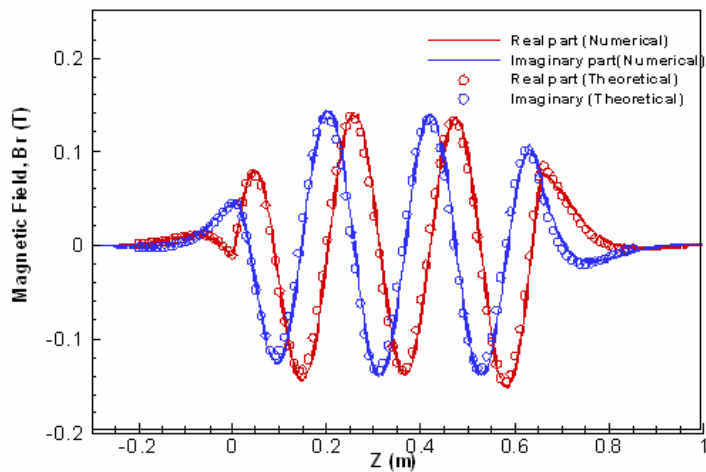
#### On-line EM Pump Literature Database

An on-line literature database has been set up on a UNLV website and now contains over 120 entries. Further work will continue this next year. The database will be expanded in terms of the number of entries, and key word searches will be incorporated into the database. This database can be found at:

<http://nstg.nevada.edu/mmrg/research/LitSurvey/EMP-Literature.html>

#### Computational Modeling

Several preliminary models of EM pumps have been developed. The results published to date from this task have focused on the calculation of the EM phenomena (current density, magnetic field, and electromagnetic body forces) in the pump. The first of these EM models was an analytic formulation of Maxwell's equations, in which the magnetic vector potential was the primary solution variable. Use of the method of separation of variables and Fourier transforms allowed the expression of the magnetic vector potential to be expressed in an integral form that could then be



*Comparison of the analytic and numeric calculations of the radial component of the magnetic flux density in the TC-1 pump along the pump axis.*

solved numerically.

The second model was developed using Comsol, a MATLAB-based platform, and relies on the finite element method to discretize and solve the partial differential equations. The software can run the finite element analysis together with adaptive meshing and error control according to a variety of iterative numerical solvers. The figures above and bottom right show a comparison of the radial and axial components of the magnetic flux density calculated in the pump from the analytic and numeric model. It should be noted that, in these calculations, the velocity of the liquid metal, which can have a significant effect on the magnetic field, was specified, not calculated via solution of the Navier-Stokes equations.

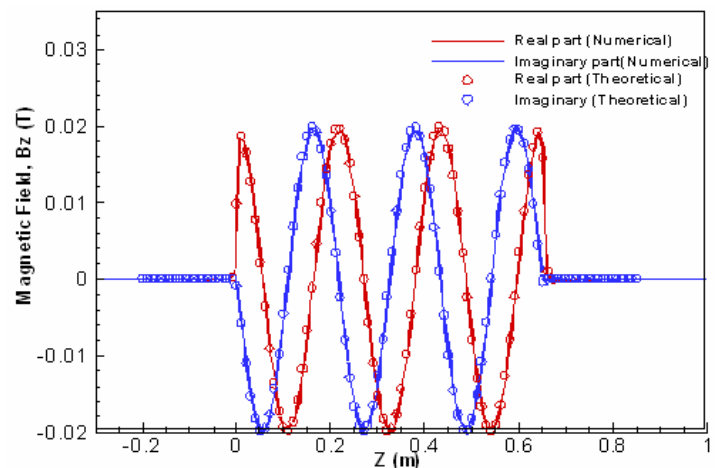
## FUTURE WORK

The next phase of the project involves development of a fully-coupled magnetohydrodynamic solver, for calculating both the EM and fluid flow phenomena in the EM pump. For this model, the EM field phenomena will be calculated using an integral formulation of Maxwell's equations, and the fluid flow phenomena will be calculated using a finite volume formulation of the Navier-Stokes equations. This model has been under development for several months and should be completed during Summer 2007.

## ACADEMIC YEAR HIGHLIGHTS

- ◆ D.P. Cook, J. Ma, H. Chen, Y. Chen, and L. Ratliff, "Numerical Modeling of EM Pump Efficiency," *Proceedings, International Mechanical Engineering Conference and Exposition, IMECE-2006*, Chicago, IL, November 5-10, 2006.
- ◆ D.P. Cook, J. Ma, H. Chen, Y. Chen, and L. Ratliff, "Numerical Modeling of EM Pump Efficiency," *Comsol Users Conference 2006*, Las Vegas, NV, 2006.

Results from the current mathematical models have shown that the efficiency of EM pumping systems can be very dependent on several operating parameters, in particular the frequency of the applied three-phase current and the inductor winding patterns. To further explore the sensitivity of the system to these parameters and to ensure the validity of the computational models that are being developed, plans to construct a lab-scale EM pumping system have been discussed. The system would be a rectangular loop, roughly 2 meters by 1 meter in dimension. The EM pump that would be providing the motive force to the fluid would be of variable frequency, allow changes in the inductor winding pattern, and have removable magnetic cores. This type of pumping system would allow extensive opportunity to validate the computational models.



*Comparison of the analytic and numeric calculations of the axial component of the magnetic flux density in the TC-1 pump along the pump axis.*

### Research Staff

Daniel P. Cook, Principal Investigator, Assistant Professor, Mechanical Engineering Department  
 Yitong Chen, Co-Principal Investigator, Associate Professor, Mechanical Engineering Department  
 Jian Ma, Co-Principal Investigator, Assistant Research Professor, Mechanical Engineering Department  
 Huajun Chen, Co-Principal Investigator, Assistant Research Professor, Mechanical Engineering Department

### Students

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 Lillian Jane Ratliff, Undergraduate Student, Electrical Engineering Department  
 Lucas Bang and Siul Ruiz, Undergraduate Students, Mechanical Engineering Department

### Collaborators

Ning Li, LBE Team Leader, Los Alamos National Laboratory



## Task 33

# Separation of Technetium from Uranium and Waste Form Synthesis

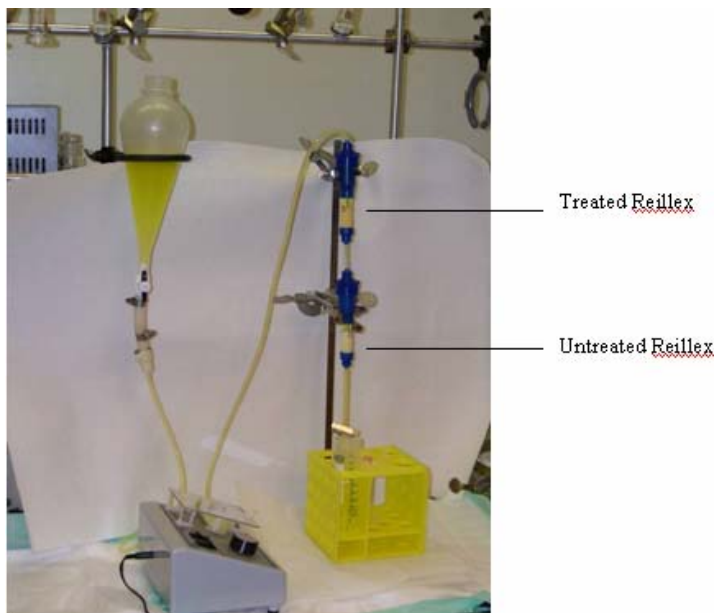
K. Czerwinski

## BACKGROUND

In the Advanced Fuel Cycle Research & Development (AFC R&D) activities, the uranium extraction (UREX+1) process is proposed as one of the most promising technique to separate transuranic elements (TRU) from light water reactor spent nuclear fuel in the years to come. The isotope  $^{99}\text{Tc}$  will be separated together with U within the first process steps. After the separation of U, Tc must be immobilized by their incorporation in a suitable storage and waste form.

A candidate process to immobilize  $^{99}\text{Tc}$  is to alloy metallic Tc with excess metallic zirconium. This material has potential advantages in terms of the future reuse of  $^{99}\text{Tc}$  and its potential transmutation. Providing a Tc storage/waste form strongly promotes the AFC R&D and the separation of TRU elements using the UREX+1 process. However, little thermodynamic data in the binary technetium–zirconium metal system exist, and only few data are available on the synthesis of Tc–Zr alloys and on their potential performance under temporary or geological storage conditions.

In this project, systematic investigations on the Tc–Zr binary metal system will be evaluated for the first time. The synthesis of metallic Tc as well as its alloys with Zr will be evaluated. In order to provide valuable data to AFC R&D, the thermodynamic equilibrium phases, as well as their performance under repository conditions, will be examined.



*Separation process with two columns.*

## RESEARCH OBJECTIVES AND METHODS

The research objectives of this project are as follows:

- Evaluate anion exchange methods for achieving the separation of Tc from U.
- Synthesize metallic Tc from the separated product.
- Synthesize and characterize Tc alloys.
- Investigate Tc-corrosion and Tc-leaching of binary Tc–Zr phases under a range of conditions.

The following experimental techniques are used in the evaluation of the solutions and solids from the experiments: ultraviolet-visible spectroscopy, time-resolved laser fluorescence spectroscopy, X-ray Absorption Fine-Structure Spectroscopy (XAFS), and microscopy.

## RESEARCH ACCOMPLISHMENTS

### Separations

Static and dynamic experiments were performed to investigate the interaction of technetium with selected anion exchange resins. The kinetic static experiments showed Reillex resin had superior Tc sorption kinetics and was selected for further study. Reillex treated by nitric acid (Resin 6) was also used in the studies.

Dynamics experiments were performed on simulated UREX solution in order to determine the separation factor for uranium and technetium and to study the possibility of a Tc elution from the resin. The one column experimental set-up consisted of a reservoir of 250 mL, linked to a peristaltic pump, with a constant flux which can be between 1.2 to 8.4 mL/min. It is connected to a small column (length = 5 cm and diameter = 1 cm) and contained 1 g of resin (Reillex HP or Resin 6).

The process is divided into 3 steps: absorption, washing, and elution. For absorption, 150 mL of the UREX solution were placed in the reservoir and pumped with a peristaltic pump through the column at a constant flow rate (2, 4 or 8 mL/min). Samples were collected into centrifugation tubes (45 mL  $\pm$  0.5 mL for the first two and 10 mL  $\pm$  0.2 mL for the others). For each sample, 10  $\mu\text{L}$  of solution were removed and mixed with 10 mL of liquid scintillation fluid in a plastic vial, and  $^{99}\text{Tc}$  was counted by liquid scintillation. The samples were eluted with a 50 mL solution of  $\text{NH}_4\text{OH}$  (1M or 2 M) and were introduced in the reservoir and poured through the column with the same constant flow rate.

Samples were collected into centrifugation tubes of 10 mL  $\pm$  0.2 mL with 10  $\mu\text{L}$  of samples were removed and mixed with 10 mL of liquid scintillation fluid for  $^{99}\text{Tc}$  analysis. For samples containing a high amount of technetium, a dilution (1/100) was necessary for the liquid scintillation analysis in order to be able to use the calibration curve. To optimize U/Tc separation, treated and un-



*Tc/Zr sample before and after arc melting*

treated resin were combined. The set-up is composed as before by a reservoir, a pump and two columns.

The absorption and washing steps were carried out with exactly the same conditions, as presented above.

Concerning the elution step, the columns are disconnected and only the first one containing the treated resin is eluted, whereas the second one is kept for a re-use and for an eventual Tc reprocessing by pyrolysis. A suitably pure Tc and U stream resulted from the experiment.

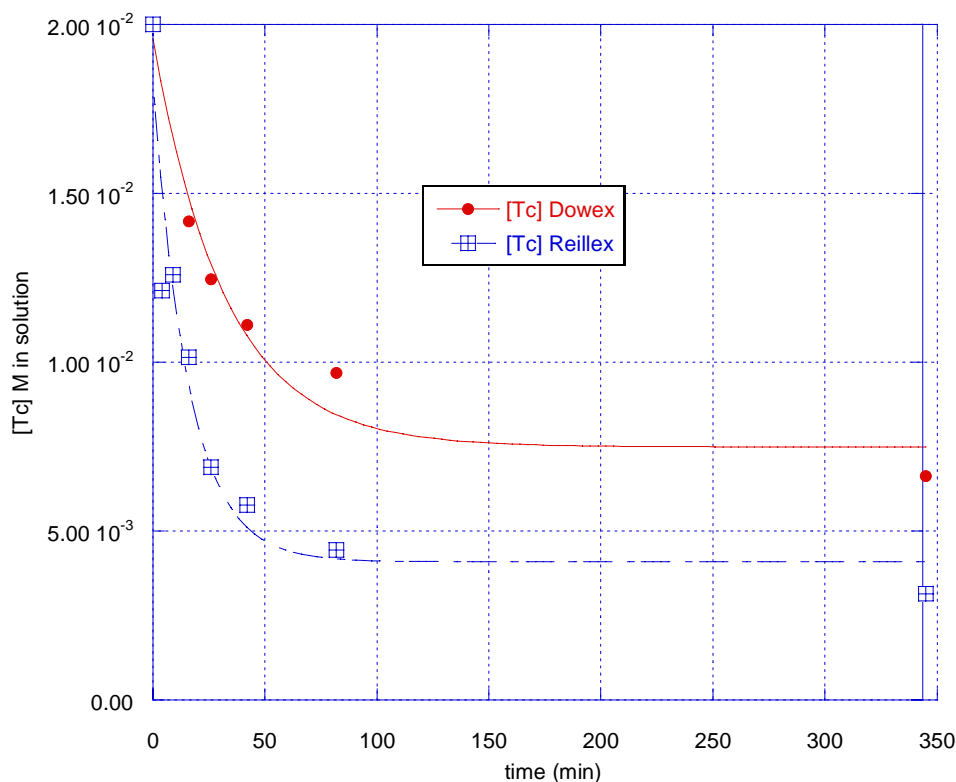
#### Solid phase synthesis

Steam reforming of pertechnetate in the presence of carbon yielded Tc metal at 700°C under Ar or N<sub>2</sub>. Alloy samples were prepared by grinding Tc and Zr metal in different ratios, from 25% to 75% Tc. Cylindrical pellets were obtained by pressing the powder and arc melting to produce the alloys. After arc melting, samples were analyzed by X-ray diffraction and optical microscopy. The alloy phases included hexagonal ( $\alpha$ -phase) and cubic ( $\beta$ -phase) Zr phases. There is a diffraction peak that does not correspond to referenced Tc or Zr phases ( $\alpha$ -Zr,  $\beta$ -Zr, Tc metal, Tc<sub>2</sub>Zr, Tc<sub>6</sub>Zr, ZrO<sub>2</sub> or TcO<sub>2</sub>). Those peaks were fitted using a theoretical phase derived from the structure of Nb<sub>3</sub>Te<sub>7</sub>. This result which reveals a new Tc-Zr phase (Zr<sub>3</sub>Tc<sub>7</sub>), should be taken with prudence and further analysis by microprobe analysis will be done in order to confirm this hypothesis.

#### **FUTURE WORK**

The further characterization of Zr-Tc alloys will be continued, including XAFS analysis. Dissolution studies to examine mechanisms

*Kinetics of TcO<sub>4</sub><sup>-</sup> removal from solution with initial [TcO<sub>4</sub><sup>-</sup>]=0.02 M by Dowex Marathon and Reillex resins*



#### **ACADEMIC YEAR HIGHLIGHTS**

- ◆ K. Czerwinski, F. Poineau, T. Hartmann, and G. Jarvinen, "Synthesis and characterization of technetium-zirconium alloys," 233rd American Chemical Society Annual Meeting, Chicago, IL, March 2007.
- ◆ F. Poineau, T. Hartmann, G. Jarvinen, and K. Czerwinski, "Synthesis and Characterization of Technetium-Zirconium Alloys Waste Forms for the UREX+1 Process," Materials Research Society, Scientific Basis for Nuclear Waste Management XXX, Boston, MA, November 27 to December 1, 2006.
- ◆ Presentation on Tc separations at Global Nuclear Energy Partnership Separations Working Group Meeting.

and characteristics of the waste forms will be performed. Based on input from national laboratory collaborators, future studies will include the Zr-Tc-Fe alloy systems as well as initial experiments on oxides.

#### **Research Staff**

Ken Czerwinski, Principal Investigator, Associate Professor, Department of Chemistry  
Frederic Poineau, Post-Doctoral Researcher, Harry Reid Center

#### **Students**

Julie du Bouchaud du Mazabrun, Graduate Student, École Nationale Supérieure de Chimie de Paris  
Ed Mausolf, Undergraduate Student, Department of Chemistry

#### **Collaborators**

Gordon Jarvinen and Doris Ford, Los Alamos National Laboratory

## Task 34

# Solution-Based Synthesis of Nitride Fuels

T.A. Sullens and K.R. Czerwinski

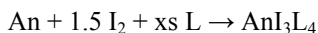
## BACKGROUND

Nitride fuels have appropriate properties for advanced fuels, including high thermal conductivity, thermal stability, solid-state solubility of actinides, fissile metal density, and suitable neutronic properties. The presence of oxide and carbide impurities that occur during the current nitride fuel synthesis limits their utility in advanced fuel cycles. The presence of these impurities can lead to the formation of phases with different properties from the bulk material, including the formation of secondary phases. Even a small amount of oxygen in the nitride fuel can reduce thermal conductivity by 10%. This limits the ability to fully develop nitride fuels for advanced reactors. To avoid the entrainment of carbides and oxides in the final actinide nitride product, a non-aqueous, carbon free solution phase route is proposed and investigated in this project.

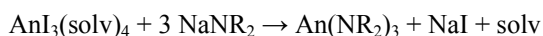
A drawback of nitride fuels involves their synthesis. For nitride fuels, the current synthetic route is carbothermic reduction from the oxide to the nitride, which is based on solid phase reactions involving a stepwise process from the metal oxide, to the carbide, and finally the nitride. This high temperature, solid-phase approach is plagued by impurities in the final nitride product and difficulties in the synthesis and fabrication steps. A direct solution-based synthesis would eliminate, or at least minimize, the impurities and other synthetic problems. The proposed solution route to nitride would also have the added benefit of providing several adjustable parameters that would allow control of the properties of the final solid product.

## RESEARCH OBJECTIVES AND METHODS

The objective of this project is to develop solution phase synthetic routes for actinide nitrides for use in nuclear fuels. In the 1970s, a synthesis for actinide nitrides was proposed based on the reaction of plutonium triiodide ( $\text{PuI}_3$ ) and uranium tetraiodide ( $\text{UI}_4$ ) with sodium metal in liquid ammonia giving  $\text{PuN}$  and  $\text{UN}$ , respectively, as the reaction products. The synthetic chemistry of trivalent actinide complexes was advanced greatly with the discovery at Los Alamos National Laboratory (LANL) of efficient routes to soluble iodide starting materials of the type  $\text{AnI}_3\text{L}_4$ , where An is uranium, neptunium, or plutonium, and L is tetrahydrofuran (thf), pyridine, dimethylsulfoxide, etc.

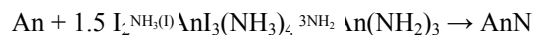


$\text{PuI}_3$  is soluble in ammonia, presumably as the ammonia adduct  $\text{PuI}_3(\text{NH}_3)_4$ . More recent efforts by ANL and LANL collaborators have investigated amido reactions with actinides to produce  $\text{An}(\text{NR}_2)_3$  complexes, where An = U, Np, Pu:



These results suggest that the amido complexes could provide a

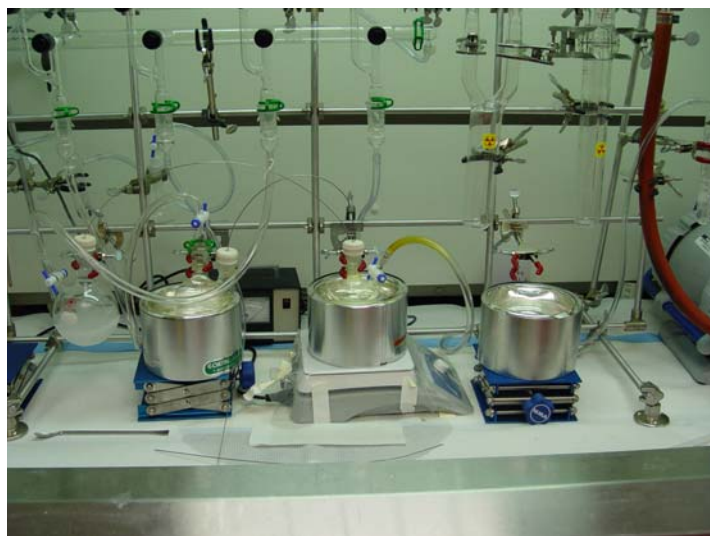
non-aqueous solution method for the synthesis of nitrides. The resulting sodium iodide is readily soluble in liquid ammonia, making separation of these products possible. From these results, a plausible route for the synthesis of nitride fuel  $\text{AnN}$  is:



where An is uranium, neptunium, plutonium or americium. To achieve the solution synthesis of actinide nitrides the fundamental chemical coordination and speciation involved in the above reaction will be examined. The non-aqueous synthetic route, based on amido chemistry, potentially provides property control over the nitride product. The resulting nitride product should be free of the impurities inherent in the carbothermic reduction technique.

The experiments are being performed by a joint research team from UNLV, LANL, and Argonne National Laboratory (ANL), with actinide experiments performed at each laboratory. This project maintains special emphasis on student participation in the project research with all team members collaborating in the educational efforts. The young researchers from UNLV have the opportunity to perform research at ANL and LANL, helping train the next generation of radiochemists and actinide scientists with experience in DOE laboratories. The synthesis of nitride fuels through this method is complementary to the ongoing carbothermic reduction syntheses being performed within the UNLV Radiochemistry program. The ANL and LANL participants are experts in synthetic actinide chemistry, including non-aqueous chemistry and materials science.

The experimental methods for the synthesis of the amido actinide species relies upon the use of inert atmosphere and elevated pressure. These conditions can be reached with the use of Schlenk



*A depiction of the Schlenk line experimental set-up for the generation and storage of liquid ammonia, solvent transfer for the dissolution of iodine, and the cannula transfer of solution for reaction with uranium.*



lines, pressure vessels, and glove boxes. A combination of these techniques is being utilized in the project. Characterization of the resulting amido species will primarily utilize X-ray diffraction, employing methods and equipment already developed by the UNLV, ANL, and LANL partnership.

Single crystal X-ray diffraction will be used for examination of final and intermediate products at the atomic level for the determination of molecular structure, atomic interaction and spacing, crystal structure, speciation, and elemental oxidation state. X-ray Powder Diffraction, high resolution Transmission Electron Microscopy in combination with Energy Dispersive X-ray Analysis, Parallel-collection Electron Energy-Loss Spectroscopy, Electron-beam Microprobe Analysis and Scanning Electron Microscopy are currently in use at UNLV and will also be used to evaluate the actinide nitrides. For complete product characterization, X-ray Absorption Fine-structure Spectroscopy will also be used for analysis. Thermal analyses (Thermogravimetric Analyzer, Differential Thermal Analyzer, and Differential Scanning Calorimetry) of the final products will also be performed at UNLV.

## RESEARCH ACCOMPLISHMENTS

The preliminary studies into the synthesis of actinide nitride fuels through a low temperature, liquid ammonia based synthesis route have been conducted on the uranium containing system, and there is good indication for the success of synthesizing uranium(III) nitride. The dissolution of iodine in ammonia is a rapid process, resulting in a pale green solution, which does not result in any observable oxidation of iodine. The cannula transfer of dissolved iodine into the reaction vessel containing U metal has been conducted with little to no residual iodine remaining in the original flask. The metal being used for these reactions has a noticeable brown/black oxide coating that prevents the formation of  $UI_3(NH_3)_x$ .

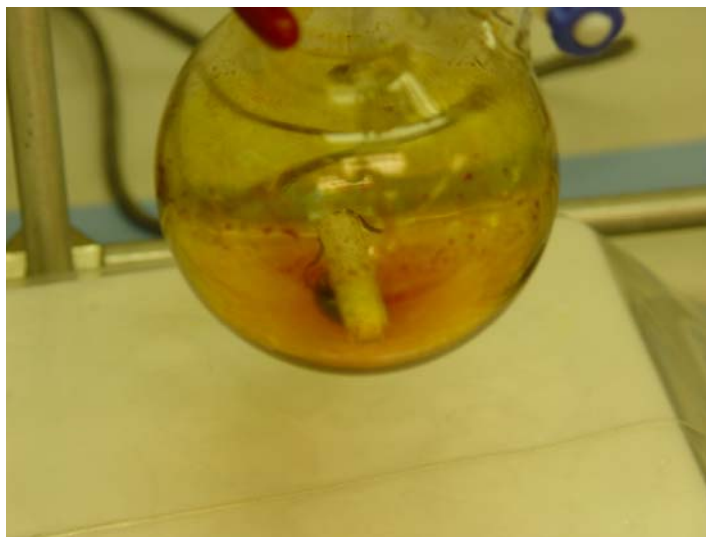
Stirring of U metal fragments with dissolved iodine in ammonia for 24 hours revealed a thickening of the oxide coating, which presumably is a result of  $O_2$  or  $H_2O$  contamination in the solvent. Procedures for cleaning the metal prior to the reaction are under development. Two measures are being taken in order to use the most purified solvent possible; the highest grade ammonia available is being obtained and several procedures are being developed to dry and deoxygenate the solvent. These actions should allow the reaction to proceed without formation of the boundary oxide layer between the two reactants.

## ACADEMIC YEAR HIGHLIGHTS

- ◆ T. Sullens and K. Czerwinski attended the 2006 Nuclear Energy Research Initiative (NERI) Fuels Review Meeting at Idaho National Laboratory, Idaho Falls, ID, August 7-8, 2006.
- ◆ This project was included in the Nuclear Energy Research Initiative 2006 Annual Report as a NERI recipient (awarded in FY06).

## FUTURE WORK

There are a number of alternate synthetic routes for producing the  $UI_3(solv)_x$  precursor to  $U(III)N$ , which are available for successful project completion should this method be ineffective. Any number of these precursors can be adapted for inclusion into the reaction process, yet these precursors will increase the likelihood of carbon inclusion and contamination into the final product. However, it is believed that the proposed procedure would be most beneficial for the desired outcome and for the introduction of a novel, viable synthetic route for accessing  $U(III)$ . Once the synthetic process is understood for the uranium species, only minor modifications are anticipated for the transuranic species.



*A depiction of dissolved iodine reacting with uranium metal after the liquid ammonia solvent has evaporated.*

### Research Staff

Tyler Sullens, Principal Investigator, Assistant Research Professor, Harry Reid Center for Environmental Studies  
Ken R. Czerwinski, Co- PI, Associate Professor, Department of Chemistry

### Students

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### Collaborators

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Dave Clark, Los Alamos National Laboratory  
Gordon Jarvinen, Los Alamos National Laboratory



# Task 35

## Criticality Studies for UREX Processes

D. Beller

### BACKGROUND

The completion of criticality experiments for mixtures of transuranic actinides (TRU—includes Np, Pu, Am, and Cm) that will be created during the separation of used nuclear fuel may be a requirement in order to construct prototype plants for the Global Nuclear Energy Partnership. In this program and the Advanced Fuel Cycle Research and Development (AFC R&D) program that supports it, economic and environmental methods are being developed to reduce the impact of waste from commercial nuclear fuel cycles.

Recycling of used fuel by chemically separating it into U, fission products, and TRU would be the first step in this new fuel cycle. Proposed mixtures and concentrations of TRU covering a wide range of conditions must be examined theoretically and experimentally to demonstrate criticality safety in advance of construction of a processing facility. Theoretical studies may be limited because of insufficient nuclear data for the rarer isotopes of Np, Pu, Am, and Cm. These data limitations include reaction cross sections in some energy regimes, thermal feedback coefficients, and delayed neutron fractions.

### RESEARCH OBJECTIVES AND METHODS

In this project, which is a collaboration between UNLV, LANL, ANL, and ORNL, criticality studies will be conducted to support the development of future fuel cycle facilities. The first step in determining requirements for criticality studies is an examination of past experiments and criticality and sensitivity studies as well as available databases. Further sensitivity studies will determine what kinds of experiments should be performed to insure criticality safety in advanced processes. This information can then be used to formulate an optimum set of experiments that can be analyzed in advance using state-of-the-art radiation transport codes. As these facilities and experiments will include complex geometries, a Monte Carlo N-Particle (MCNP) transport code will be used in these sensitivity, scoping and design studies. The work may also require generation of new cross section libraries and thermal scattering coefficient databases. Future criticality studies may include cross section sensitivity studies and design of critical experiments including dilute mixtures of Pu, mixed higher actinides in solution, and fuels.

### ACADEMIC YEAR HIGHLIGHTS

- ♦ L. Lakeotes, R. LeCounte, D. Beller, and R. Boehm, “Higher Actinide Cross-Section Sensitivity and Criticality Studies for the UREX+1 Process,” oral presentation by L. Lakeotes at the ANS Student Conference, Corvallis, Oregon, March 31, 2007.
- ♦ Students and faculty participated in the Advanced MCNPX Workshop at UNLV where criticality studies and cross section perturbation techniques were discussed.

### RESEARCH ACCOMPLISHMENTS

The project was initiated in September 2006. Discussions occurred with LANL, ORNL, and ANL regarding project scope and direction. The appropriate division of effort between cross-section sensitivity studies and design of required criticality experiments, such as measurement of thermal feedback coefficients in dilute mixtures of plutonium with varying isotopic constituents, needs to be determined. The project will likely focus on sensitivity studies. At UNLV, separations processing facilities and components will be concentrated on, as opposed to critical cores.

One conceptual study could focus on the capability to measure thermal feedback coefficients in dilute mixtures of plutonium with varying isotopic constituents. Another could involve the modeling of a liquid- or solid-core critical assembly to assess the ability to measure integral critical parameters with small quantities of TRU, rather than a full core of fuel containing TRU. Students collected information on code systems and references on criticality and sensitivity studies and to research cross section uncertainties for Am and Cm at room temperature in uranium extraction (UREX) separations processes.

The SCALE code system was acquired for processing cross sections for sensitivity studies. MCNP, MCNPX, SCALE, and data libraries were loaded for processing cross sections and conducting sensitivity studies.

### FUTURE WORK

During the following year SCALE and MCNP/MCNPX will be used to investigate cross section sensitivity of UREX process and conceptual integral experiments.

#### Research Staff

Denis Beller, Principal Investigator, Research Professor, Mechanical Engineering Department

#### Students

Ryan LeCounte, Lawrence Lakeotes and Timothy Beller, Graduate Students, Mechanical Engineering Department  
Tanya Sloma, Undergraduate Student, Mechanical Engineering Department

#### Collaborators

Richard McKnight, Argonne National Laboratory (ANL)  
Michael Dunn, Nuclear Data Division, Oak Ridge National Laboratory (ORNL)  
David Hayes, Los Alamos National Laboratory (LANL)  
Thomas Ward, UNLV Russian Collaboration Science Adviser, TechSource, Inc.

## Task 36

# Evaluation of Cs/Sr Waste Form for Long Term Storage and Disposal

G. Cerefice and L. Ma

## BACKGROUND

In order to maximize the utilization of the proposed repository facility, the short-term decay heat generated by high-level waste must be removed from the waste stream. The proposed waste management baseline strategy for the GNEP program calls for the separation of cesium and strontium from used nuclear fuel in order to minimize the short-term heat loading in the repository facility. The separated waste stream will be converted to an aluminosilicate waste form, stored for decay (approximately 300 years), then managed as low-level radioactive waste.

The goal of this project is to examine two potential concerns regarding the long-term performance of a proposed cesium/strontium waste form. To facilitate long-term storage, up to 300 years, the disposal containers will need to be able to survive for the entire storage interval. The first aspect of the project will explore the potential interaction of the aluminosilicate waste form with the storage canister materials to determine if there is any corrosion or chemical interaction concerns for the storage of the materials.

At the end of the storage interval, most of the  $^{137}\text{Cs}$  in the waste form will have decayed to its daughter,  $^{137}\text{Ba}$ . While this decay provides a significant reduction in the decay heat generated by the waste form, it poses a new concern. Barium is hazardous, and is identified by the U.S. Environmental Protection Agency (EPA) as a hazardous constituent under the Resource Conservation and Recovery Act (RCRA). To dispose of any material containing a RCRA-identified constituent, the material must be demonstrated to be durable enough to prevent the release of the hazardous component or must be treated as hazardous waste. For the Cs/Sr waste stream, failure to contain the barium within the waste form would require disposal as a mixed waste stream, greatly increasing the disposal costs. Understanding the potential impacts of radioactive damage, high storage temperatures, and the crystallographic impacts of the decay transmutation itself on the performance of the waste form 300 years from now poses a significant challenge.

## RESEARCH OBJECTIVES AND METHODS

The research effort at UNLV will be divided into materials compatibility and waste form performance subtasks. The materials compatibility subtask will examine the potential for chemical interactions between the waste form material and proposed structural materials for the disposal container (carbon steel, stainless

steel, etc.). The waste form performance subtask will examine the leach resistance of the waste form, with particular attention to barium retention. The performance subtask will also work with the ANL team to develop the cold analog samples for comparison with the aged  $^{137}\text{Cs}$ -bearing aluminosilicate.

To examine the potential for waste form-storage materials interactions, coupons of potential container materials (carbon steel, 316L stainless steel, Inconel 617, and Zircalloy-2) will be contacted with the Cs/Sr-loaded aluminosilicate waste form material. These coupons will be exposed at fixed temperatures for up to 6 months. The samples will be analyzed for weight loss as well as structural changes to determine if any material-material interactions would be expected for this waste form.

The performance of the waste form will be evaluated using the Toxic Constituent Leaching Protocol (TCLP), established by the EPA as a standard analysis to determine if a material requires disposal as a hazardous waste. The resistance of the waste form to leaching will be examined following the TCLP, with a particular focus on barium retention. Standard dissolution/leaching tests will also be performed for comparison. To evaluate the impact of radiologically produced barium in the waste form, an archived sample of  $^{137}\text{Cs}$ -bearing aluminosilicate material from ANL will be used to examine the chemical environment of the Ba. Analog cold samples will be prepared at UNLV for comparison and baseline measurements, and experimental protocols will be evaluated with the cold samples to evaluate the feasibility of performing leach testing on the hot, archived sample.

## RESEARCH ACCOMPLISHMENTS

This effort represents a new project started in May 2007 with a kick-off meeting between the UNLV researchers and the national program collaborators. Since this meeting, the test plan and sample matrix has been developed, and the procurement for the metal coupons has been initiated.

## FUTURE WORK

For the next academic year, the material chemical interaction experiments will be started to explore the corrosion of potential container materials in contact with the waste form. Samples of the waste form will be synthesized using single components of the waste stream to determine the speciation of the Cs, Sr, Y, Ba and Zr within the waste form by X-ray diffraction and electron microscopy.

### Research Staff

Gary Cerefice, Principal Investigator, Assistant Research Professor, Radiochemistry Ph.D. Program  
Longzhou Ma, Assistant Research Professor, Harry Reid Center for Environmental Studies

### Students

To be determined.

### Collaborators

Michael Kaminski, Argonne National Laboratory (ANL)

## UNLV TRANSMUTATION RESEARCH PROGRAM EVENTS

### *June 13, 2006*

E. Philip Horwitz, PG Research Foundation, Inc., gave a seminar entitled “Alpha Emitters: From Earth to Moon to Man.”

### *August 2006*

Robert O’Brien graduated with a Master of Science in Materials and Nuclear Engineering becoming UNLV’s second Nuclear Engineering graduate.

### *August 20-23, 2006*

The UNLV Student Section of the American Nuclear Society had their annual field trip. This year they went to Los Alamos National Laboratory and included stops in Albuquerque and Sante Fe, NM.

### *August 30, 2006*

Micha Polak, Ben-Gurion University of the Negev, gave a seminar entitled “Alloy nanocluster compositional structure and heat-capacity based on TB coordination-dependent bond energetics and the statistical-mechanical FCEM approach.”

### *September 27, 2006*

Alan Dobson and Chris Phillips, Energy Solutions, gave a seminar on the British recycling program to the UNLV Radiochemistry Group.

### *September 29 - October 1, 2006*

Eleven graduate students and seven faculty members staffed an informational booth at the Town of Pahrump Fall Festival. This is the program’s major community outreach to discuss nuclear issues with the citizens of Nye County, Nevada.

### *October 4, 2006*

American Nuclear Society President Harold McFarlane gave a presentation in Las Vegas on the nuclear industry.

### *October 5, 2006*

Rhonda Hopkins, NSTec, presented a seminar at UNLV entitled “Scientific Work Conducted by the Remote Sensing Laboratory.”

### *October 12, 2006*

Riland Carson, Remote Sensing Laboratory, presented a seminar at UNLV entitled “Remote Sensing Laboratory (Part 2): Technical Symposium.”

### *October 24-25, 2006*

UNLV faculty participated in a DOE-Academia meeting in Chicago on DOE Nuclear Energy University Programs.

### *November 18, 2006*

Two M.S. Materials and Nuclear Engineering students presented an exhibit on the HP RACE Target for UNLV Engineering freshman recruitment for about 50 students and parents.

### *December 21-24, 2006*

Two faculty members, Yury Korovin and Vladimir Artisyuk, from the Institute for Nuclear Power Engineering, Obninsk, Russia visited UNLV to investigate potential collaboration on a textbook and research.

### *December 27, 2006*

Bob Summers, NSTec, gave a seminar on missions at the Nevada Test Site.

### *January 4, 2007*

David Ashley, the new UNLV President, visited the Harry Reid Center to meet with division directors and tour the facilities. He particularly expressed his interest in hearing about the Transmutation Research Program.

### *January 8-12, 2007*

The UNLV College of Engineering hosted an Advanced MCNPX Workshop. Attendees included a large contingent from UNLV, plus staff members from Los Alamos, Nevada Test Site, Idaho State University, and other organizations.

### *January 12, 2007*

Vladimir Novosselov, Ural Subsidiary of Federal Government Service Academy, Chelyabinsk, Russia, visited UNLV to discuss the history of the former Soviet Union nuclear fuel cycle.

### *February 1, 2007*

Todd Allen, University of Wisconsin, visited UNLV and toured facilities as part of a User Facility study for DOE-NE.

### *March 1, 2007*

Tyler Sullens was hired after a search for a Research Professor in Radiochemistry as the replacement for Thomas Hartmann who accepted a faculty position at Idaho State University.

### *March 25-29, 2007*

Nine Radiochemistry program students and faculty presented papers at the American Chemical Society conference in Chicago, IL.

### *April and May, 2007*

A GNEP poster was prepared and displayed at the Las Vegas Grand Prix (April 6-8), the Pahrump Earth Day Festival (April 21), and the Las Vegas Family and Kids Expo (May 26-27).

### *April 12, 2007*

A tour of the Nevada Test Site was organized for the UNLV community. Two bus loads of mainly students and staff participated in the tour.

### *April 16, 2007*

Jill Duggan and Annabelle Malins from the United Kingdom embassy gave presentations entitled “The Energy Challenge – Moving to a Low Carbon Future: The UK experience in developing climate policy.”

### *April 23-26, 2007*

Tom Ward, GNEP liaison and TRP science adviser visited UNLV to discuss infrastructure and potential future aspects of the UNLV program.

### *May 1-2, 2007*

UNLV hosted the GNEP Economic Analysis Working Group meeting.

## Transmutation Research Program Financial Statement

<b>Program Administration</b>	<b>FY01</b>	<b>FY02</b>	<b>FY03</b>	<b>FY04</b>	<b>FY05</b>	<b>FY06</b>	<b>TOTAL</b>
Program Support							
Labor	\$187,305	\$348,324	\$564,755	\$452,274	\$575,395	\$515,340	\$2,643,393
Other Costs	\$121,779	\$72,336	\$115,047	\$108,013	\$139,019	\$75,000	\$631,194
LANL Subcontract	\$150,000	\$162,500	\$0	\$0	\$0	\$0	\$312,500
SRNL Subcontract	\$0	\$0	\$0	\$0	\$70,250	\$0	\$70,250
Infrastructure Augmentation							
New Hires	\$112,692	\$240,648	\$433,832	\$391,028	\$691,846	\$360,000	\$2,230,046
Facilities	\$1,492,446	\$799,837	\$838,661	\$604,933	\$394,910	\$624,654	\$4,755,441
Academic Programs	\$0	\$0	\$0	\$179,122	\$154,527	\$210,858	\$544,507
International Collaboration	\$144,973	\$377,175	\$155,200	\$121,700	\$13,565	\$76,000	\$888,613
<b>Subtotal</b>	<b>\$2,209,195</b>	<b>\$2,000,820</b>	<b>\$2,107,495</b>	<b>\$1,857,070</b>	<b>\$2,039,512</b>	<b>\$1,861,852</b>	<b>\$12,075,944</b>
<b>Student Research Tasks Totals</b>	<b>\$790,805</b>	<b>\$2,499,180</b>	<b>\$1,752,505</b>	<b>\$1,642,930</b>	<b>\$1,928,488</b>	<b>\$2,098,148</b>	<b>\$10,712,056</b>
<b>Totals</b>	<b>\$3,000,000</b>	<b>\$4,500,000</b>	<b>\$3,860,000</b>	<b>\$3,500,000</b>	<b>\$3,968,000</b>	<b>\$3,960,000</b>	<b>\$22,788,000</b>

### Student Research Task by Task

	<b>FY01-06</b>		<b>FY04</b>	<b>FY05</b>	<b>FY06</b>	<b>TOTAL</b>		<b>FY05</b>	<b>FY06</b>	<b>TOTAL</b>
Task 1	\$424,291	Task 17	\$165,253	\$156,770	\$148,921	\$470,944	Task 28	\$119,694	\$77,097	\$196,791
Task 2	\$483,361	Task 18	\$149,704	\$228,998	\$179,151	\$557,853	Task 29	\$151,217	\$100,596	\$251,813
Task 3	\$576,563	Task 19	\$140,865	\$109,349	\$111,884	\$362,098	Task 30	\$144,201	\$126,420	\$270,621
Task 4	\$432,679	Task 20	\$103,587	\$177,101	\$112,539	\$393,227	Task 31	\$0	\$90,973	\$90,973
Task 5	\$271,950	Task 21	\$106,290	\$142,928	\$45,296	\$294,514	Task 32	\$0	\$92,511	\$92,511
Task 6	\$369,218	Task 22	\$56,921	\$91,522	\$21,299	\$169,742	Task 33	\$0	\$178,666	\$178,666
Task 7	\$453,388	Task 23	\$79,941	\$135,153	\$79,814	\$294,908	Task 34	\$0	\$176,199	\$176,199
Task 8	\$350,090	Task 24	\$124,228	\$71,195	\$75,517	\$270,940	Task 35	\$0	\$134,785	\$134,785
Task 9	\$221,001	Task 25	\$91,545	\$133,114	\$59,211	\$283,870	Task 36	\$0	\$15,680	\$15,680
Task 10	\$243,371	Task 26	\$135,776	\$117,525	\$122,040	\$375,341				
Task 11	\$181,019	Task 27	\$79,950	\$120,944	\$104,258	\$305,152				
Task 12	\$281,975									
Task 13	\$424,273									
Task 14	\$313,998									
Task 15	\$247,563									
Task 16	\$247,643									

### Infrastructure Facilities Augmentation

	<b>FY01-02</b>	<b>FY03</b>	<b>FY04</b>	<b>FY 05</b>	<b>FY06</b>	<b>Total</b>
Electron Microanalysis and Imaging Laboratory	\$105,313	\$63,000	\$63,000	\$63,000	\$63,000	\$357,313
Materials Performance Laboratory	\$227,493	\$0	\$0	\$0	\$0	\$227,493
Transmission Electron Microscope	\$1,459,369	\$321,582	\$150,000	\$166,914	\$150,000	\$2,247,865
ICP – Atomic Emission Spectrometer	\$100,163	\$0	\$0	\$0	\$0	\$100,163
Lead-Bismuth and Other Molten Materials Facilities	\$234,198	\$121,579	\$217,227	\$66,843	\$141,654	\$781,501
Machining System and Equipment	\$72,619	\$22,500	\$934	\$0	\$0	\$96,053
Flow Visualization System (Task 2)	\$22,207	\$0	\$0	\$0	\$0	\$22,207
Pyrolizer, Baths, and Controller (Task 15)	\$20,921	\$0	\$0	\$0	\$0	\$20,921
Prof. B.J. Das Startup Package Equipment	\$50,000	\$0	\$49,972	\$0	\$0	\$99,972
Actinide Chemistry Laboratory	\$0	\$260,000	\$123,800	\$98,153	\$270,000	\$751,953
Oxygen Control System	\$0	\$50,000	\$0	\$0	\$0	\$50,000
<b>Totals</b>	<b>\$2,292,283</b>	<b>\$838,661</b>	<b>\$604,933</b>	<b>\$394,910</b>	<b>\$624,654</b>	<b>\$4,755,441</b>

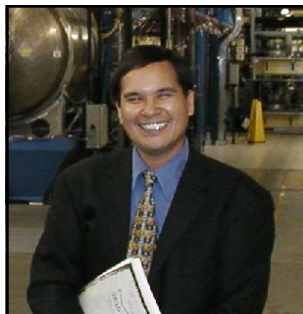
### International Collaboration

	<b>FY01-02</b>	<b>FY03</b>	<b>FY04</b>	<b>FY 05</b>	<b>FY06</b>	<b>Total</b>
Khlopin Radium Institute Contracts	\$342,550	\$23,950	\$0	\$0	\$0	\$366,500
International Science and Technology Center	\$87,500	\$98,250	\$51,700	\$800	\$11,700	\$249,950
International Collaboration Program Coordination	\$92,098	\$33,000	\$70,000	\$12,765	\$64,300	\$272,163
<b>Totals</b>	<b>\$522,148</b>	<b>\$155,200</b>	<b>\$121,700</b>	<b>\$13,565</b>	<b>\$76,000</b>	<b>\$888,613</b>



# Photo Gallery

## Transmutation Research Program Administration



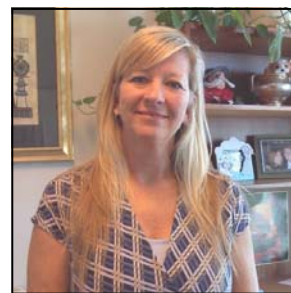
**TRP Director  
Anthony E. Hechanova**



**TRP Deputy Director  
Gary S. Cerefice**



**TRP Finance Director  
Patricia Rugeiro**



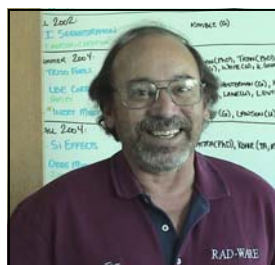
**TRP Finance Director  
Leisa Rodriguez**



**Assistant/Coordinator  
Rebecca Arbour**



**Finance Assistance  
Hallie Lyons**



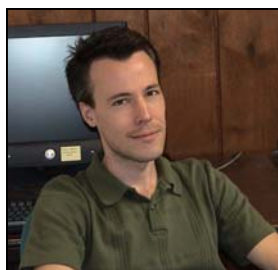
**Laboratory Director  
Thomas O'Dou**



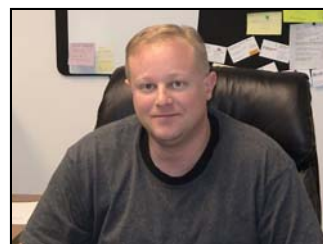
**Laboratory Manager  
Trevor Low**



**Webmaster  
John Knoten**



**HRC Network Admin  
Kris Davidson**



**HRC Travel Coordinator  
Joseph Zimmerman**



**Project Assistance  
Kathy Lauckner**

**Not pictured:**  
Ruby Bynum  
Cristalyne Estella

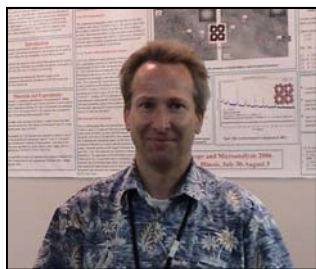


**Program Developer  
Steven Curtis**



**International Programs  
Adviser  
Thomas Ward**

## Transmutation Research Program Staff, Faculty Researchers and Students



**Group Leader  
Structure & Solid Phase Analysis  
Thomas Hartmann**  
(Accepted faculty position at Idaho  
State University Fall 2006)



**Group Leader  
Radiochemistry  
Ken Czerwinski**



**Group Coordinator  
Materials for Nuclear  
Applications, Ning Li (LANL)**



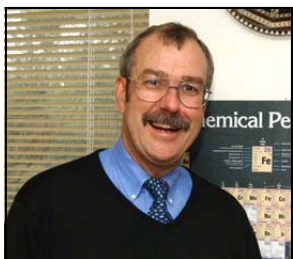
**Assistant Research Professor  
Molten Materials Research  
Jian Ma**



**Assistant Research Professor  
Radiochemistry  
Tyler Sullens**



**Assistant Research Professor  
Materials  
Longzou Ma**



**Visiting Professor  
Radiochemistry  
Al Sattelberger**



**Post Doctoral Researcher  
Cynthia Gong**



**Post Doctoral Researcher  
Frederic Poineau**

**Not pictured:**  
Leslie Jardine, Russian Program Coordinator

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### Task 1:

---



Yitung Chen  
Associate Professor  
Associate Director, NCACM  
Mechanical Engineering Department



Darrell W. Pepper  
Professor  
Mechanical Engineering Department  
Director, NCACM



Taide Tan



Randy Clarksean  
Adjunct Professor  
Mechanical Engineering Department

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Yulien Chen  
Paul Lawson

---

Not pictured



Xiaolong Wu

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### Task 2:

---



Robert A. Shilll, Jr.  
Associate Professor  
Electrical and Computer  
Engineering Department



William Culbreth  
Associate Dean for Research  
College of Engineering

Mohamed B. Trabia  
Chair  
Mechanical Engineering  
Department



Anoop George



Satishkumar  
Subramanian



Qin Xue



Myong Holl



Greg Loll



### Task 3:



John Farley  
Professor  
Department of Physics



Dale Perry  
Adjunct Professor  
Lawrence Berkeley National Lab

Allen Johnson  
Assistant Professor  
Department of Chemistry



Umar Younas



Brian Hosterman



Dan Koury



Thao Trung Ho



Julie Manzerova



Denise Parsons



Lindsay Wylie



Chris Harland



Stacy Sidle

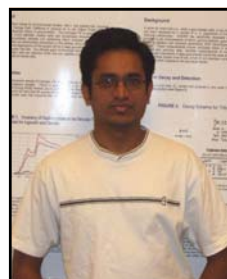
### Task 4:



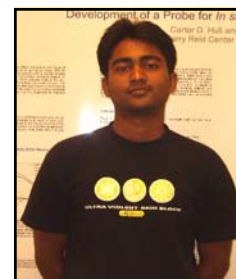
Ajit Roy  
Professor  
Department of Mechanical Engineering



Mohammad Hossain



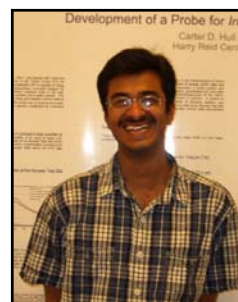
Sudheer Sama



Venkataramakrishnan  
Selvaraj



Ramprashad Prabhakaran



Phandi Gudipati

Nikata Agarwal  
Aaron Tippetts

Not pictured



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### Task 5:

---



Samir Moujaes  
Associate Professor  
Department of Mechanical Engineering

Yitung Chen  
Associate Professor  
Associate Director, NCACM  
Department of Mechanical Engineering



Kanthi Dasika



Chao Wu

Narain Armbya

Not pictured



Guanjun Li

---

### Task 6:

---



Denis Beller  
Research Professor  
Department of Mechanical Engineering



Timothy Beller



Brice Howard



Dean Curtis



Steve Curtis



Shruti Patil

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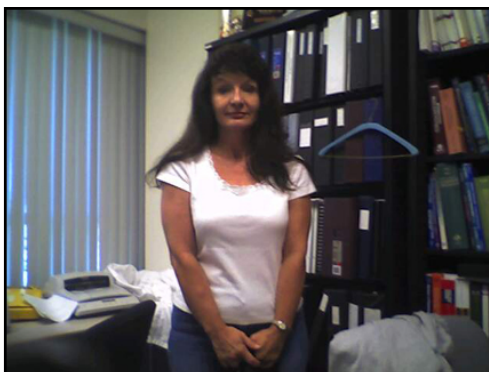
### Task 7:

---



Phillip Patton  
Associate Professor  
Department of Health Physics

Mark Rudin  
Associate Professor  
Department of Health Physics



Deanna Tuttle

---

Tserenpagma Chaoui  
Ashley Gann  
Sung Yop Kim  
Jeffrey Wyler  
John Shanahan  
Yayun Song

---

Not pictured

---

### Task 8:

---



Yitung Chen  
Associate Professor  
Associate Director, NCACM  
Mechanical Engineering Department

Sean Hisieh  
Research Associate Professor  
Mechanical Engineering Department



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Sushma Gujjula  
Sridhar Munaga

---

Not pictured



Darrell W. Pepper  
Professor  
Mechanical Engineering Department  
Director, NCACM



Jianhong Li



Haritha Royyuru



Lijian Sun

## Task 9:



Georg Mauer  
Professor  
Department of Mechanical Engineering



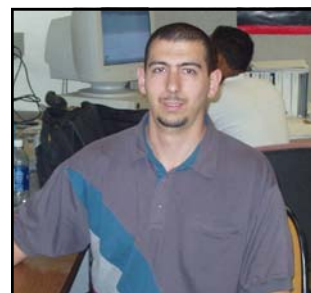
Caroline Wiejak  
Visiting Scholar



Richard Silva



Jae-Kyu Lee



Jamil Renno

## Task 10:



Ajit Roy  
Professor  
Department of Mechanical Engineering

Brendan O'Toole  
Associate Professor  
Department of Mechanical Engineering



Venkata Potluri



Srinivas Kukatla

Prad Koppula  
Raymond Kozak

Not pictured



Mark Jones



John Motaka



Martin Lewis



Bhagath Yarlaga



## Tasks 11 & 12:



William Culbreth  
Associate Dean for Research  
College of Engineering

Denis Beller  
Research Professor  
Mechanical Engineering Department



Robin Jenkins  
Ashraf Kaboud

Not pictured



Robert O'Brien



Suresh Sadineni



Daniel Lowe

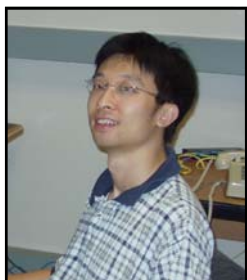


Trevor Wilcox



Elizabeth Bakker

## Task 13:



Yingtao Jiang  
Assistant Professor  
Department of Electrical and Computer Engineering

Bingmei Fu  
Assistant Professor  
Department of Mechanical Engineering

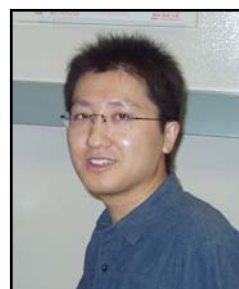


Yi Lu  
Shahidur Rahaman

Not pictured



Jian Ma  
Assistant Research Professor  
Department of Mechanical Engineering



Xiaolong Wu



### Task 14:



Ajit Roy  
Professor  
Department of Mechanical Engineering



Vikram Marthandam

Raghunandan Karamcheti  
Bhagath Yarlagadda

Not pictured



Satish Dronavalli



Silpa Budugur



Anand Venkatesh



Srinivas Chanda



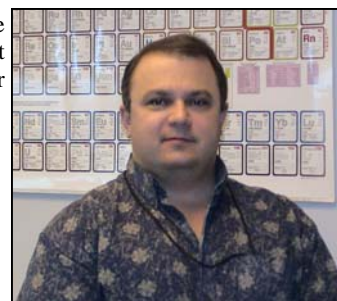
Subhra Bandyopadhyay

### Task 15:

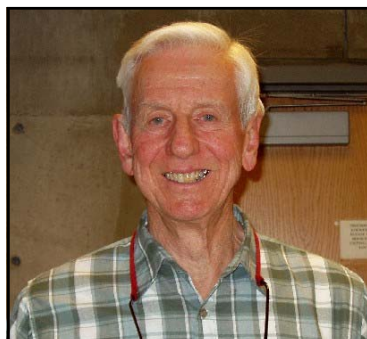


Spencer Steinberg  
Professor  
Department of Chemistry

Gary Cerefice  
Research Scientist  
Harry Reid Center



Ginger Kimble



David Emerson  
Emeritus Professor  
Department of Chemistry

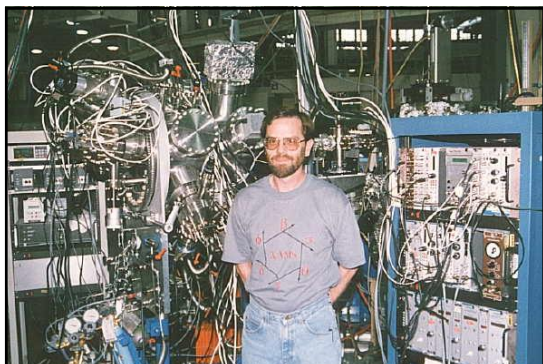


James Dorman



Nancy Birkner

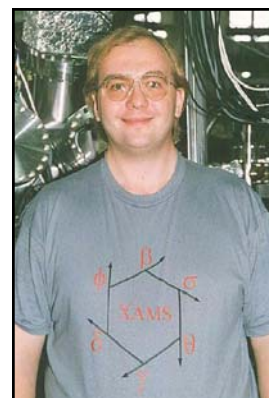
## Task 16:



Dennis Lindle  
Professor  
Department of Chemistry



Dale Perry  
Adjunct Professor  
Department of Physics



Oliver Hemmers  
Assistant Research Professor  
Department of Chemistry

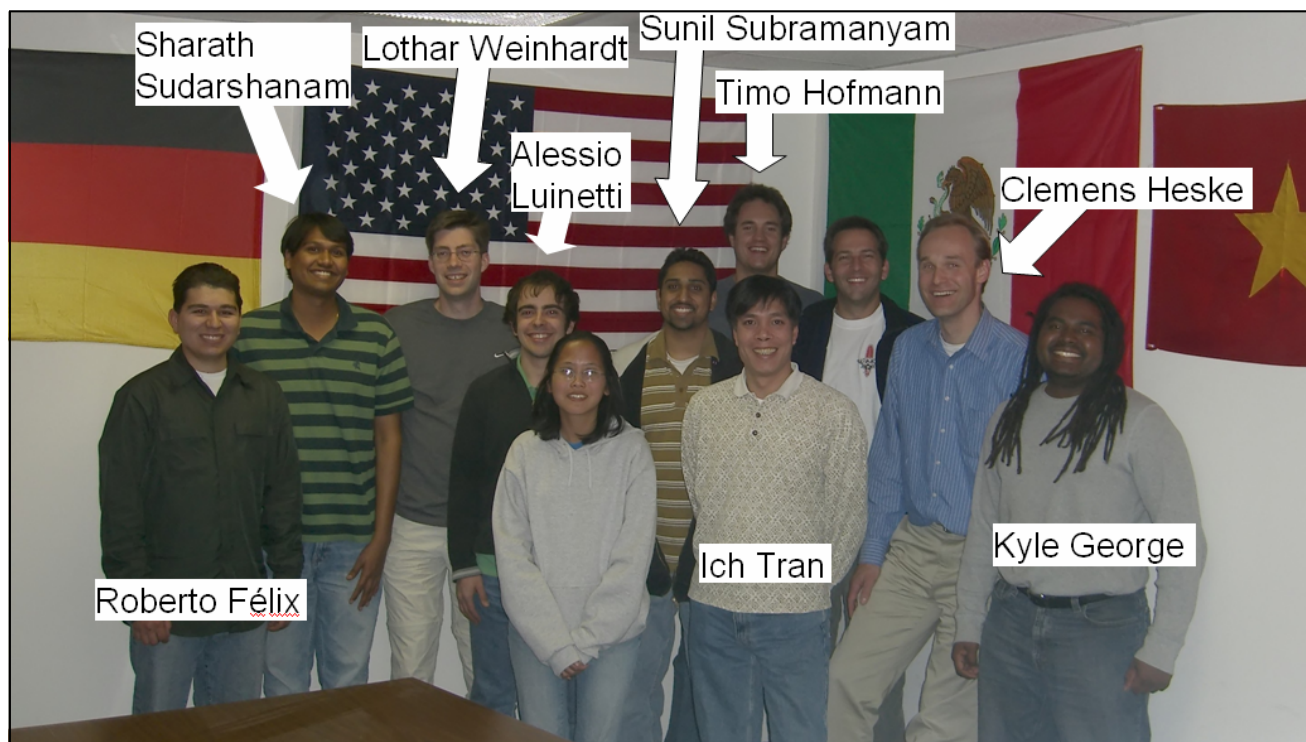


Chinthaka Silva



Chirantha Rodrigo

## Task 17:



Lothar Weinhardt  
Post-Doctoral Fellow  
Department of Chemistry

Clemens Heske  
Associate Professor  
Department of Chemistry



## Task 18:



John Farley  
Professor  
Department of Physics

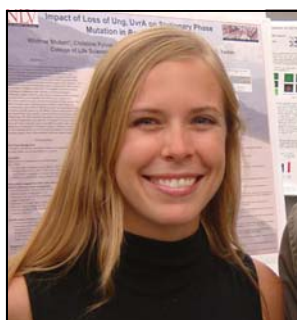


Thao Trung Ho

Allen Johnson  
Assistant Professor  
Department of Chemistry



Dan Koury



Jenny Welch



Timothy Lane



Brian Hostermann

## Task 19:



Ken Czerwinski  
Associate Professor  
Department of Chemistry

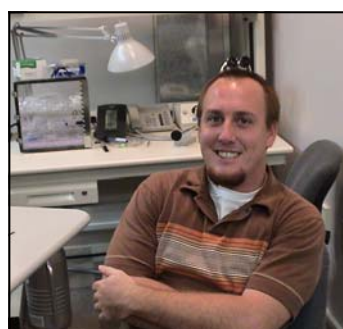
Thomas Hartmann  
Staff Scientist  
Harry Reid Center

Deborah Callway

Not pictured



Frederic Poineau



Kiel Holliday

### Task 20:



Ajit Roy  
Professor  
Department of Mechanical Engineering



Pankaj Kumar



Sreenivas Kohir



Debajyoti Maitra

### Task 21:



Yitung Chen  
Associate Professor  
Department of Mechanical Engineering

Jichun Li  
Assistant Professor  
Department of Mathematics

Chaiyod Soontrapa  
Jinsuo Zhang

Not pictured



Huajun Chen  
Postdoctoral Researcher  
Department of Mechanical Engineering



Taide Tan



---

### Task 22:

---



Georg Mauer  
Professor  
Department of Mechanical Engineering



Koushik Damera

---

Kyle Gohres  
Tobias Kotthaeuser  
Prathima Sajja

---

Not pictured

---

### Task 23:

---



Biswajit Das  
Associate Professor  
Department of Electrical and Computer  
Engineering



Arghya Banerjee



Tan Wu

---

Kishore Sreenivasan  
Rani Krishna  
Nilanjan Halder  
Lillian Ratliff

---

Not pictured

## Task 24:



Yitung Chen  
Associate Professor  
Department of Mechanical Engineering

Sean Hisieh  
Research Associate Professor  
Mechanical Engineering Department



Jianfei Wu

Not pictured



Ling Kwan



Ming Chang



Matthew Hodges



Ruilong Li

## Task 25:



David Hatchett  
Assistant Professor  
Department of Chemistry

Ken Czerwinski  
Associate Professor  
Department of Chemistry



Sujanie Gamage

Not pictured



Sandra Elkouz



Wendy Pemberton

---

### Task 26:

---



Ken Czerwinski  
Associate Professor  
Department of Chemistry

---

Mari Bonaud  
Michel Draye  
Ira Racoma  
Lena Wright

---

Not pictured



Cynthia Gong



Wendy Pemberton



Amber Wright

---

### Task 27:

---



Denis Beller  
Research Professor  
Department of Mechanical Engineering



Evgeny Stankovskiy



Timothy Beller & Ryan LeCounte set up the High-Power RACE Target experiment at the Idaho Accelerator Center.



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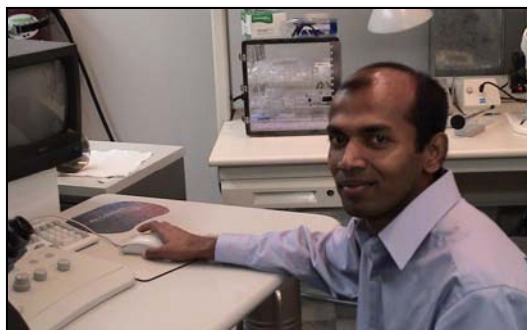
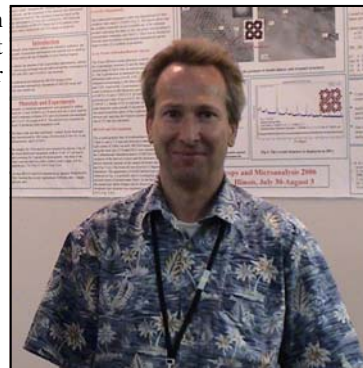
### Task 28:

---



Ken Czerwinski  
Associate Professor  
Department of Chemistry

Thomas Hartmann  
Staff Scientist  
Harry Reid Center



Chinthaka Silva

---

### Task 29:

---



Gary Cerefice  
Research Scientist  
Harry Reid Center

Ken Czerwinski  
Associate Professor  
Department of Chemistry



Jeremy Maute

Not pictured



Nicholas Smith

### Task 30:



Denis Beller  
Research Professor  
Department of Mechanical Engineering

Warnick Kernan  
Lawrence Lakeotes  
Pavan Attur  
Luis Durani  
Ryan LeCounte

Not pictured



Timothy Beller



Quinten Newell

### Task 31:



Jian Ma  
Assistant Research Professor  
Department of Mechanical Engineering

Woosoon Yim  
Professor  
Department of Mechanical Engineering



Joon Soo Lee  
Assistant Research Professor  
Department of Mechanical Engineering



Xiuju (Julia) Tan

### Task 32:



Daniel Cook  
Assistant Professor  
Department of Mechanical  
Engineering



Yitung Chen  
Associate Professor  
Department of Mechanical Engineering

Jian Ma  
Assistant Research Professor  
Department of Mechanical Engineering



Huajun Chen  
Postdoctoral Researcher  
Department of Mechanical  
Engineering

Lucas Bang  
Lillian Ratliff  
Matthew Cutler  
Chensong Dai  
Siul Ruiz

Not pictured

### Task 33:



Ken Czerwinski  
Associate Professor  
Department of Chemistry

Thomas Hartmann  
Staff Scientist  
Harry Reid Center



Frederic Poineau



Julie Gostic

Julie du Bouchau du Mazaubrun

Not pictured

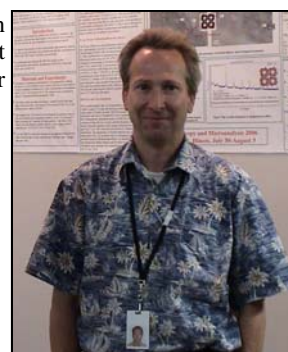


### Task 34:



Tyler Sullens  
Assistant Research Professor  
Department of Mechanical Engineering

Thomas Hartmann  
Staff Scientist  
Harry Reid Center



Ken Czerwinski  
Associate Professor  
Department of Chemistry



Edward Mausolf

### Task 35:



Denis Beller  
Research Professor  
Department of Mechanical Engineering



Timothy Beller

Lawrence Lakeotes  
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### Task 36:



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# Acronyms

ACS	American Chemical Society	FLUENT	Computational Fluid Dynamics Code
ADSS	Accelerator-driven subcritical systems	GNEP	Global Nuclear Energy Partnership
ADTTA	Accelerator-Driven Transmutation Technologies and Applications	GUI	Graphical user interface
AFC	Advanced Fuel Cycle	HAZ	Heat Affected Zone
AFCI	Advanced Fuel Cycle Initiative	HE	Hydrogen embrittlement
AHA	Acetohydroxamic acid	HEPA	High efficiency particulate air
ALI	Annual limit on intake	HLM	Heavy Liquid Metals
ALIP	Annular, Linear Induction Pump	HR	High resolution
AMAD	Activity median aerodynamic diameter	HTGR	High Temperature Gas-Cooled Reactor
AMPT	Advance in Materials and Processing Technologies	HTMEF	High Temperature Materials Experiments Facility, UNLV
AMUSE	Argonne Model for Universal Solvent Extraction	IAC	Idaho Accelerator Center, Idaho State University
ANL	Argonne National Laboratory	IC	Ion Chromatography
ANS	American Nuclear Society	ICONE	International Conference on Nuclear Engineering
ASM	American Society of Metals	ICRP	International Commission on Radiological Protection
ASME	American Society of Mechanical Engineers	IEEE	Institute of Electrical and Electronics Engineers, Inc.
ASTM	American Society for Testing and Materials	INL	Idaho National Laboratory
CAD	Computer aided design	IPPE	Institute for Physics and Power Engineering
CAINE	Computer Applications in Industry and Engineering	IR	Infrared
CCD	Charge-coupled device	ISM	Induction skull melter
CEA	French Atomic Energy Commission	ISRS	International Symposium of Research Scholars
CFD	Computational fluid dynamics	ISTC	International Science and Technology Center
CL	Constant load	ISU	Idaho State University
CPP	Cyclic potentiodynamic polarization	IYNC	International Youth Nuclear Congress
CTD	Chemical Technology Division	KRI	Khlopin Radium Institute, St. Petersburg, Russia
CV	Cyclic Voltammogram	KRI-KRISI	Khlopin Radium Institute Research Industrial Enterprise, St. Petersburg, Russia
CW	Cold-worked	LANL	Los Alamos National Laboratory
DAC	Derived air concentration	LANSC	Los Alamos Neutron Science Center
DAQ	Data Acquisition	LBE	Lead-bismuth eutectic
DC	Dose coefficient	LFS	Laser Fluorescence Spectroscopy
DCAL	Dose and risk calculation software	MATLAB	A software system integrating mathematical computing and visualization
DCB	Double-cantilever beam	MCNP	Monte Carlo n-particles code
DELTA	Development of Lead-Bismuth Target Applications (test loop at LANL)	MCNPX	Monte Carlo n-particles code, extremely high-energy version
DOE	U.S. Department of Energy	MPAC	Materials Protection, Accounting, and Control
DSA	Dynamic Strain Ageing	MPI	Message passing interface
DSC	Differential scanning calorimetry	MS&T	Materials Science and Technology
DTA	Differential thermal analysis	MS SQL	Microsoft Standard Query Language
ECS	Electrochemical Society	MS VB	Microsoft Visual Basic
EDAX	Energy dispersive x-ray spectroscopy	MSZ	Magnesia Stabilized Zirconia
EDS	Energy dispersive spectrometry	NACE	National Association of Corrosion Engineers
EDX	Energy Dispersive X-Ray Analysis	NE	Office of Nuclear Energy
EELS	Electron energy loss spectrometry	NEDHO	Nuclear Engineering Department Heads Organization
%El	Percent elongation	NERI	Nuclear Energy Research Initiative
ENSDF	Evaluated nuclear structure data file		
EUROTRANS	European research program for the transmutation of high level nuclear waste in an accelerator driven system		
FCC	Fullerene containing carbon		
FEM	Finite Element Method		
FGR	Federal Guidance Report		
FL	Fusion-Line		
FLEX	Fluoride extraction process		



NICEST	Neutrons in Solid-State Chemistry and the Earth Sciences Today and Tomorrow	UHV	Ultra High Vacuum
NMDS	Neutron multiplicity detector system	UNLV	University of Nevada, Las Vegas
NMR	Nuclear Magnetic Resonance	UREX	Uranium extraction process
NOM	Natural organic matter	UREX+	Uranium extraction process plus
NTS	Nevada Test Site	UT	University of Texas
NUBASE	A nuclear properties database	UTS	Ultimate tensile strength
ORNL	Oak Ridge National Laboratory	UV	Ultra-violet
OTA	Oxygen Thermodynamic Activity	UV-Vis	UV-visible
PANI	Polyaniline	XAFS	X-ray absorption fine-structure spectroscopy
PAS	Positron annihilation spectroscopy	XML	Extensible markup language
PEELS	Parallel energy loss spectroscopy	XPS	X-ray photoelectron spectroscopy
PNNL	Pacific Northwest National Laboratories	XRD	X-ray diffraction
PUREX	Plutonium extraction process	YS	Yield strength
PVM	Parallel virtual machine	YSZ	Yttria-stabilized zirconia
%RA	Percent reduction in area		
RACE	Reactor-accelerator coupled experiment		
RADDB	Radiological Data Base		
RCRA	Resource Conservation and Recovery Act		
R&D	Research and Development		
RELAP	Plant Safety Modeling Code		
RGA	Residual gas analyzer		
RSL	Remote Sensing Laboratory		
RT	Room temperature		
RTIL	Room Temperature Ionic Liquid		
SAMPE	Society for the Advancement of Materials and Process Engineering		
SCA	Sub Critical Assembly		
SCALE	Standardized Computer Analyses for Licensing Evaluation code		
SCC	Stress corrosion cracking		
SDS	Slowing Down Spectrometer		
SEE	Secondary electron emission		
SEM	Scanning electron microscope		
SFR	Sodium-Cooled Fast Reactor		
SFTF	Spent Fuel Treatment Facility		
SNS	Spallation Neutron Source		
SRNL	Savannah River National Laboratory		
SS	Stainless steel		
SSR	Slow-strain-rate		
STAR-CD	A commercial computational fluid dynamics software package		
SXF	Soft X-ray Fluorescence		
TBP	Tributylphosphate		
TC-1	Target Complex 1		
TEM	Transmission electron microscope		
TFSI	bis(trifluoromethylsulfonyl)amide		
TG/DSC	Thermogravimetry and Differential Scanning Calorimetry		
TOF-SIMS	Time of Flight Secondary Ion Mass Spectrometer		
TRIGA	Training, Research, Isotopes, General Atomics		
TRISO	A silicon carbide and pyrocarbon composite coating		
TRLFS	Time Resolved Laser-Induced Fluorescence Spectroscopy		
TRP	UNLV Transmutation Research Program		
TRPSEMPro	TRP System Engineering Model Program		
TRU	Transuranic actinides		
TTF	Time-to-failure		





## **References**

UNLV Transmutation Research Program references, current activities and other miscellaneous information can be found on the TRP website at:

<http://aaa.nevada.edu>

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