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2006

University of Nevada, Las Vegas Transmutation Research Program Annual Report Academic Year 2005-2006

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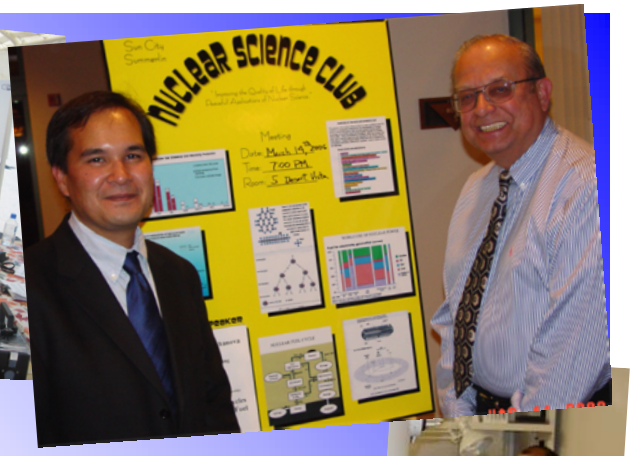
University of Nevada, Las Vegas

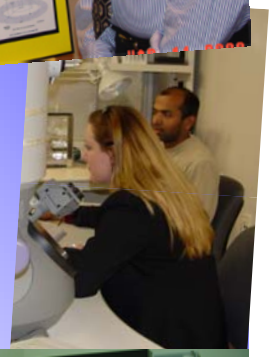
Transmutation Research Program

Annual Report

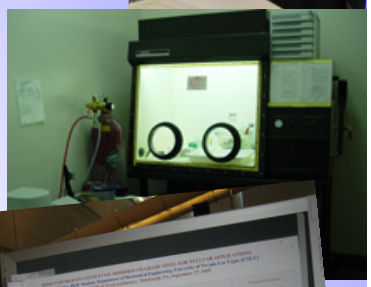
Academic Year 2005-2006

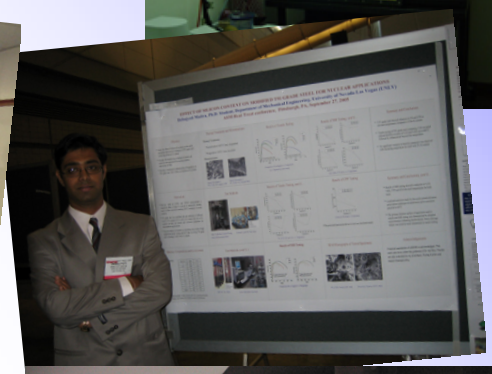
Harry Reid Center for Environmental Studies

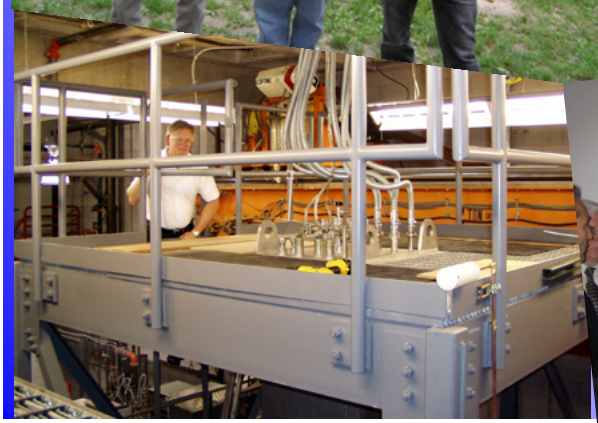




University of Nevada, Las Vegas Transmutation Research Program Annual Report Academic Year 2005-2006







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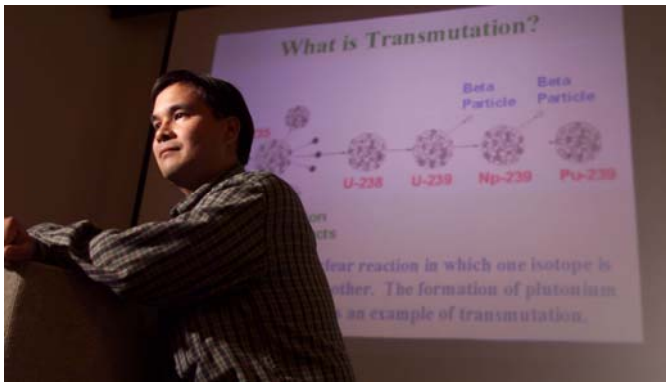
Letter from the Director



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

UNLV
UNIVERSITY OF NEVADA LAS VEGAS

It is my pleasure to present the UNLV Transmutation Research Program's fifth annual report that highlights the academic year 2005 – 2006. Supporting this document are the many technical reports and scientific papers 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 fifth year of our program, we saw amazing growth in the Radiochemistry Ph.D. program with a total of 12 students in the second year of the program (twice the number we anticipated in the program proposal). In the back of this issue, under Infrastructure Augmentation, you will find some news about the new academic programs sponsored by the TRP. Since our inception, the program has sponsored to their conclusion 38 M.S. and 2 Ph.D. degrees. The program supported 47 graduate students and 23 undergraduates in 6 academic departments across the UNLV scientific and engineering communities in the academic year 2005-2006.

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 transmutation.

The primary role of the UNLV program in the national effort is the training of 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-one independent student research tasks, supporting 47 graduate students and 23 undergraduates, were 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-added priority area on material protection and accounting and control.

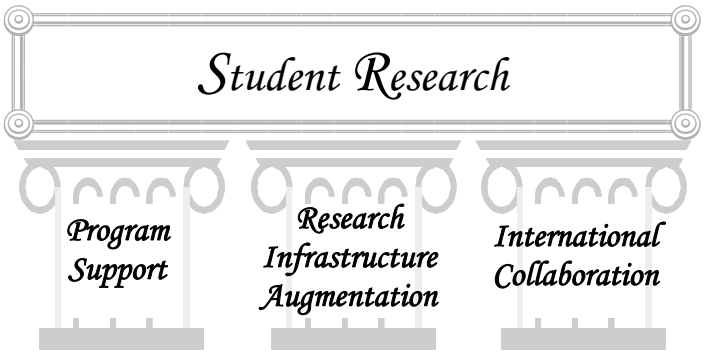
UNLV graduate students, from left, Daniel Lowe, Robert O'Brien, Joydeep Pal, and Debajyoti Maitra staff a booth at the ANS Student Conference at Rensaellaer Polytechnic Institute in Troy, NY March 30 to April 1, 2006.

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

UNLV students and faculty staffed an informational booth on radioactivity and nuclear waste management at the Fall Festival in the Town of Pahrump, October 1 and 2, 2005. Pictured above are postdoctoral scholar Cynthia Gong, graduate student Amber Wright, and MIT graduate student Lisa Mullen (currently finishing her research in the laboratories at UNLV. Pictured below are UNLV Research Professor Thomas Hartmann (second from left) and graduate student Julie Gostic (far right) speaking to interested members of the community at the Pahrump Fall Festival.

Program Overview



UNLV Transmutation Research Program Components

student research projects, coordination with the national and international 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 team of Russian scientists from the Institute for Physics and Power Engineering in Obninsk, Russia, who successfully installed a Russian-built lead-bismuth loop. In addition, a new project entitled "Preparatory Work for the Systematic Measurements and Evaluation of Minor Actinide Nuclear Data" was initiated with the Research Coordinative Center on the Problem of Muon Catalyzed Fusion and Exotic Quantum Systems in Moscow, Russia.

The international collaboration component also supported three joint research proposals: two between UNLV and the Khlopin Radium Institute (UNLV Tasks 15 and 16) and one with the Ben Gurion University of the Negev (Task 19).

Radiochemistry pioneer Darlene Hoffman (fourth from the right) visits with Radiochemistry Ph.D. students at UNLV on October 5, 2005.

The program support component sponsored a number of workshops and meetings this year between UNLV researchers and 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 ANS Student Conference at Troy, New York and the American Chemical Society's Radiochemistry Workshop in Atlanta, Georgia.

The official grand opening of the Transmission Electron Microscopy User Facility took place on October 7, 2005. Pictured above are UNLV top administrators observing Research Professor Longzhou Ma (seated) demonstrate the use of the TEM.

Students and faculty sponsored by the TRP from Ben Gurion University of the Negev with TRP Director at a conference in Zagreb, Croatia, June 2005. From left, graduate student Emil Fridman, UNLV TRP Director Anthony Hechanova, Professor Sion Koren, and graduate student Sergei Kolesnikov.

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) program. In February 2006, the Bush administration announced a broad program that effectively expanded the AFCI program and accelerated the development of commercial-scale facilities. The goals of the national program are to:

- Reduce America's dependence on foreign sources of fossil fuels and encourage economic growth.
- Improve our environment.
- Recycle nuclear fuel using new technologies to recover more energy and reduce waste.
- Encourage prosperity, growth and clean development around the world.
- Utilize the latest technologies to reduce the risk of nuclear proliferation worldwide.

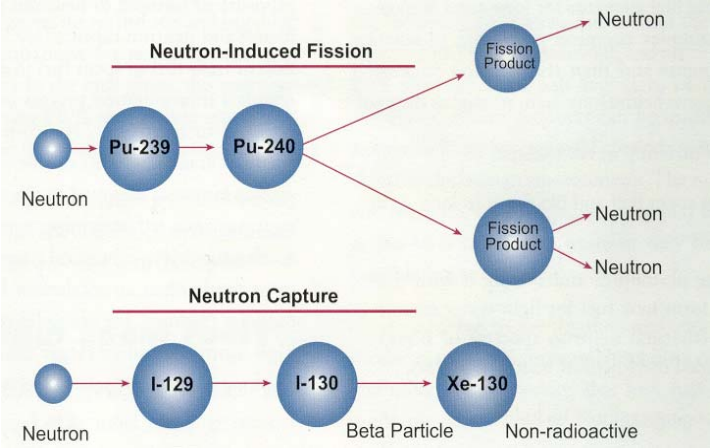
The Global Nuclear Energy Partnership logo. More information about the national program can be found at www.gnep.energy.gov.

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.

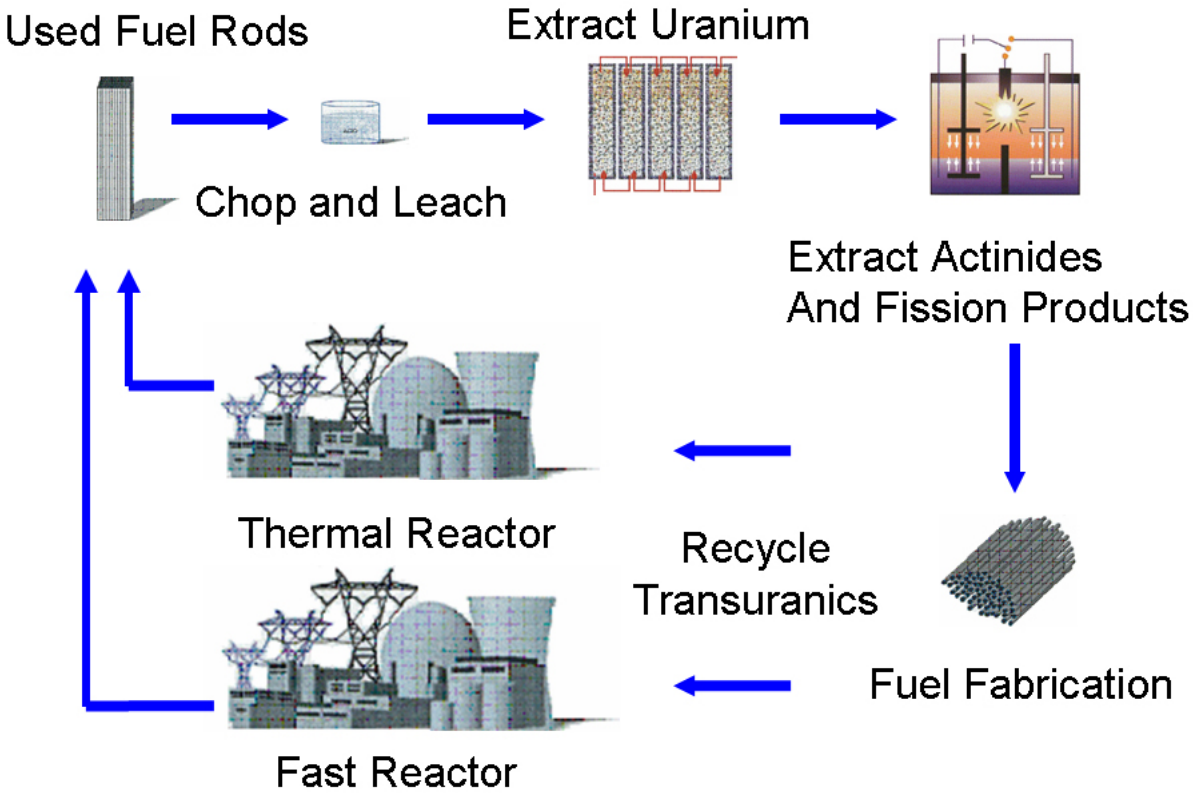
Neutron-Induced Fission (top): a neutron is captured by a fissile actinide (e.g. Plutonium-239) and is induced to split (or fission).

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.

Benefits from Transmuting Nuclear Waste

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

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.

REDUCE, REUSE, RECYCLE, RESEARCH

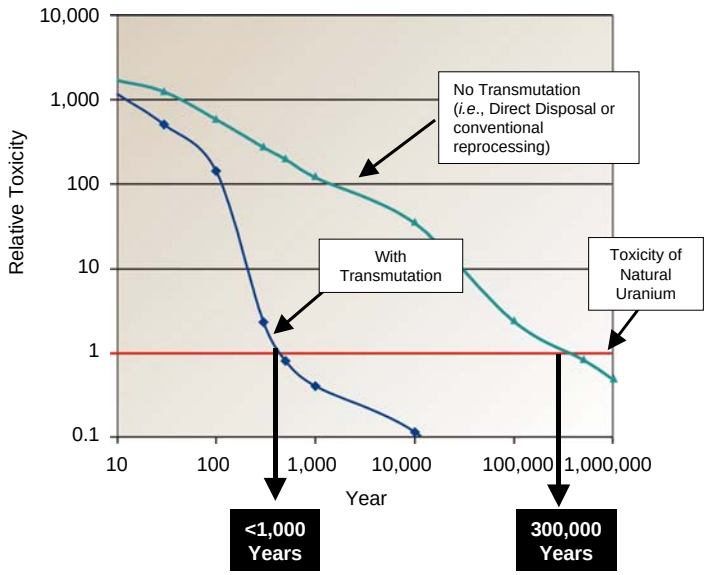
(1) The initial amount of high-level radioactive waste will be reduced by virtue of separation (only two percent of used nuclear fuel is highly radioactive, the rest, if separated, can be classified as low-level or non-radioactive).

(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.

(5) The accelerator process will provide a powerful proton source that could be used in medical therapy and to produce isotopes for a variety of applications such as: medical isotopes, industrial isotopes and research isotopes.



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

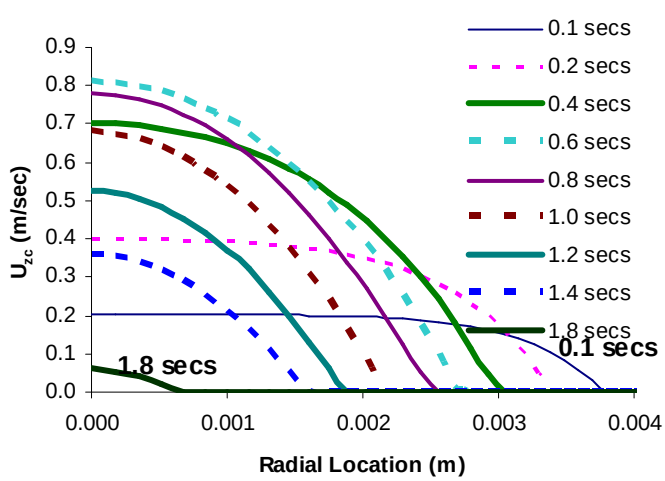
Development of the induction-heating model: Modeling efforts centered on the development of the governing equations, incorporating these equations into computer codes, setting up a test problem, and making preliminary calculations for the geometry of interest. Detailed analyses were conducted for an Induction Skull Melter (ISM) 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, inter-facial heat transfer coefficient = 2,000 W/m^2-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," *ICHMT 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.

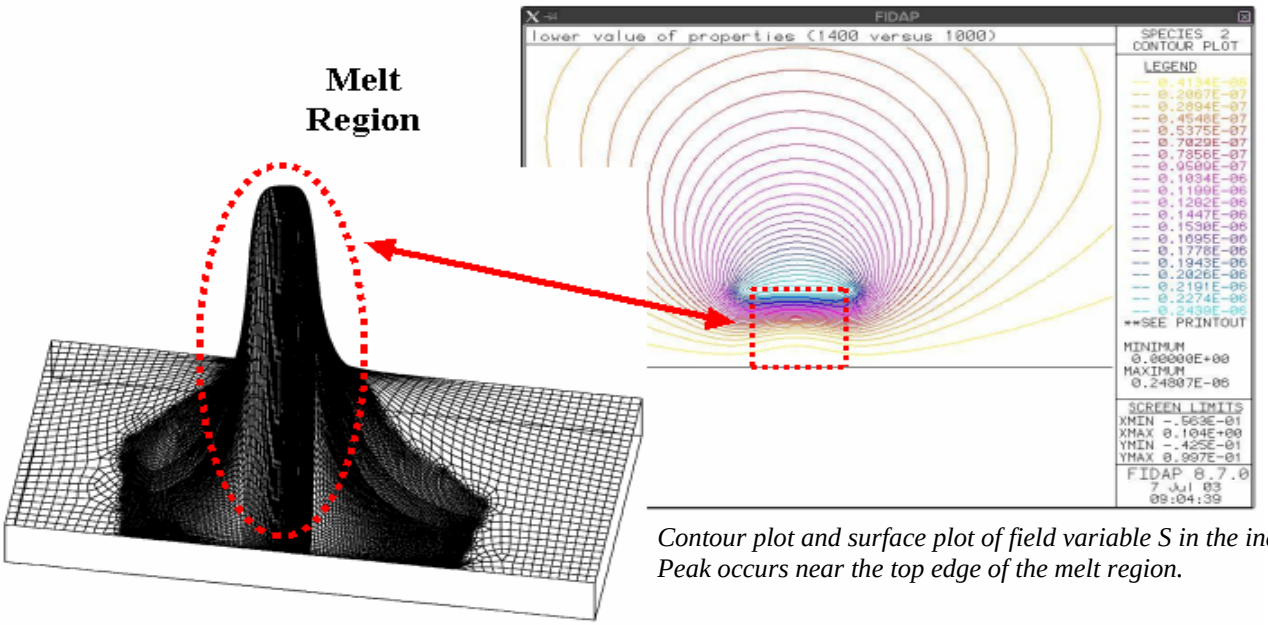
T. Tan, R. Clarksean, Y. Chen, S. Hsieh, and M. Meyer, "Simulating the Induction Heating Process in an Induction Skull Melter for Casting Metallic Fuel," *ICONE-12*, Arlington, VA, April 25-29, 2004.

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

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Randy Clarksean, Adjunct Professor, Mechanical Engineering Department

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Taide Tan and Xiaolong Wu, Graduate Students, Mechanical Engineering Department
Yulien Chen and Paul Lawson, Undergraduate Students

Collaborators

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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

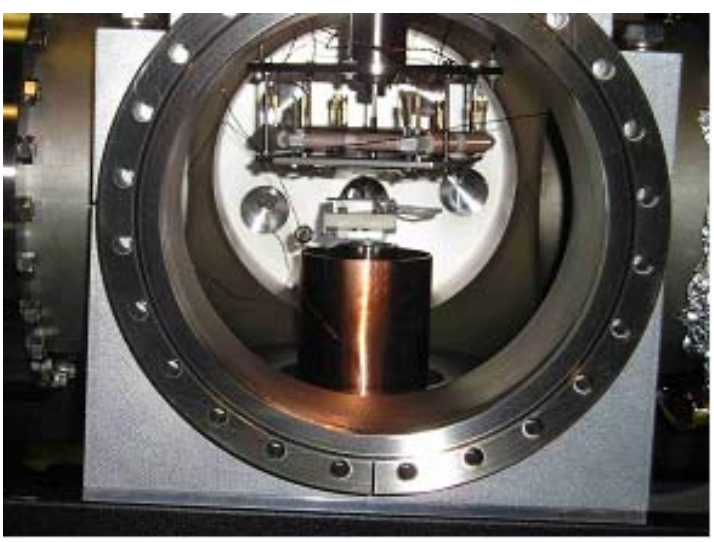
One of the key technologies for the deployment of accelerator-driven transmutation systems is the accelerator itself. Elliptical superconducting niobium cavities are used to increase the efficiency of the high-power accelerators needed to support the transmutation mission.

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 ideal properties.



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.

A Monte Carlo secondary electron microscopy (SEM) 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 a UHV 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

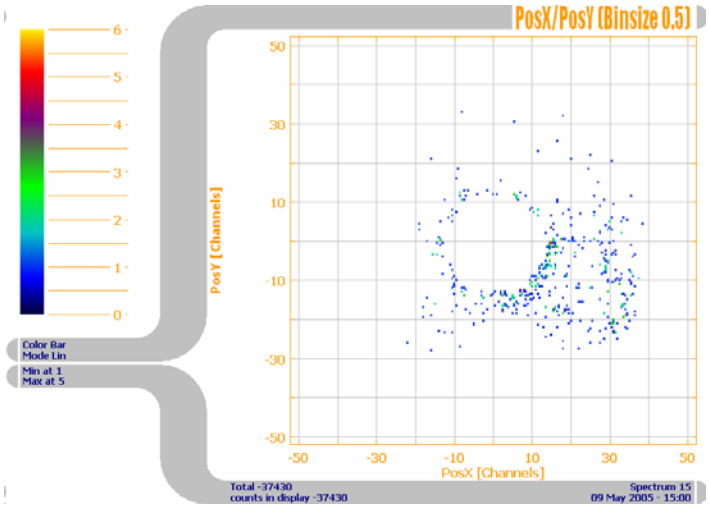
Monte Carlo SEE Code Development and Modifications: A Monte Carlo secondary electron emission code based on the "Single Scatter" approach was obtained from Dr. David Joy of both ORNL and the University of Tennessee. The "Single Scatter" approach follows the primary electron and each generation of secondary 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 (Secondary Electron Emission) 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 secondary electron emission (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 niobum 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 with in 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 Sumbramanian, 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*, ASME 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," ANS Student Conference, April 1-4, 2004, Madison, WI. (Outstanding Student Paper Award)

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Collaborator

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Task 3

Corrosion of Steel by Lead Bismuth Eutectic

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

BACKGROUND

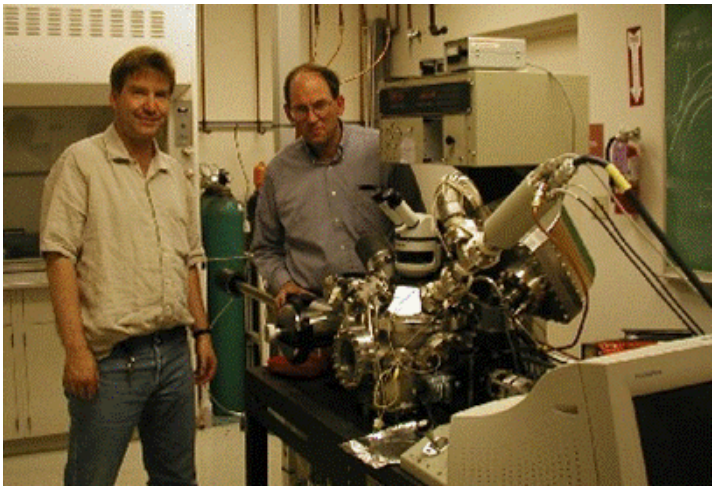
There is an active international interest in lead-bismuth eutectic and similar liquid lead systems because of the relevance to the transmutation of nuclear waste, fast reactors, and spallation neutron sources.

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 (SEM), Energy Dispersive X-ray (EDAX) spectroscopy, X-ray Photoelectron Spectrometry (XPS), and laser Raman spectrometry.



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

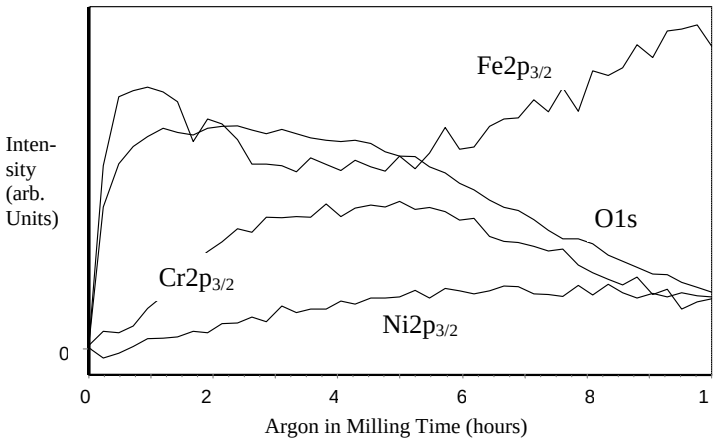
These techniques, applied to the steel surface, have probed the surface morphology, elemental composition, and oxidation states as a function of position. Chemical alterations and resulting chemical species were studied at the steel surface. Additionally, the experimental facilities at the Advanced Light 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

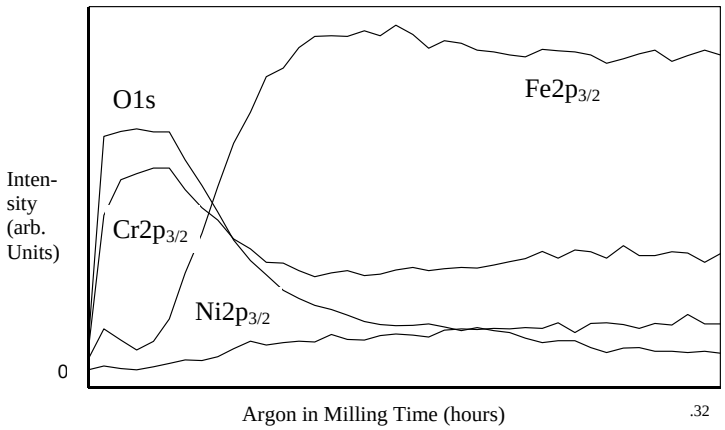
Several samples were compared having the same or similar compositions (standard nuclear grade 316/316L) but different surface preparation, including cold-rolled, annealed and a special low-corrosion treatment, "D-9." The cold-rolled sample had an order of magnitude less corrosion (i.e., both lower oxidation 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 IPPE 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 INL. Several unique features were observed: at low silicon concentrations in the starting alloy, the silicon was found as a silicate (SiO_3^{--}). As the concentration of silicon increased in the starting alloy, a layer containing silica (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.



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 (LBE) 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 (LBE) 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," ANS Topical Mtg. on Accelerator Applications, AccApp/ADTTA01, Reno, NV, Nov. 2001.

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Thao Trung Ho and Julia Manzerova, Graduate Students, Department of Chemistry
Denise Parsons and Lindsay Wylie, Undergraduate Students, Department of Physics
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Task 4

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

A.K. Roy

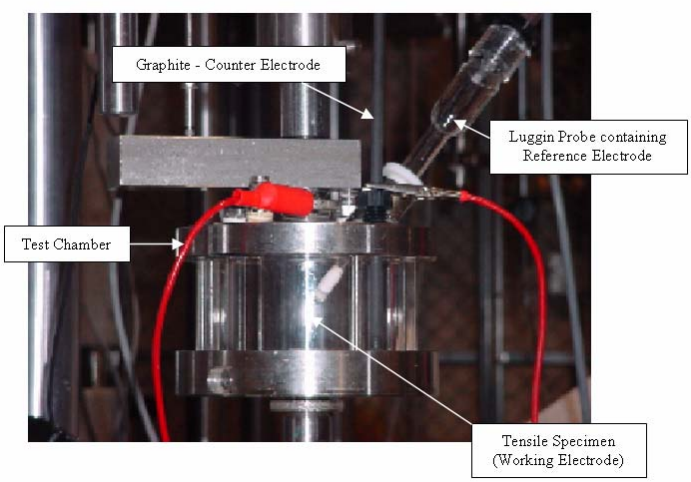
BACKGROUND

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.

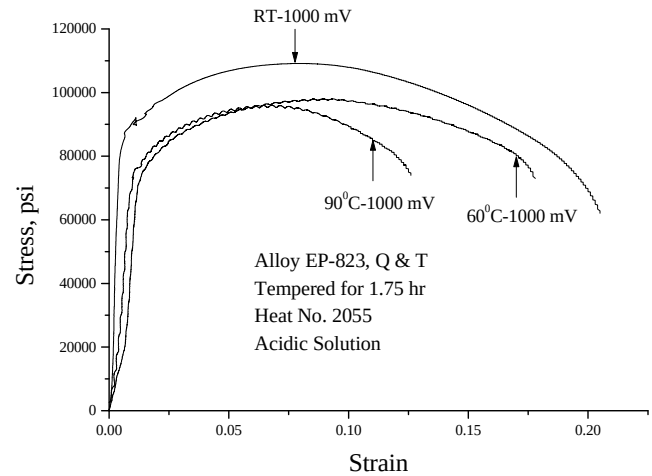
Accelerator-driven transmutation systems involve bombarding a target material such as molten lead-bismuth-eutectic (LBE) by a proton beam, thereby producing neutrons. The molten LBE target will be contained in a subsystem structural container made of a suitable material such as Alloys HT-9, EP-823, and 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 (CPP) were employed to evaluate these corrosion phenomena. The susceptibility of these alloys to HE was evaluated by applying cathodic potential while 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.



Controlled Potential Test Setup



Stress vs Strain under Controlled Potential.

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 (σ_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 σ_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 (σ_{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 σ_{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 (σ_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 σ_f value was increased due to plastic constraint resulting from triaxial stress field at the notch.
- The magnitude of %El, %RA, TTF, and σ_f was reduced under

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*, ASM International, (In Review).

A.K. Roy, M. K. Hossain, R. Prabhakaran and S. Sama, "Environment-Assisted Cracking of Structural Materials under Different Loading Conditions," *Corrosion*, 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," 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 (IYNC) 2004, 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," 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," TMS 2004, 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," ANS 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," 204th Meeting of the Electrochemical Society (ECS), 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," ANS 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 10th 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 (SNS)-JINS-NICEST 2003, 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.

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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-ε 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.

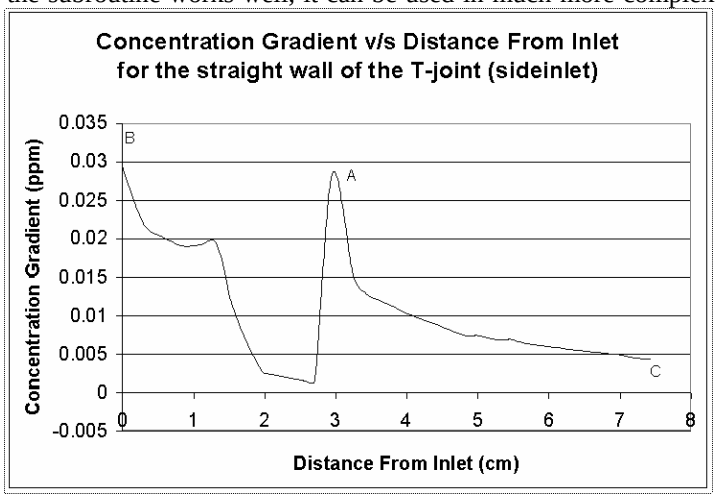
The k-ε Chen model which works better with high Re number flows and predicts some of the peculiar flow features relevant to sudden expansions where eventually vortex generation is expected at the backward step.

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 Fe_3O_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.



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

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," ANS National Conference, 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," NURETH-10, South Korea Oct. 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," ICAPP Conference, Hollywood Florida, ANS, June 2002.

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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

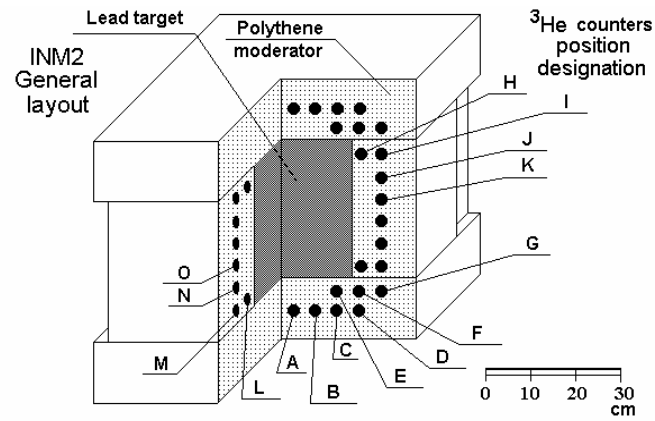
A prototype modular Neutron Multiplicity Detector System (NMDS) with 64 ^{3}He gas counting tubes was developed to measure the neutron multiplicity of scaled lead accelerator targets. Its modularity allows it to be configured for a variety of experiments to measure neutron multiplicity from different 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}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}He as well as fractional capture in Pb and polyethylene were calculated. A ^{252}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 n/s ±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 ~600 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 deadtime, a deadtime 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 deadtime 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 deadtime. 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*, OECD/NEA, 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 Particle and Nuclei International Conference (PANIC05)*, Santa Fe, New Mexico, October 24-28, 2005.

D. Curtis, D. Beller, C. Hull, A, Rimsky-Korsakov, and T, Ward, "Modeling Neutron Multiplicities in a 60-element ^{3}He Detector System," *Proc. of the Sixth International Meeting on Nuclear Applications of Accelerator Technology (AccApp'03)*, 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 & Transmutation (OECD/NEA), 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 3He 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," ANS Conference, Reno, NV, November 11-15, 2001.

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Alexander Rimsky-Korsakov, Director, V.G. Khlopin Radium Institute

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).

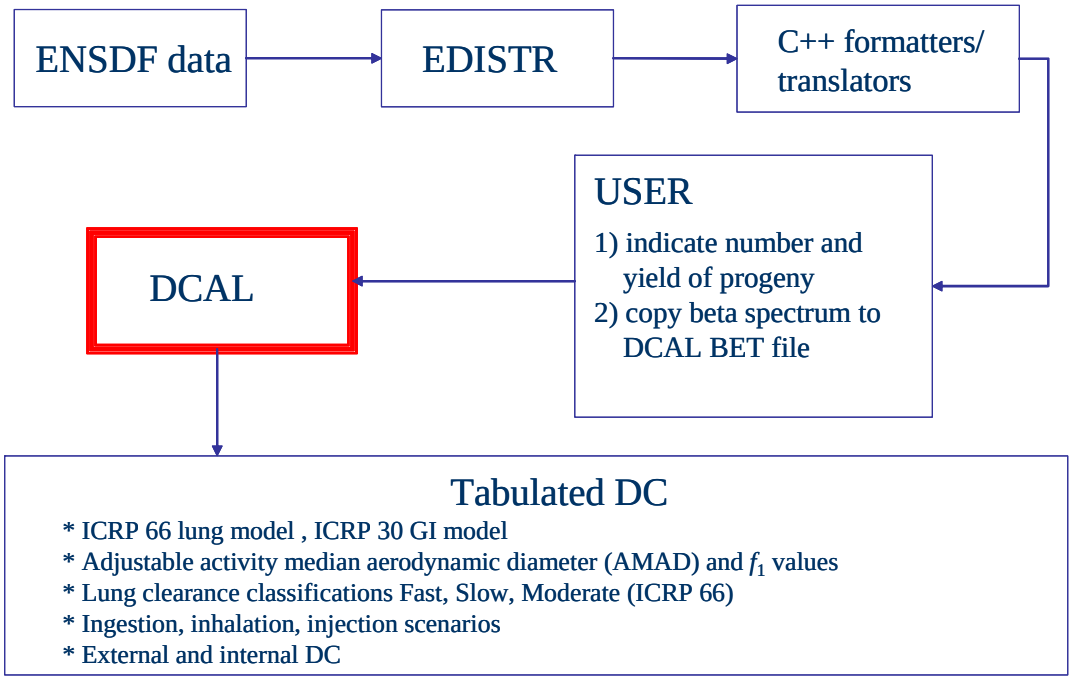
RESEARCH OBJECTIVES AND METHODS

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 (ICRP), 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 Coefficients 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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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 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 TRP 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. The demonstration code from

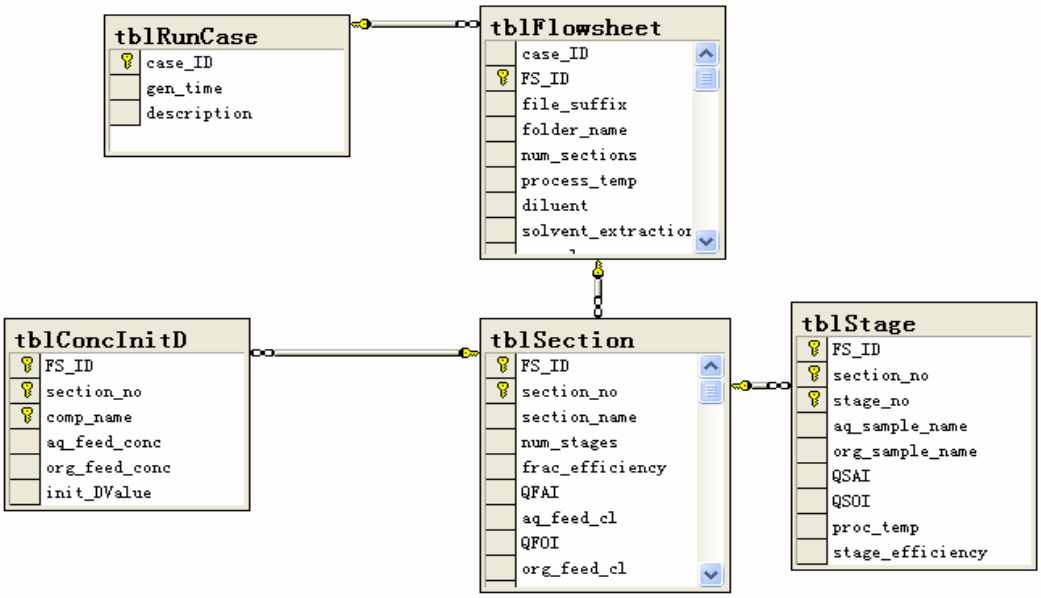


Diagram for the Structure of the Database Design.

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.

Conference Proceedings:

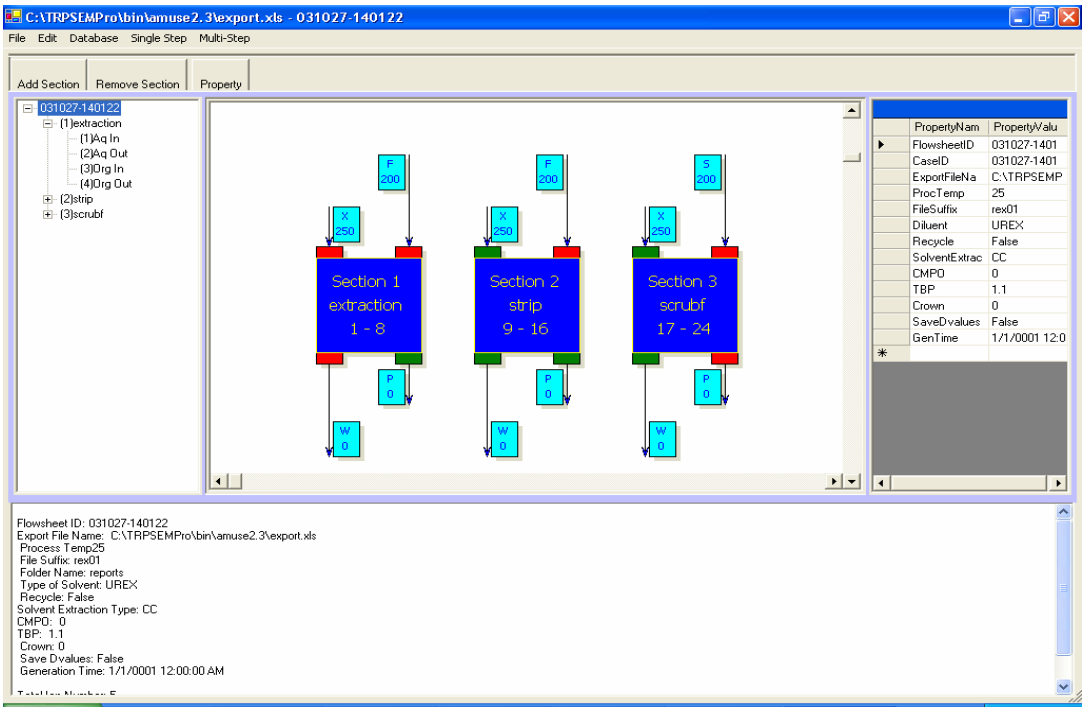
"Development of Systems Engineering Model for Spent Fuel Extraction Process," IMECE 2004, International Mechanical Engineering Congress and Exposition Conference, Anaheim, CA, November 13-19, 2004.

L. Sun, Royyuru, H., Hsieh, S., Chen, Y., Clarksean, R., Vandegrift, G., Copple, J., and Laidle, J., "Development of Systems Engineering Model for Spent Fuel Extraction Process," *ICAPP-04*, Pittsburgh, PA USA, June 13-17, 2004.

H. Royyuru, Sun, L., Chen, Y., Hsieh, S., Clarksean, R., Pepper, D., Vandegrift, G., Copple, J., and Laidle, J., "Development of Systems Engineering Model For UREX Process," ASME International Mechanical Engineering Congress and Exposition, Washington, DC, November 16-21, 2003.

H. Royyuru, Sun, L., Chen, Y., Hsieh, S., Clarksean, R., Pepper, D., Vandegrift, G., Copple, J., and Laidle, J., "Development of Systems Engineering Model For UREX Process," *AccApp'03: Accelerator Applications in a Nuclear Renaissance*, San Diego, CA, June 1-5, 2003.

L. Sun, Chen, Y., Clarksean, R., and Laidler, J., "The Development of a Systems Engineering Model for the DOE Advanced Accelerator Applications Program," *International Congress on Advanced Nuclear Power Plants*, embedded topical meeting at the ANS Summer Meeting, Hollywood, Florida, 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

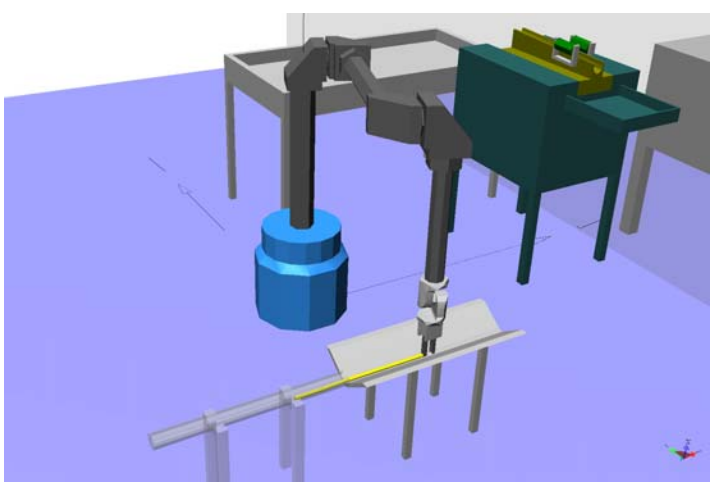
BACKGROUND

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.

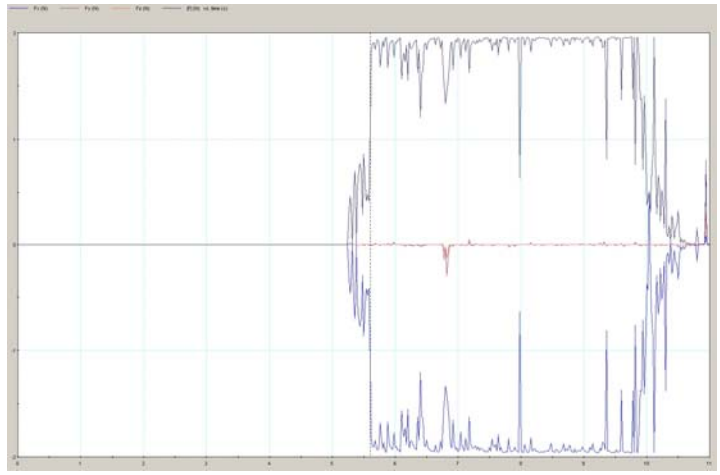
RESEARCH OBJECTIVES AND METHODS

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 prevent human presence near processes.



The Wäelischmiller robot inserts the fuel pins in the cladding tube.



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

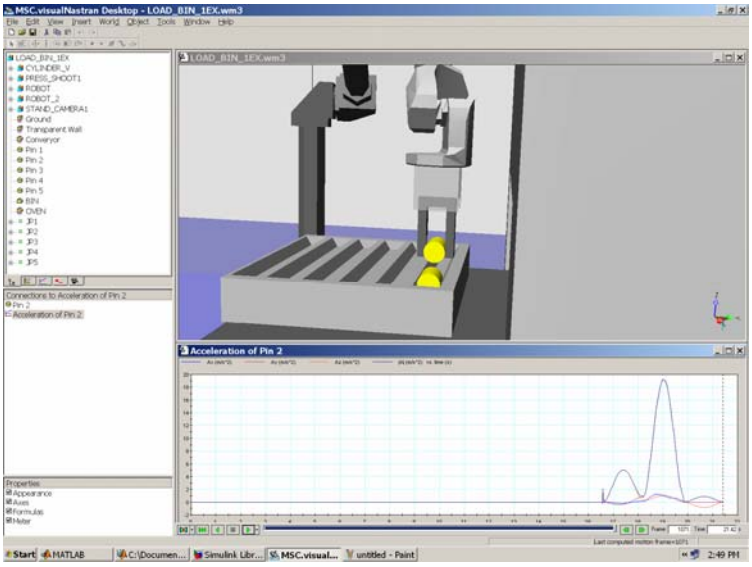
The research work was divided into several tasks and subtasks:

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^2.

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 CAD 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 (AI) 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.

Journal Article:

J.K. Lee and G. Mauer, "Feature-Based Pattern Recognition and Object Identification for Telerobotics," submitted to IEEE/ASME *Journal of Mechatronics* in August 2004.

Conference Proceedings:

G.F. Mauer and J. Renno, "Virtual Testing of Robotic Assembly Processes for Hot Cells," *Proceedings*, 10th International Conference on Robotics & 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*, CAINE 2002 conference, San Diego, CA, November 2002.

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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-molbdenum (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.

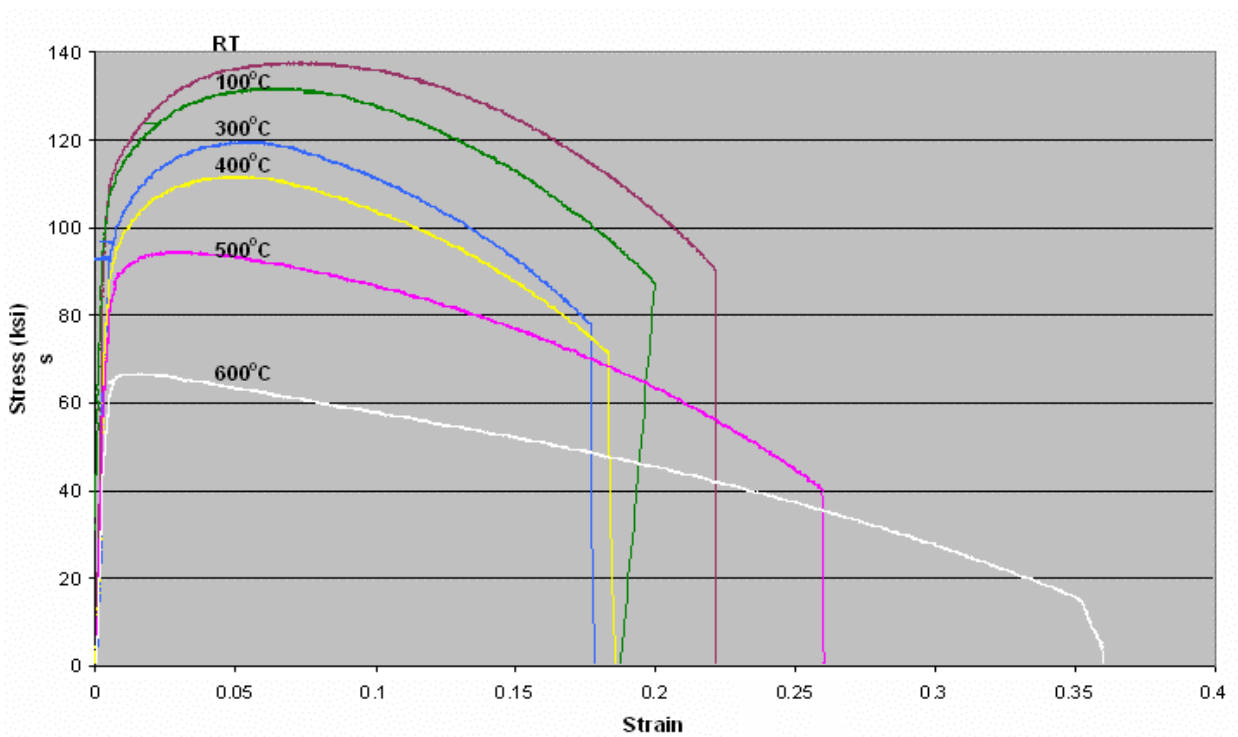
RESEARCH OBJECTIVES AND METHODS

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} sec^{-1} according to the 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 (YS), and ultimate tensile strength (UTS) 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.

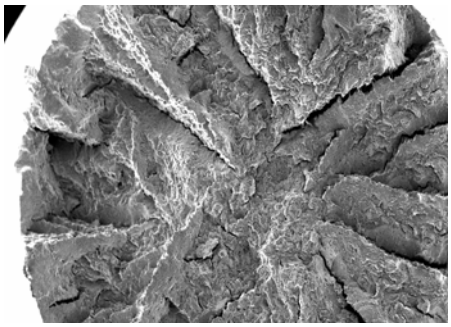
RESEARCH ACCOMPLISHMENTS

The significant conclusions drawn from this investigation are summarized below:

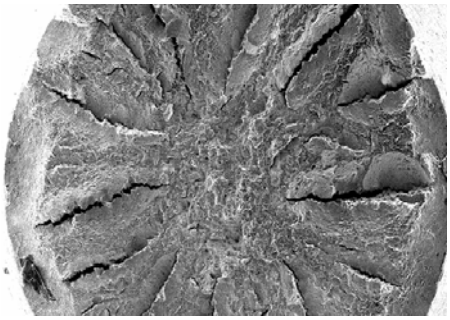
- The hardness of all three austenitized and quenched alloys were significantly reduced due to tempering, showing a gradual reduction with increasing tempering time.
- The magnitude of the yield, ultimate and failure stress were gradually reduced with increasing temperature, showing significant reductions 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, the magnitude of these parameters was enhanced due to increased plastic flow.



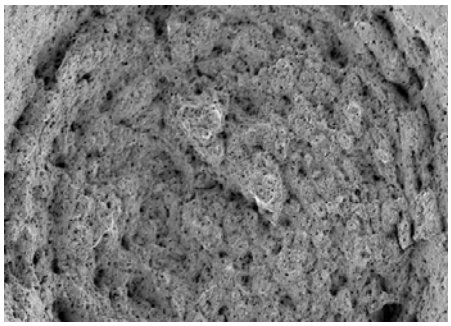
Stress-strain curves for Alloy HT-9 at different temperatures.



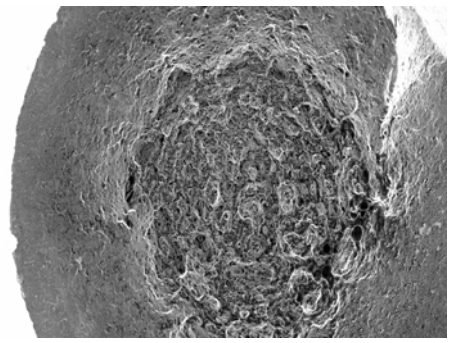
Room Temperature



100°C



300°C



600°C

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

- 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, ASM 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 (SAMPE) 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_{eff}, to prevent a possible sustained fission reaction. Maintaining k_{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.

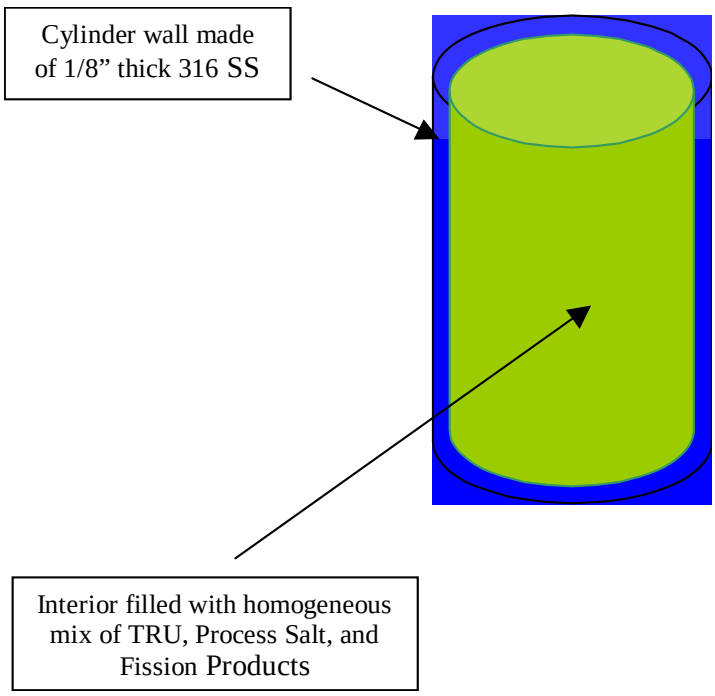
RESEARCH OBJECTIVES AND METHODS

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_{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_{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_{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_{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_{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_{eff} as a function of the relative concentrations of process salt, TRU actinides, and fission products. The research team analyzed the cesium/strontium waste stream, the plutonium/neptunium waste stream, and the americium/curium waste stream.

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 .

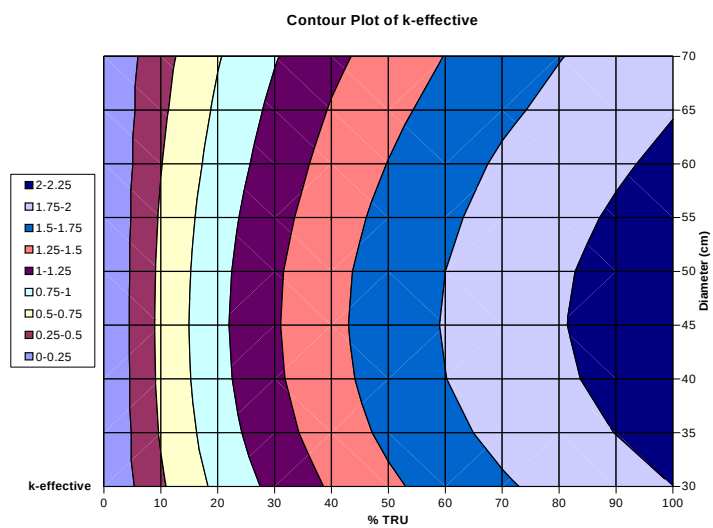
Reports:

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.

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_2O_3 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_2O_3 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_2O_3+Cm_2O_3		Criticality		Heat Transfer	
Cylinder		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.



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

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George F. Vandergrift, III, Senior Scientist, Chemical Technology Division, Argonne National Laboratory

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 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 LANCSE 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 LANCSE 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.

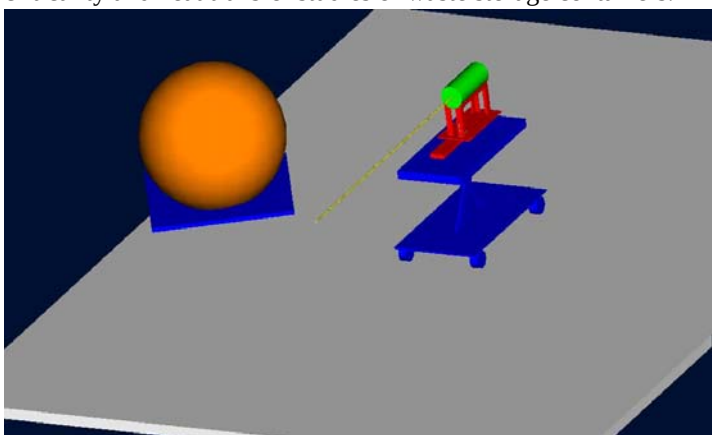
Extensive studies on how MCNPX performs with respect to MPI (Message Pass Interface) and PVM (Parallel Virtual Machine) have been run. PVM was no longer supported by the LANL team after 2005, hence more emphasis was placed on how MCNPX runs with MPI on a Beowulf system.

Parallelization of MCNPX for a Parallel Virtual Machine was completed. Message Passing Interface (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.



Schematic of the experimental facility at LANSCE used for modeling.

With the help of Trevor Wilcox, a doctoral student in mechanical 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

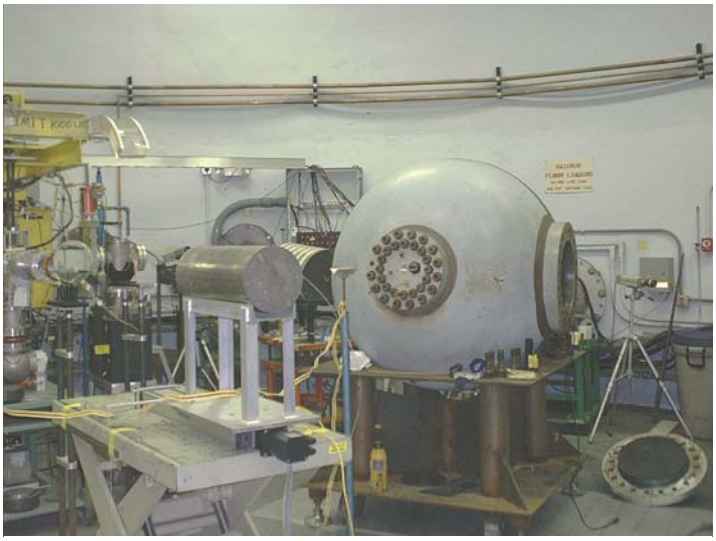
Thesis Generated:

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.

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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:

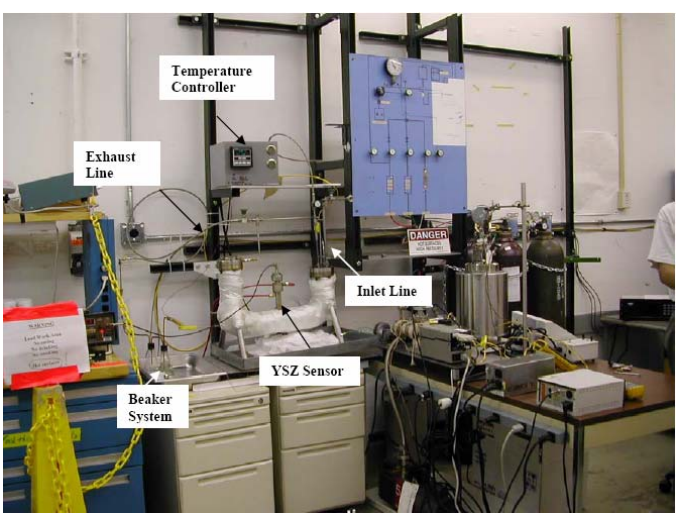
- To generate calibration curves of voltage versus oxygen concentration for the YSZ oxygen sensor system under various temperatures in liquid LBE.
- To determine the sensor characteristics of the YSZ sensor system.
- To determine oxygen dissolving rates in LBE under different temperatures in vitro.
-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

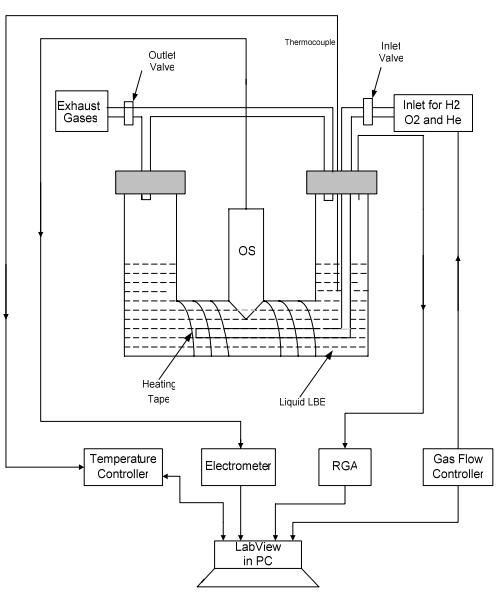
The first experimental set up consisted of a temperature controlled U-shape container, gas supplies and exhaust, a residual gas analyzer (RGA), a high-impedance electrometer, and a PC for data acquisition. The container is tightly sealed from the outside atmosphere using a conflat flange except for gas 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 ^{o}C). In addition, direct injection of O_2/H_2 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 (Si3N4) ceramic. Silicon Nitride has high temperature strength, creep resistance,



The first sensor calibration experimental setup.



oxidation resistance, and it is not wetted by any molten metal. On top of those, compared to many other ceramic materials, Si_3N_4 has good mechanical strength.

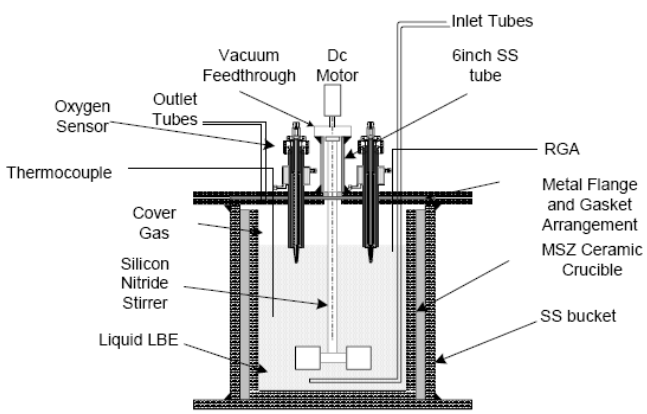
Oxygen Sensor Calibration Results

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°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 Bi_2O_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.



Schematic of the second sensor calibration experimental setup.

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," *Proc. 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," *Proc. of 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," *Proc. of 10th International High-Level Waste Management Conference*, Las Vegas, March 30-April 3, 2003.

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Task 14

Use of Positron Annihilation Spectroscopy for Stress-Strain Measurements

A. K. Roy

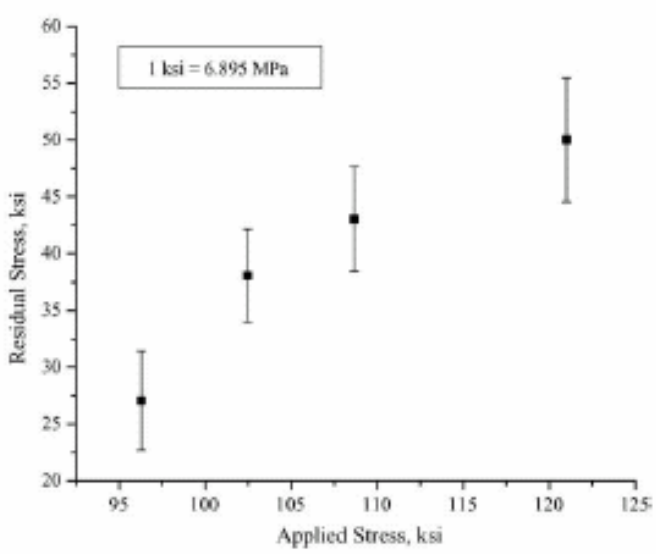
BACKGROUND

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.

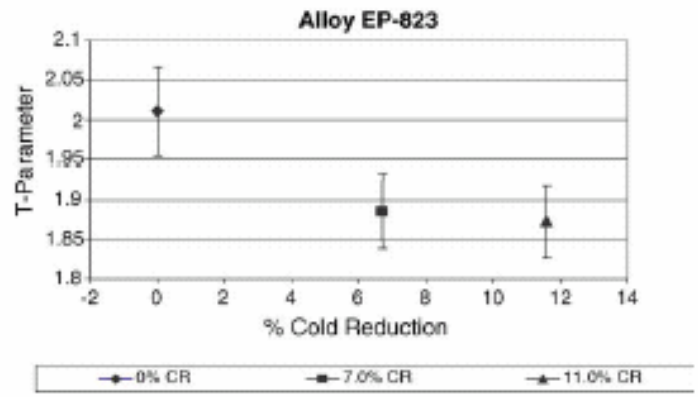
This project is focused on the evaluation of residual stresses in target structural materials by the state-of-the-art destructive and non-destructive techniques. In addition, microstructural evaluations have also been performed by metallographic techniques. More recently, the effect of post-weld-thermal-treatments (PWTT) on the internal stresses in welded specimens has been studied. Further, the characterization of defects by transmission electron microscopy (TEM) has been performed.

RESEARCH OBJECTIVES AND METHODS

The primary objective of this task is to evaluate the feasibility of the characterization of residual stresses in plastically-deformed and welded structural materials using a new nondestructive technique based on positron annihilation spectroscopy (PAS). The



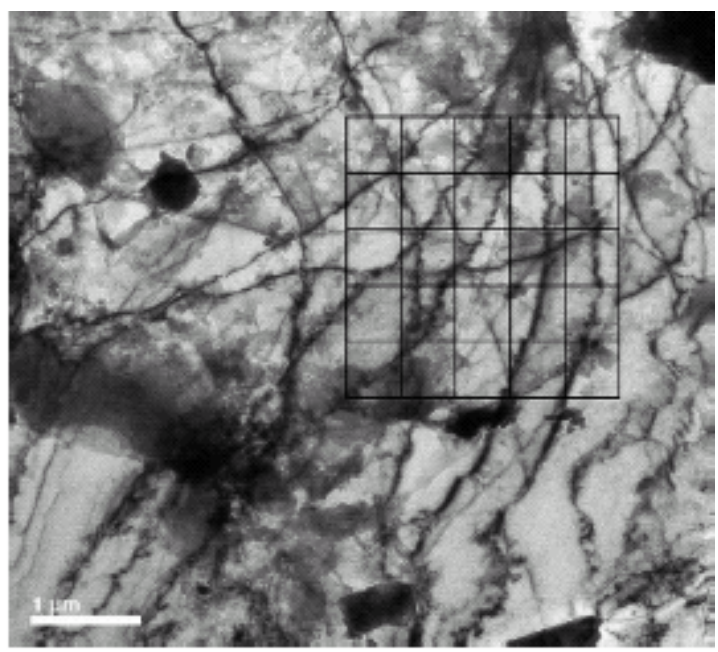
Residual stress versus applied stress using neutron diffraction.



Effect of % cold reduction on T-parameter (PAS).

residual stresses measured by a modified PAS method have been compared to those measured by three other techniques namely, the ring-core (RC, destructive), X-ray diffraction (XRD, non-destructive), and neutron diffraction (ND, 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 (LBE) nuclear coolant needed for fast spectrum operations of an accelerator-driven transmutation system (ADS). Type 304L SS is a universally-known corrosion resistant low-carbon iron-nickel-chrome



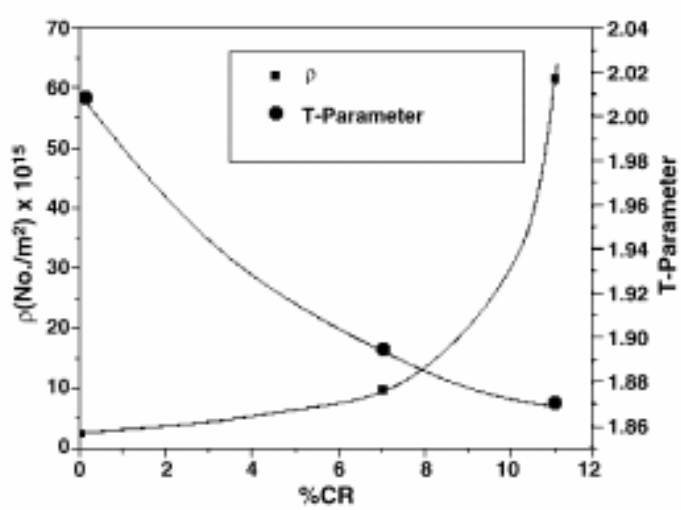
TEM micrograph of Alloy EP-823 used to determine ρ by the line intersection method.

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 and TEM, respectively.

RESEARCH ACCOMPLISHMENTS

The significant results obtained to date are summarized as follows:

- The residual stresses, characterized in all three tested materials in terms of the PAS line-shape parameters (*S, W and* T) exhibited consistent patterns.
- The residual stresses in cylindrical calibration specimens under tensile loading were enhanced at increasing applied stresses, showing a gradual enhancement in the *S*-parameter.
- The extent of residual stress in terms of the *W*- and *T*-parameter was enhanced at higher applied stresses, showing a gradual reduction in both parameters.
- The overall data revealed that the residual stresses generated inside the cylindrical specimens of all tested materials were enhanced at higher applied loads, irrespective of the testing technique.
- The PAS data on the cold-reduced plates of Alloy EP-823 showed reduced *T*-parameter value with increasing level of cold deformation, indicating higher residual stresses .
- The TEM micrographs of the cold-reduced plates were characterized by the presence of dislocations and carbide precipitates, irrespective of the cold-reduction level.



Variation of ρ and T-parameter with percent cold-reduction.

ACADEMIC YEAR HIGHLIGHTS

- Theses Generated:

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

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

- Journal Publications:

  A. K. Roy, S. Bandyopadhyay, S. B. Suresh, and D. Wells, "Comparison of Residual Stress in Martensitic Alloys by Nondestructive Techniques," *Materials Science and Engineering A,* Elsevier Science, Vol. 419, March 2006, pp. 372-380.

  A. K. Roy, S. Bandyopadhyay, S. B. Suresh, D. Maitra, P. Kumar, D. Wells, L. Ma, "Relationship of Residual Stress to Dislocation Density in Cold-Worked Martensitic Alloy," *Materials Science and Engineering A,* Elsevier Science, Vol. 416, January 2006, pp. 134-138.

  A. K. Roy, A. Venkatesh, S. Dronavalli, V. Marthandam, D. Wells, F. Selim, and R. Rogge, "Residual Stress Measurements in Welded and Plastically Deformed Target Structural Materials," *Journal of ASTM International*, June 2005, Vol. 2, No. 6, pp. 1-13.

- Conference Publications:

  A. K. Roy, S. Bandyopadhyay, S. B. Suresh, and D. Wells, "Characterization of Residual Stresses in Structural Materials for Nuclear Applications," ASME Conference, PVP 2005, Denver, CO, July 2005.

- The dislocation density (ρ) was gradually enhanced almost by an order of magnitude due to the reduction of thickness by cold-rolling from 0 to 7-11%, respectively.

FUTURE WORK

- Characterization of residual stress by the PAS method in welded specimens before and after PWTT.
- Characterization of microstructures and defects (dislocations) in welded specimens of similar and dissimilar metals by TEM.

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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

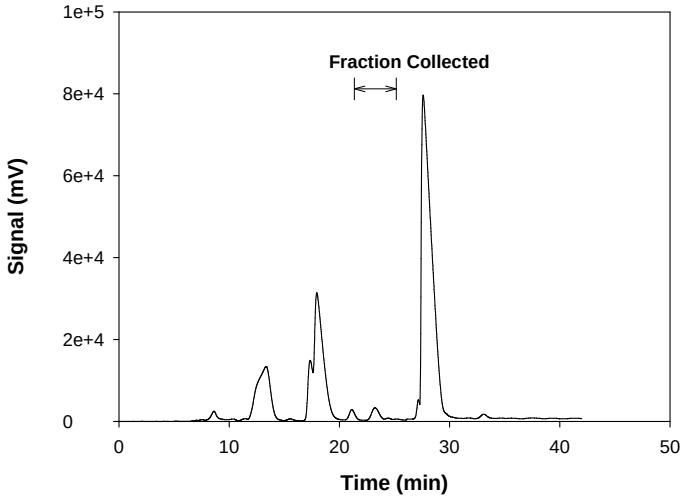
BACKGROUND

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.

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 spaghnum 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.



An example chromatogram from pyrolysis of 0.05 g of iodinated alkali lignin at 400 °C.

RESEARCH OBJECTIVES AND METHODS

The stability of the association of iodine with FCC and NOM products are 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.

The following are the specific research objectives and goals:

- Develop bench-scale experimental set-up and procedures for simulating 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 are developed and prepared by the KRI Research Industrial Enterprise (KIRSI). The KRI-KIRSI team research the impacts of process parameters on sorption of iodine, and examine the material properties, such as how iodine attaches to the FCC compounds. The KRI-KIRSI team also examines 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

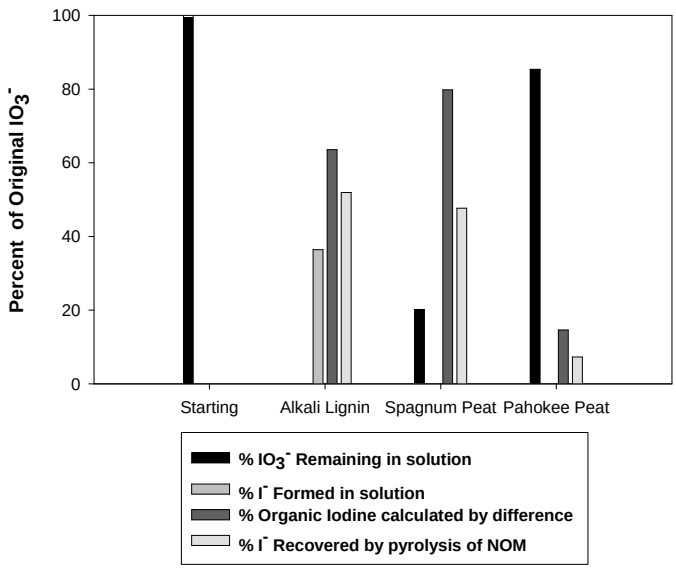
Observations of the reduction of iodate by NOM were continued. Incorporation of iodine into various forms of NOM and various model compounds was demonstrated. Several methods for trapping iodine to further demonstrate that iodine or HOI was an intermediate in this process were utilized. Iodine trapping with N,N –dimethylaniline and selective oxidation of leuco crystal violet was also utilized. Kinetic measurements of this process were taken.

Utilizing preparative gas chromatography, it was demonstrated that methyl iodide that was released by pyrolysis (of .05 to 0.5 grams of OM) could be purified and recovered.

Several methods for the conversion of methyl iodide to sodium iodide were explored. The Würst reaction was attempted and was not successful. Methyl iodide reacted rapidly with several nucleophiles including thiourea, mercapto ethanol. Methyl iodide could be easily reacted with GT-73 resin (mercaptan containing resin) in the sodium form. The result of this reaction was the release of sodium iodide that could be rinsed free of the resin.

The methyl pyridinium resin was prepared. Further experiments demonstrated that iodide could be recovered from aqueous solution and converted to methyl iodide by pyrolysis. Competitive effects from other aqueous anions were observed.

A number of potential reducing organic compounds as candidates for iodate reduction were examined. Lignin phenols and carbohydrates did not seem to be viable candidates. Hydroquinone however, rapidly reduces iodate to iodide. Furthermore, iodine (or HOI) was demonstrated to be an intermediate in this process and can be trapped as an organoiodine compound. For example a solution of hydroquinone and iodate can iodinate p-hydroxybenzoic acid or vanillic acid. It can be routinely observed that diphenolic moieties are produced during pyrolysis of lignin and other forms of NOM. Others have evoked this functionality to explain the redox properties of humic and fulvic acids.



Distribution of iodine after iodate-NOM experiments at room temperature and pH 2.

It was demonstrated that iodide can be trapped in NOM in the presence of manganese dioxide (g-MnO2). The oxidation of iodide to iodine (or I_3^-) can be observed at moderate pH (4-9). Also, it was demonstrated that at pH 7 iodide is incorporated into NOM in the presence of MnO_2. Observations indicate that the reaction occurs when microcrystalline MnO_2 (prepared by us) is utilized. Reagent grade MnO_2 does not appear to promote this reaction.

FUTURE WORK

It has been proposed that the reaction of NOM with iodide in the presence of various forms of MnO_2 be continued, and the effect temperature and pH on this reaction be investigated.

ACADEMIC YEAR HIGHLIGHTS

- Steinberg S.M., Kimble G.M., Schmett G.T., Emerson D.W., *Abiotic reaction of iodine and iodate with sphagnum peat*. Preprints of Extended Abstracts presented at the ACS National Meeting, American Chemical Society, Division of Environmental Chemistry, 45(1), 476-481, 2005.
- Steinberg S.M., Kimble G.M., Schmett G.T., Emerson D.W., *Abiotic Reaction of Iodate and Iodine with Natural Organic Matter*. University of Nevada, Las Vegas: Las Vegas, NV. Presented at ACS 40th Western Regional Meeting, Anaheim, CA, January 22-25, 2006.
- Steinberg S.M., Kimble G.M., Schmett G.T., Emerson D.W., Turner M.F.*, Rudin M., *Immobilization of Fission Iodine by Reaction with Insoluble Natural Organic Matter*. Presented at MARC VII, Honolulu, HI, April 3-7, 2006.
- Steinberg S.M., Kimble G.M., Schmett G.T., Emerson D.W., *Abiotic Reaction of Iodate with Sphagnum Peat and Other Natural Organic Matter*. Presented at MARC VII, Honolulu, HI, April 3-7, 2006.

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Task 16

Evaluation of Fluorapatite as a Waste-Form Material

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

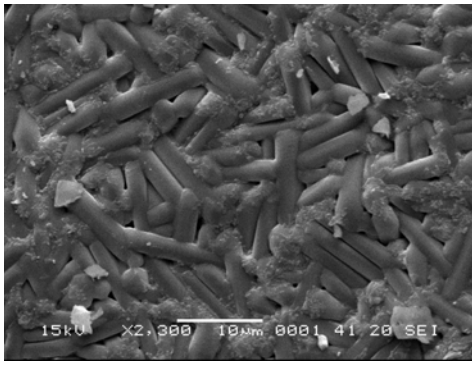
BACKGROUND

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, or 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 (UF_6). In the FLEX process, the used TRISO fuel is reacted with zirconium fluoride salt, forming UF_6 and the fluoride salts of the actinides and fission products. At process temperatures, the UF_6 volatizes 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 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.



SEM micrograph of Ca_4SrFap (annealed sample).

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:

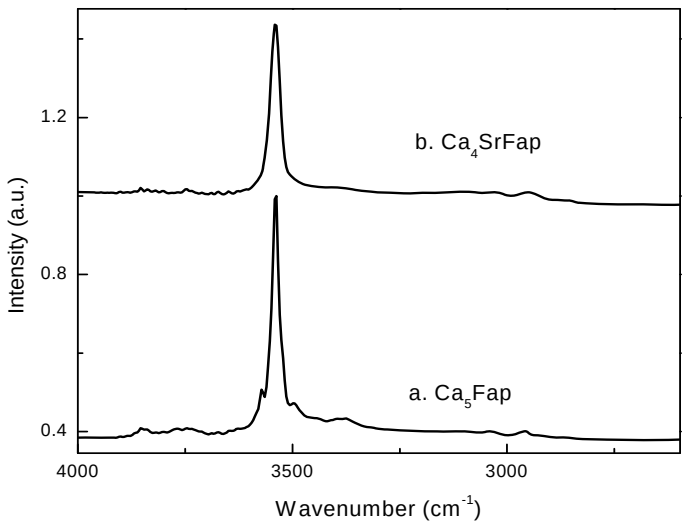
- To develop a waste matrix for the disposal of the fission product waste stream from the FLEX process;
- To develop a process to make synthetic fluorapatite that incorporates the FP-bearing ZrF_4 salt;
- To develop a fundamental understanding of the chemistry of this new waste form in order to better 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



IR spectra of Ca_5Fap and Ca_4SrFap 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 Spectroscopy, SEM, XRD, 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.

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.

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.

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Task 17

Interaction between Metal Fission Products and TRISO Coating Materials

C. Heske

BACKGROUND

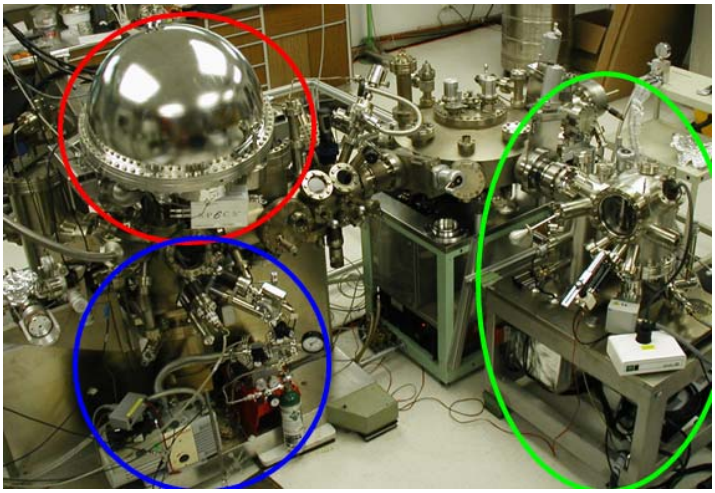
In this project the chemical bonding and interface formation of metal fission products with the coating materials used in TRISO fuel particles is investigated. A combination of surface- and bulk-sensitive spectroscopic methods are used to analyze intermediate chemical phases at the interface, intermixing/diffusion behavior, and the electronic interface structure as a function of material (metal and coating materials) and temperature.

The interface formation of Pd, Cs, and Ag with SiC and pyrolytic carbon is studied in detail. Using the SiC single crystals and TRISO coating materials as substrates, interfaces are prepared under controlled conditions in an ultra-high vacuum environment and are studied with a photoelectron spectroscopy, Auger electron spectroscopy, Inverse Photoemission, X-ray emission spectroscopy, and X-ray absorption spectroscopy. Recent additions to the experimental approach include microscopic techniques (Transmission Electron Microscopy, Scanning Tunneling Microscopy, Atomic Force Microscopy) and local scanning tunneling spectroscopy.

RESEARCH OBJECTIVES AND METHODS

The research results of this project are expected to:

- Give valuable information about failure mechanisms of TRISO particles and fission product transport.
- Derive strategies to tailor the interface properties for an optimization of TRISO particles in terms of, e.g., chemical and long-term stability.
- Give, through simulating experiments, indications for optimized irradiation testing and post-irradiation examinations within the AFCI effort at ORNL.



Bird's eye view of the modified multi-chamber ultra-high vacuum apparatus. Red: replacement electron analyzer; blue: inverse photoemission setup, green: scanning probe microscope.

The experiments use two different experimental apparatuses, namely a multi-chamber ultra-high vacuum system at UNLV, and the SXF endstation at Beamline 8.0 at the Advanced Light Source Lawrence Berkeley National Lab. In the past project year, significant improvements of the UNLV system could be implemented. Several upgrades could be installed, in particular a new state-of-the-art electron analyzer, a partially custom-built inverse photoemission (IPES) set-up, and, very recently, a scanning probe microscope (all instruments are funded through other projects). In particular the replacement of the electron analyzer now allows us to take reliable electron spectra at a significantly increased count rate, while avoiding the saturation effects, software communication problems, and background issues of the old analyzer. The achievable signal-to-noise ratio is now improved by several orders of magnitude, while also improving the spectral resolution greatly. The IPES set-up now allows investigation into the conduction band, and hence gives valuable information about the interface formation from the viewpoint of the unoccupied electronic states. The new scanning probe microscope will, once fully commissioned, give insights into the sample morphology and chemical and electronic structure on a *local* (i.e., for single crystal systems, *atomic*) scale.

RESEARCH ACCOMPLISHMENTS

In the second year of the project, focus was placed on a detailed analysis and description of the Pd/SiC interface formation process. This description is documented in the Masters thesis of Goverdhan Gajjala, which was successfully defended at the UNLV Department of Electrical Engineering. As an example, a series of X-ray photoelectron spectroscopy (XPS) survey spectra, that were taken for a SiC single crystal substrate after introduction into the system, after sputter-cleaning with Ar^+ ions (2 keV), and after several Pd deposition steps are illustrated. In this particular case, the Pd deposition was performed at approx. 800 degrees C to simulate elevated temperatures in TRISO fuel. Furthermore, the SiC surface was very strongly sputtered, which induces a significant number of structural defects at the surface and is hence intended to simulate real SiC surfaces. An example of a detailed UV photoelectron spectroscopy (UPS) study of the corresponding samples is also provided, indicating how the electronic surface structure is converted from an adsorbate-induced character to a semiconductor (SiC) to a metallic thin film (for increasing Pd overlayer thickness). A detailed analysis of the valence band maxima and Fermi edges, together with a study of the work function (which can be derived from the secondary electron cutoff in the UPS spectra) gives detailed insight into the electronic structure of the Pd/SiC interface, which can be interpreted in view of pronounced intermixing effects, as well as the formation of an electronic Schottky barrier.

In the thesis of Goverdhan Gajjala, the results obtained from the sample series are compared with a similar series that was obtained

at room temperature. Furthermore, the first experimental series, which was taken at the University of Wuerzburg (before relocation of the instrument to UNLV), can be well compared. In all cases, the presence of two additional carbon species at the interface was found, one associated with a short-range charge transfer (the actual chemical bonding) and a longer-range interdiffusion species (in addition to the expected SiC bulk species). Combining all spectral regions (in XPS and UPS), a detailed picture of the Pd/SiC interface formation can be painted, in particular when taking additional soft X-ray emission and absorption data into account, which was taken in the experimental campaigns at the Advanced Light Source.

FUTURE WORK

The Pd/SiC results are currently being prepared for publication in a peer-reviewed journal. For this purpose, some additional data is currently collected in order to allow a reliable quantitative analysis of the bonding and interdiffusion processes. This is necessary since the old electron analyzer showed several age-related electronic problems.

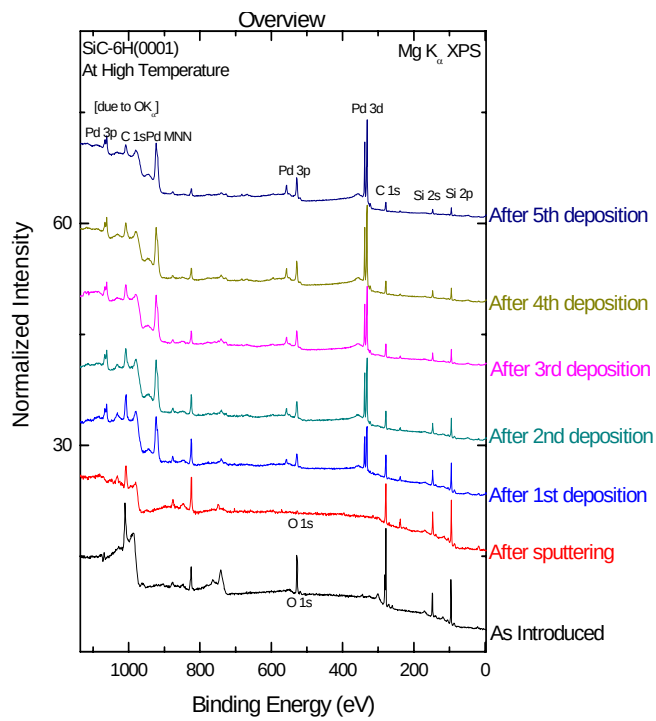
As mentioned above, the electron analyzer has been replaced by a modern state-of-the-art instrument (SPECS PHOIBOS 150MCD) that not only allows a much more reliable quantitative analysis, but also a significantly improved energy resolution, shorter accumulation time, and drastically enhanced signal-to-noise ratio. These experiments will be very important to reproduce and calibrate some of the experiments presented in G. Gajjala's thesis before they are published in a peer-reviewed journal.

In addition to completing the existing Pd/SiC data set, the investigation of the Cs/SiC interface is being prepared – a Cs evaporator has been designed and is currently being constructed by Sharath Sudarshanam. Again, these studies will be performed as a function of external parameters such as deposition/diffusion temperature, surface/interface modification, SiC preparation method, etc.

Further studies will focus on other material combinations, in particular Ag and SiC, as well as various metals (Pd, Ag, Cs, …) and their interaction with the pyrocarbon layers in TRISO fuel. By combining these studies, a deeper knowledge and a more comprehensive picture of the chemical properties of interfaces in TRISO fuels and the interaction of metallic fission products with TRISO coating layers are expected.

ACADEMIC YEAR HIGHLIGHTS

- G. Gajjala, "Interaction Between Pd and SiC: A Study for TRISO Nuclear Fuel," Masters Thesis, Department of Electrical & Computer Engineering, UNLV, April 2006 (submission), May 2006 (defense).
- C. Heske, "Soft X-ray spectroscopy of compound semiconductors: how to reveal the chemical and electronic properties of buried interfaces," Tutorial at the Florida American Vacuum Society Meeting, Orlando, FL, March 2006.
- C. Heske, "X-ray spectroscopy of buried things: interfaces, liquids, and dirty powders", Stanford Synchrotron Radiation Lab Workshop on Soft X-ray Science, Stanford, CA, February 2006.
- C. Heske, "Soft X-ray spectroscopy of compound semiconductors: how to reveal the chemical and electronic properties of interfaces and buried layers", Pacifichem 2005, Honolulu, HI, December 2005 (featured in an article in Chemical & Engineering News 84, 35 (2006)).



XPS survey spectra of an as-introduced SiC-6H(0001) single crystal surface, after 2 keV Ar^+ ion sputtering, and after several Pd deposition steps at approx. 800°C.

Research Staff

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Lothar Winhardt, Post-Doctoral Fellow, Department of Chemistry

Students

Goverdhan Gajjala and Varun Marepally, Graduate Students, Department of Electrical Engineering
Timo Hofmann and Ich Tran, Graduate Student, Department of Chemistry
Jared White 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

This effort is a continuation of the work of Task 3 (see pages 10 and 11), and the same overview applies. Advanced nuclear processes such as the transmutation of nuclear waste, fast reactors, liquid-metal-cooled reactors, and spallation neutron sources require advanced materials systems to contain them. The required structural materials must be stable in the presence of non-moderating coolants. A prime candidate for such a coolant is Lead Bismuth Eutectic (LBE). Materials in these systems must be able to tolerate high neutron fluxes, high temperatures, and chemical corrosion. Unfortunately, LBE corrodes stainless steel.

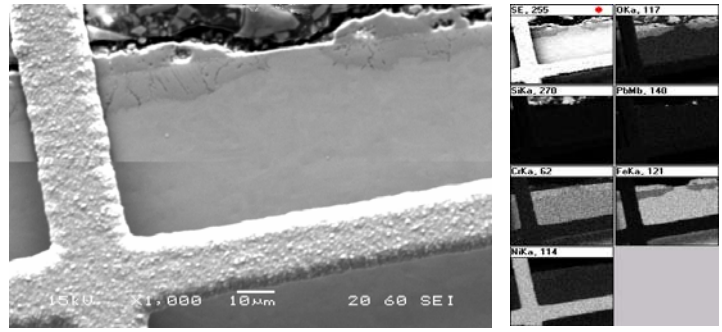
The corrosive behaviors of structural materials in LBE are not well understood. The Russians have over 80 reactor-years experience with LBE coolant in their Alpha-class submarine reactors. The Russians found that the presence of small amounts of oxygen in the LBE significantly reduced corrosion, but a fundamental understanding is incomplete. The formation and breakdown of protective (or non-protective) oxide layers in a steel/LBE is a key materials question.

RESEARCH OBJECTIVES AND METHODS

Samples of steel exposed to LBE were examined using various types of surface microscopy: Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDAX), X-ray Photoelectron Spectrometry (XPS) with sputter depth profiling (SDP), and Laser Raman Spectroscopy. The objectives are (1) to examine the morphology and composition of the oxide layer, its elemental and chemical composition, and its relation to the bulk material, (2) to probe the formation, nature, composition, breakdown, passivation, and healing of oxide layers on steel exposed to LBE, and (3) thereby gain insight into the fundamentals of corrosion of steel by LBE.

The following 8 activities were conducted:

- The UNLV group has continued collaborations with the LANL group, which has an LBE loop ("DELTA" loop). Samples of steel that were exposed to LBE at the DELTA loop at LANL were analyzed.
- Silicon has been proposed as a component to improve the corrosion resistance of steel in LBE systems. Si-containing steel that was exposed to LBE by Eric Loewen at INL was examined.
- A bay in the chemistry building, CHE 112C, was converted into the High Temperature Materials Experimental Facility (HTMEF).
- An experimental apparatus, the Liquid Metal Corrosion Experiment (LMCE) is being built.
- Gas phase experiments, using a tube furnace, has been started.
- An existing ion beam apparatus will be restarted to produce mass-selected ion beams. These will be used for isotopic labeling experiments for studying diffusion rates of iron, oxygen, nickel, and chromium atoms in steel matrices at elevated temperatures. Detection will be accomplished using the SIMS-TOF experiment at the EMSL laboratory at PNNL.
- A laser Raman experiment was designed to examine the chemical species present in oxide films produced in steel/LBE corrosion experiments.
- Corrosion of D-9 steel, which is a proprietary surface treatment, was studied.



D-9 shows failure of the thin oxide and formation of duplex oxide in localized patches. The iron moved outside the original metal surface to form Fe_3O_4 (as shown by Raman spectroscopy) and the chromium stayed in place to form an iron/chromium oxide which undercuts the thin oxide.

RESEARCH ACCOMPLISHMENTS

Approximately 250 DELTA loop samples were analyzed using SEM and EDAX. This was important to the LANL research group, which was having some issues controlling the crucial oxygen level in their DELTA loop.

The silicon-containing steel samples at INL were examined using SEM, XPS, and SDP. Samples with four different concentrations of silicon were examined. Silicon was found in the form of elemental silicon (in the metal), in the form of silica (SiO_2) at the bottom of the oxide layer, and silicates in the oxide. A layer of silica formed between the oxide and the bulk metal. The details were written up and published in the peer-reviewed *Journal of Nuclear Materials*.

Renovation of room CHE 112C into The High Temperature Materials Exposure Facility (HTMEF) was largely completed. This included renovating the floor, walls, air conditioning, and utilities. Experiments can now start in the HTMEF. The first two experiments will be the LMCE and the gas-phase experiments.

Construction continues on the Liquid Metal Corrosion Experiment (LMCE). This experiment will be placed in the HTMEF.

The first experimental results using the gas-phase experiment were obtained, using a quartz tube in a tube furnace, containing a steel sample and a copper/copper oxide pellet to determine the oxygen level.

The Raman experiment obtained its first results. The Raman technique allows determination of the chemical species (e.g., Fe_2O_3 or Fe_3O_4) while other techniques (XPS, EDAX) can only yield elemental composition (e.g., Fe and O are present but not what chemical species). Graduate student Brian Hosterman used the Raman experiment to demonstrate that the iron oxide in a sample exposed by the Russian collaborators was Fe_3O_4 and not Fe_2O_3.

Technical Summary

Investigations of steels samples exposed to LBE in a Russian test loop, as well as samples from other sources, are continuing.

It was found that very similar steels can show very different corrosion behavior in concert with different protective oxide morphology: slow corroding steels have a thin, high chromium surface layer similar to the initial oxide, while the faster corroding steels have a duplex oxide, magnetite above an iron-chromium oxide which is ~10x thicker than the thin protective oxide.

Inhibition of the conversion from protective thin oxide to less protective duplex oxide may lead to improved service life. Recently, an investigation of D9 steel, which has intermediate corrosion resistance, was finished. It was found that the oxide was primarily thin, with patches of duplex oxide.

The conversion from protective thin oxide to less protective duplex oxide seems to occur at localized sites. Further, the boundary between the chromium free magnetite layer and the chromium containing iron-chromium oxide is the same as the original metal surface – i.e. the chromium does not move nearly as rapidly as the iron does.

This means that the failure sites of the thin oxide in D9 are not healing to form thin oxide, in contrast with previous work on cold rolled 316 steel which did show healing to reform thin oxide. Control of the localized failure mode and understanding the healing mechanism may lead to improved corrosion resistance.

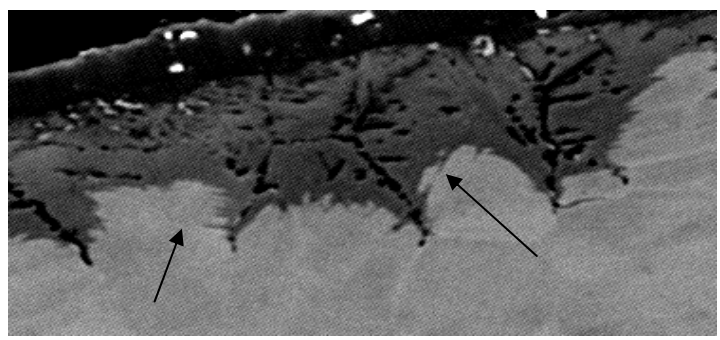
ACADEMIC YEAR HIGHLIGHTS

- 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 316/316L stainless steel by lead–bismuth eutectic (LBE) at elevated temperatures. II. Initiation of duplex oxide formation in D-9 alloy," presentation by Allen Johnson at the AFCI materials working group, March 2006, Santa Fe, NM

The migration channels for oxygen into and iron out of the iron-chromium oxide layer can be observed. Anisotropic etching of the underlying metal grains by the oxygen diffusing into the duplex oxide were noted, indicating some crystal planes seem to be more subject to oxidation than other planes. This opens another possible mechanism for improvement of oxidation resistance: If metal grains at the surface are oriented by shear between the underlying metal and the surface (by cold rolling, for example), the steel may become more resistant to formation of the thicker, non-resistant oxides.

FUTURE WORK

Development of the HTMEF and LMCE will continue, with experiments to follow. Gas phase experiments will provide useful baseline studies of low oxygen concentration corrosion of these systems. The Raman microscopy will allow in-situ characterization of the crystal phase of corrosion products in the oxide layers. Collaborative efforts with LANL will continue, with particular interest in new materials and new processes (the ion beam collaboration).



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

Faculty
Allen Johnson, Principal Investigator, Assistant Professor, Department of Chemistry
John Farley, Professor, Department of Physics

Students
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Thao Trung Ho, Graduate Student, Department of Chemistry
Jenny Welch and Timothy Lane, Undergraduate Students, Department of Physics

Collaborators
Ning Li, LBE Project Leader, Los Alamos National Laboratory
Peter Hosemann, Visiting Scientist, Los Alamos National Laboratory
Eric P. Loewen, Idaho National Engineering and Environmental Laboratory

Task 19

Dissolution, Reactor, and Environmental Behavior of ZrO_2-MgO Inert Fuel Matrix

K. Czerwinski

BACKGROUND

There has been a recent resurgence of interest in different oxide fuel types (Th, inert matrix, Pu fuel) as potential advanced fuel for Generation IV nuclear energy systems that can be operated to relatively high burnups at lower costs than current UO_2 fuels. These fuels can also be formed to incorporate transuranics elements in the matrix, acting as a host for these elements. 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_2 has been examined. The inclusion of ZrO_2 is expected to increase chemical stability and radiation resistance. 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_2 matrix to achieve desirable reprocessing properties. A candidate oxide is MgO.

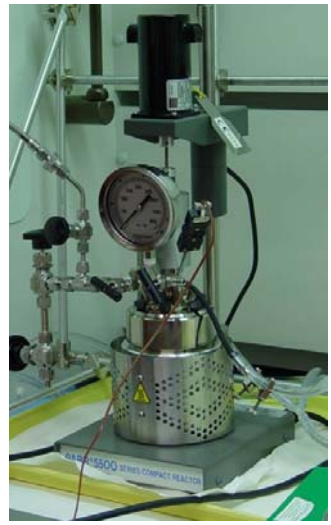
Inert fuel matrices containing a mixture of ZrO_2 and MgO have not been studied. It is proposed that such an inert fuel matrix will have reactor behavior and reprocessing properties desirable for an advanced fuel.

RESEARCH OBJECTIVES AND METHODS

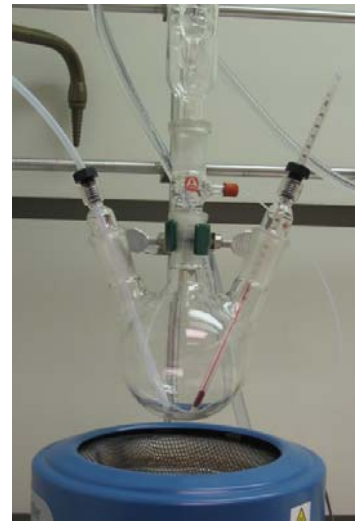
This project examines inert fuels containing ZrO_2 and MgO as the inert matrix, with the relative amount of MgO varied from 30 % to 70 % in ZrO_2. Reactor physics calculations are used to examine suitable quantities of burnable poisons from the candidate elements Gd, Er, or Hf with reactor grade Pu providing the fissile component, with up to 10 % of ^{239}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_2 inert fuels. 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 of MgO-ZrO_2 ceramics containing burnable poison and fissile composition. Synthesis is based on a precipitation method. Characterization of ceramics will include density, X-ray diffraction, surface area analysis, X-ray absorption fine structure spectroscopy, 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.



Pressure Vessel



Acid Reflux Vessel

RESEARCH ACCOMPLISHMENTS

Zirconium Ceramic Fuel

Prototype zirconium ceramic fuel was produced through several reproducible steps. The entire range of Mg to Zr from 0 – 92.5% with Ce at 5% and Er at 2.5% has been synthesized using the precipitation method previously described. It was shown that 10% Mg with 5% Ce, 2.5% Er and 82.5% Zr is enough to fully stabilize the Zirconia to a cubic structure and produce a single phase. From x-ray diffraction the maximum amount of Mg that can be incorporated into the Zr matrix with the Ce and Er is 28% Mg, after which a second Mg phase called periclase begins to build in.

Microprobe analysis confirmed that the periclase MgO phase is pure as suggested by XRD. The microprobe analysis of the ZrO_2 phase showed a constant level of MgO at around 5%, while the concentration of CeO_2 increased from 5% to 14%, and $ErO_{1.5}$ concentrations increased from 2.5% to 12%. Since the CeO_2 to $ErO_{1.5}$ ratio dropped below 2:1 at the lower concentrations of ZrO_2, it suggests that CeO_2 is the first to precipitate out of the ZrO_2 phase.

Pressure Vessel Sampling Method

A pressure vessel was fitted with a custom sample draw tube constructed from stainless steel components. The setup allows *in-situ*

sampling throughout the experiment and samples will be analyzed by ICP-AES and/or ICP-MS, depending on constitution.

Ceramic Solubility in Reprocessing Conditions

Two systems were constructed for the purpose of simultaneous studies of ceramic fuel pellet solubility. The apparatus is designed to reflux nitric acid for extended periods of time without harm to most components. Future studies involving this apparatus can include elemental analysis of the ceramic constituents.

Pressure vessel studies have shown that the pellet is physically destroyed within 48 hrs. However, there are no species dissolved in quantities greater than 1ppm. It is possible that uranium containing ceramics will prove a more interesting study due to the possibility of oxidizing the UO_2 to soluble UO_2^{2+}. Acid dissolution in boiling H_2SO_4 was successful in dissolving all species of the ceramic within 48 hrs. The dissolution follows first order kinetics as expected.

XRD of uranium containing ceramics showed some slightly different characteristics than the cerium ceramics. UO_2 and Er_2O_3 are not mutually soluble, unlike CeO_2 and Er_2O_3 which are mutually soluble. The Uranium containing ceramics did show the same trends and phases as Cerium containing ceramics other than solubility in Er_2O_3. An equal amount of corundum was mixed with sample to evaluate how much amorphous material was contained within the sample. A large amount of the sample is not seen by the XRD, resulting in apparently more corundum than sample.

Soxhlet apparatus to compare corrosion resistance and to determine long-term behavior.

Soxhlet Solubility Studies

To determine the corrosion resistance of the ceramics, fuel pellets are placed in a Soxhlet apparatus, and the pellets are continuously contacted with distilled hot water (65-70°C). The specific mass loss will be determined over an extended time period (typically 2,000 hrs). The long-term goal of the solubility and corrosion studies is not only to provide thermodynamic and kinetic data, but also to provide a suitable strategy for the reprocessing of inert matrix fuels. The soxhlet has produced information on corrosion properties, ability to absorb water, and the extent to which Mg is hydrated.

ACADEMIC YEAR HIGHLIGHTS

- K.S. Holliday, T. Hartmann, K. Czerwinski, "Zirconium-magnesium oxides as inert matrix fuels," and A.D. Wright, K. Holliday, G.W.C. Silva, C.-M. Gong, T. Hartmann, K. Czerwinski, "Using radiochemistry to couple nuclear fuel development with separations and repository behavior for the advanced fuel cycle," 231st ACS National Meeting, Atlanta, GA, March 26-30 2006
- A. Wright, K. Holliday, C. Gong, T. Hartmann, and K. Czerwinski, "Radiochemistry in the US Advanced Fuel Cycle Initiative: Coupling Nuclear Fuel Development to Separation and Repository Behavior," Michigan State University, December 2005.

FUTURE WORK

Further synthesis and characterization of $MgO\text{-}ZrO_2$ ceramics will be performed with the use of U and Pu as the fissile materials. The resulting ceramics will be characterized with a range of methods including density, X-ray diffraction, microscopy, surface area analysis, and XAFS (XANES and EXAFS). The results will be applied to behavior in high temperature water, acid, and environmental conditions and the data will be incorporated into models.

Research Staff

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Kiel Holliday and Earl Wolfram, Graduate Students, Department of Chemistry (Radiochemistry Ph.D. Program)
Wendy Pemberton and Deborah Calloway, Undergraduate Students, Department of Chemistry

Collaborators

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Emil Fridman and Sergei Kolesnikov, Graduate Students, Ben Gurion University of the Negev
Mitchell Meyer, Idaho National Laboratory

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

Recent studies at the Los Alamos National Laboratory (LANL) involving martensitic Alloy EP-823 containing different silicon content have revealed a beneficial effect of Si on corrosion resistance in a molten lead-bismuth-eutectic (LBE) environment. Since very little data exist in the open literature on the beneficial effect of Si on the corrosion resistance of martensitic alloys, a research task was initiated to explore the role of Si not only on the corrosion resistance but also on high-temperature deformation and radiation-induced embrittlement of modified T91 (9Cr-1Mo-0.24V) grade stainless steels.

This task is primarily focused on the evaluation of the effect of Si content on the susceptibility of modified 9Cr-1Mo-0.24V steel to stress corrosion cracking (SCC) and localized cracking in both molten lead-bismuth eutectic (LBE) and an aqueous solution of acidic pH.

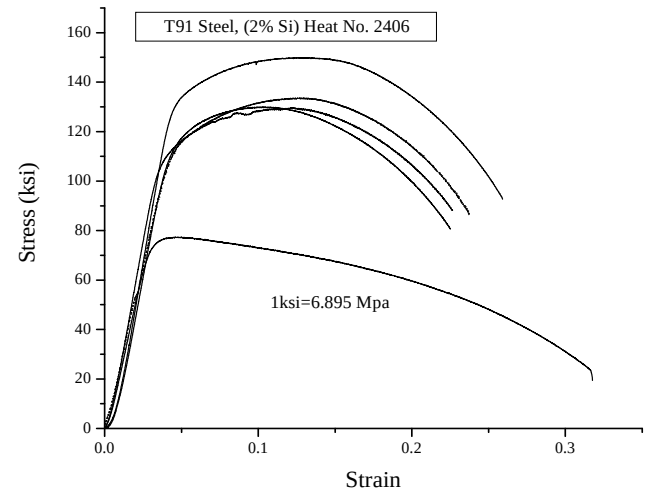
Further, significant efforts are in progress to characterize the deformation mechanism of modified T91 grade steel as a function of temperature and strain rate. Simultaneously, surface analyses of the tested materials are ongoing using state-of-the-art techniques including scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

RESEARCH OBJECTIVES AND METHODS

Four different experimental heats of ASTM A213 Type T91-grade alloy steels (similar to Mod9Cr-1Mo) with different Si content (0.48, 1.02, 1.55 and 1.88 weight percent) have been melted by a vacuum-induction-melting (VIM) practice at the Timken Research Laboratory. An additional four heats containing higher Si content were also melted by the VIM practice, which are also being studied for detailed metallurgical and corrosion characterization. All eight heats were subsequently processed into rectangular and square bars by forging and hot-rolling. These bars were then austenitized, oil-quenched, and tempered to achieve fine-grained and fully-tempered martensitic microstructure.

Tensile testing of T91 grade steels having Si content ranging between 0.48 and 1.88 weight percent were completed, as a function of temperature relevant to the transmutation process. The role of strain rate on the tensile properties is also under investigation. The tensile properties are being interpreted in terms of the yield strength (YS), ultimate tensile strength (UTS), percent elongation (%El), and percent reduction in area (%RA). The morphology of failure at the primary fracture surface is being investigated by SEM as a function of the testing temperature.

In order to better understand the plastic deformation of all four heats, TEM is being employed to characterize the nature of imperfections such as dislocations. Simultaneously, the microstructural variations are being investigated by using both TEM and optical microscopy (OM).



Engineering stress-strain (s-e) diagram vs. temperature.

The susceptibility of the test materials to SCC has been investigated in the presence of molten LBE using self-loaded specimens (C-Ring/U-Bend) at LANL. Simultaneously, SCC testing involving all four heats is in progress at UNLV in the presence of an acidic aqueous solution at temperatures ranging between ambient and 90ºC.

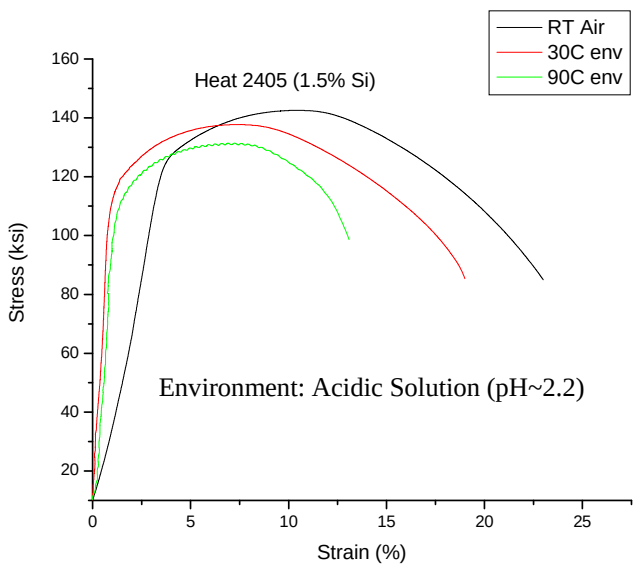
The localized corrosion susceptibility of these materials has also been investigated by cyclic potentiodynamic polarization (CPP) technique. The CPP testing has enabled the development of an understanding on localized corrosion behavior in terms of the corrosion potential (E_{corr}) and the critical pitting potential (E_{pit}).

SEM has been used to analyze the extent and morphology of failure at the primary fracture surface of the specimens tested under a slow-strain-rate (SSR) condition. The cracking susceptibility has been expressed in terms of the true failure stress, time to failure and ductility parameters (%El and %RA).

RESEARCH ACCOMPLISHMENTS

- The tensile data indicates that the magnitudes of both YS and UTS were gradually reduced with increasing temperature, as anticipated. However, there was a gradual drop in the failure strain in the temperature regime of ambient to 400ºC.

- The gradual reduction in failure strain in the susceptible temperature regime has often been cited to be the result of work hardening resulting from the diffusion of interstitial solute elements onto the dislocations near the grain boundaries. This phenomenon, known as dynamic strain ageing, is also a function of strain rate used during plastic deformation under tensile loading.
- At 550ºC, there was an increase in ductility in terms of failure strain, possibly due to enhanced plastic flow even under an identical strain rate of $5x10^{-4}$ s^{-1}.
- In view of the minimum failure strain noted at 400ºC within the susceptible temperature regime (ambient to 400ºC) for all four alloys, testing was performed under three additional strain rates of 10^{-2}, 10^{-3} and 10^{-4} s^{-1} at this temperature. The resultant data indicate that the maximum failure strain at this temperature was observed at a strain rate of 10^{-4} s^{-1}, suggesting that this could be the critical strain rate at or below which the concept of DSA may not be prevalent.
- The results of SSR testing in an acidic solution (pH~2.2) suggest that the cracking susceptibility was enhanced at 90ºC in terms of the reduced time to failure and failure strain.
- SEM study on self-loaded C-Ring specimens revealed a separation of grains possibly due to the decohesion of surface layers resulting from their interaction with the molten metal (LBE). Intergranular brittle crack was seen on the convex side of this specimen, which also revealed the presence of lead, as observed by energy dispersive spectroscopy (EDS).



Stress-strain diagram in Slow-Strain-Rate testing.

ACADEMIC YEAR HIGHLIGHTS

- Thesis Generated:
  Harish Krishnamurthy, "Metallurgical and Corrosion Characterization of a Martensitic Stainless Steel as a function of Silicon Content," M.S. Thesis, December 2005.

- Conference Publications:
  P. Kumar, D. Maitra, A.K. Roy, "Metallurgical and Corrosion Studies of Modified T91 Grade Steel," MRS Spring Meeting, San Francisco, CA, April 2006.
  P. Kumar, D. Maitra, S. Kohir, "Metallurgical and Corrosion Characterization of T91 Grade Steel versus Silicon Content," ANS Students' Conference, RPI, NY, April 2006.
  P. Kumar, D. Maitra, H. Krishnamurthy, "Effect of Silicon Content on Modified T91 Grade Steel for Nuclear Application," ASM Heat Treat Conference, Poster Presentation, Pittsburgh, PA, September 2005.
  P. Kumar, D. Maitra, H. Krishnamurthy, "Effect of Silicon Content on Metallurgical and Corrosion Properties of Martensitic Stainless Steel," ANS Students' Conference, Columbus, OH, April 2005.

FUTURE WORK

- Tensile properties evaluation of materials at 300ºC under different strain rate conditions.
- Comparative analyses of tensile data at 300 and 400ºC under different strain rates.
- Determination of dislocation density under different experimental conditions as a function of Si content.
- Analyses of metallurgical microstructures as a function of Si content and metallurgical variables.
- Determination of the temperature dependence on critical pitting potentials, ductility parameters and true failure stress in corrosion studies.
- The determination of the effect of controlled electrochemical potential on the SCC susceptibility.
- Performance of charpy impact testing to determine the ductile-to-brittle transition temperature.
- Determination of the effect of radiation on the tensile properties of T91 grade steels.
- Characterization of fracture toughness (compact tension) and crack growth rate (double cantilever beam).

Research Staff

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Task 21

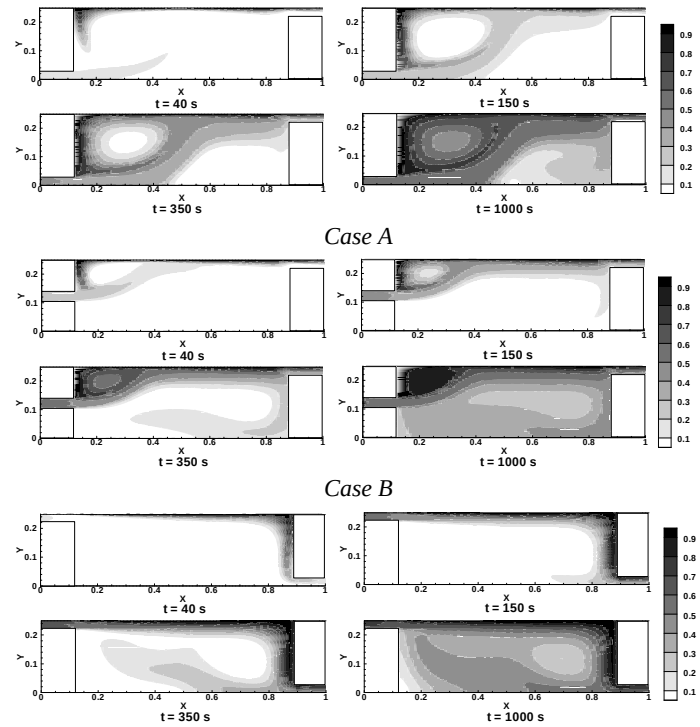
Theoretical Modeling of Protective Oxide Layer Growth in Non-isothermal Lead Alloy Coolant Systems

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-alloys coolant system. However, in a practical coolant loop, the proper oxygen level depends not only on thermal factors but also on hydraulic factors (system operating temperature, temperature profile, flow velocity, etc.). In addition, the oxygen distribution in a non-isothermal leadalloys coolant system is still unclear. The optimal oxygen levels still need to be investigated.



Oxygen concentration contours at different times (t = 40, 150, 350 and 1000 s) for different convection mode. Re = 1143 and Sc = 5 for all cases.

The goal of this research project is to provide a basic understanding of the protective oxide layer behaviors and to develop oxide layer growth models of steels in non-isothermal leadalloys (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 leadalloys nuclear coolant systems. The research project, therefore, is aimed at filling the gaps of protective oxide layer growth and the oxygen concentration level before lead-alloys nuclear coolant is ready for programmatic implementations and industrial applications.

RESEARCH OBJECTIVES AND METHODS

The research objectives are:

- To elucidate the mechanism of the protective oxide layer growth of steels in static, non-isothermal flowing lead-alloys coolant systems with oxygen concentration level control.
- To elucidate the mechanism of mass transport of oxygen, 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 process on the 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

<u>Numerical analysis on oxygen transport in LBE system</u>

The Lattice Boltzmann simulations of oxygen transfer in the liquid lead alloy system were performed to investigate the enhancement of the oxygen transport by force convection. To mix the oxygen uniformly and quickly, the forced convection is proposed to enhance the oxygen transport with a cover gas scheme. The

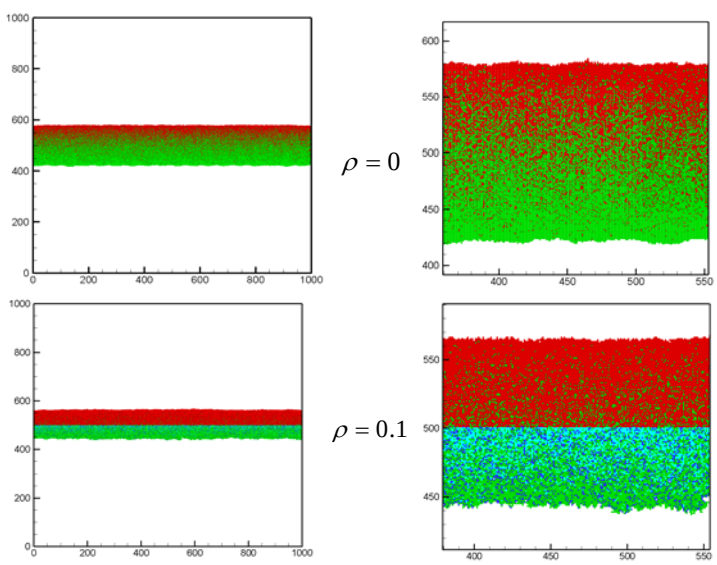
oxygen control technique with cover gas scheme is formulated. To optimize efficient mixing of the oxygen, three different forced convection flow patterns on the oxygen transport are investigated.

Stochastic modeling on morphology of oxide layer growth.

A cellular automaton model, which combines the surface growth and internal oxidation, was created to explain the oxidation mechanism of steels in liquid lead-alloys. Based on Rebertson's theory, the morphology of steel under the mechanism of corrosion and oxidation under lead-alloy environment is modeled by a cellular automaton method, which uses the simple mathematical model to investigate self-organization in statistical mechanics, and especially suitable for complex systems. A global random walk method is included to characterize the diffusion process of iron. Working on the mesoscopic level, three main processes, which include the corrosion of the substrate, the diffusion of iron species across the oxide layer and precipitation of iron on the oxide layer, are included. In contact with liquid lead alloy, a piece of steel (mainly Fe and Cr) is corroded. The oxide layer is formed by one part of the corroded steel at the local place where corrosion occurs. Meanwhile, the remaining part of iron starts to diffuse across the oxide layer till they reach the layer boundary where they precipitate as new oxide product.

Numerical modeling on the oxygen-diffusion controlled oxide layer growth model

The numerical modeling of the oxygen-diffusion controlled oxide layer growth model was developed. This moving boundary problem was solved by finite difference method with transformation of the dependent variables and the coordinates. Also, the numerical code was benchmarked with available publication results.



Snapshots of the simulated layer in the presence of corrosion and surface growth. They correspond to 2.5×10^4 time step.

ACADEMIC YEAR HIGHLIGHTS

- "Modeling corrosion and precipitation in non-isothermal LBE Pipe/Loop Systems," was published in *Journal of Nuclear Science and Technology*, 2005, 42(11): 970-978.
- "Oxygen Control Technique in Molten Lead and Lead Bismuth Eutectic Systems" was submitted to Nuclear Science and Engineering, 2006, in press.
- "Numerical analysis of corrosion behavior and oxygen transport in the nature convection Lead-Bismuth flow" was present in 2005 ASME International Mechanical Engineering Congress, November 5-11, 2005, Orlando, FL.
- "Theoretical modeling and numerical simulation of the corrosion/precipitation process in non-isothermal pipe system" was present in 2005 ASME International Mechanical Engineering Congress, November 5-11, 2005, Orlando, FL.
- "Modeling one oxygen transfer in the forced convection lead-bismuth eutectic flow" and "Corrosion and precipitation Process in non-isothermal LBE pipe/loop system" were present in ICAPP'06, Reno, NV, June 4-8, 2006.

Theoretical modeling on oxidation with scale removal in LBE system

An oxidation model with scale removal in LBE system was developed. The common kinetics of the oxide layer thickness and weight change per unit area depend on the pre-oxide thickness and the critical spallation thickness of the oxide. The steady state thickness was found to be a function of the operation conditions, such the materials, oxygen concentration, the flow velocity and the temperature.

FUTURE WORK

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

- Illustration of the erosion-corrosion process mechanisms in oxygen control lead-alloys systems.
- Identification of the protective oxide layer growth under corrosion and oxidation mechanism with using stochastic methods.
- Optimal operation conditions for oxygen control lead alloys systems.
- Analytical models for various limiting process regimes.
- Development of correlations and tools for calculation of the oxidation rate, oxygen concentration level and distribution, and oxygen consumption.

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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 was divided into several tasks:

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 performed using the MSC.visualNastran and ProEngineer simulation software tools. To date, the modeling of dispersion and TRISO fuels 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 is to 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

A fabrication process simulation model with several Waelischmiller robots in a hot cell was developed and coupled with MatLab control software. Matlab provides the interface with the robot and is used to control the system. The simulation renders a realistic simulation of the forces and torques present during robot motion. A 3-D manufacturing process simulation using CAD models and the Newtonian dynamics of the moving components has been developed.

The simulations are numerically extensive, and a single simulation can require hours to complete, depending on the complexity of the model. The speed of the simulation has been increased substantially through continuous equipment upgrades, which were essential in enabling more detailed model refinements without undue elongation of simulation run times.

Analysis of Fabrication Plant Reliability

Given the large quantities of transuranic waste to be transmuted, an automated manufacturing process will likely be required for transmuter fuel fabrication. An analysis and simulation of various design configurations is conducted on a robotic powder-process manufacturing hot cell which had been designed and analyzed previously. Work cell layouts with redundant robots, and reliability analyses of the resulting alternative layouts directly effect production operations and costs by reducing plant down times, compared to a hot cell manufacturing plant without redundancy. Methods for the assessment of plant reliability and optimization strategies for optimizing the work cell layout with redundant robots were investigated. An analysis of different plant configurations as well as quantitative decision criterion for plant selection by means of a cost function that considers both plant reliability and capital cost were conducted. The performance of various selected layouts was simulated in order to

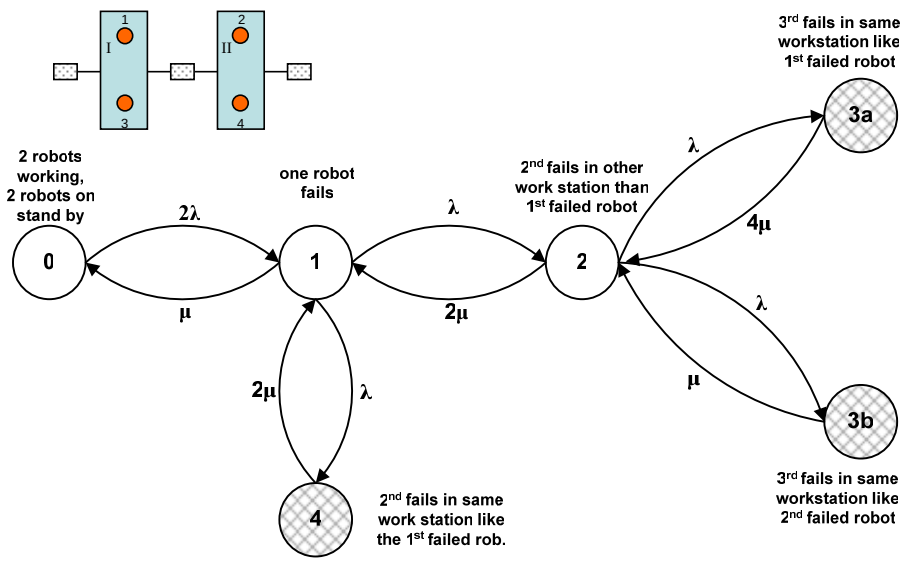
verify the overall plant performance and to study conceivable accident scenarios.

Randomly occurring robot failures and their subsequent repairs are modeled as Markov processes. This is a system with two possible states, operating or failing, and system availability and reliability can be calculated.

Plant Layout Options

Both powder and metallic processing methods of transmuter fuel manufacturing will likely require two robots for material handling inside the work cell. Redundancy is introduced by adding one or more robots. When adding one robot, it must be configured to assume two distinct alternate base positions, so that it can assume the functions of the failed device.

In a four robot configuration, two robots are placed on standby. The redundant robot takes over for the failed robot in the case of one failing robot at any one location. If the replacement robot fails at the same work station as the first failure (before completion of repair the first failed) the entire system fails. Assuming that the robots do not fail while on standby, the availability and resulting reliabilities of the four robot work cell over a time period can be calculated.



Markov Model of Hot Cell Layout with two redundant robots.

ACADEMIC YEAR HIGHLIGHTS

- G.F. Mauer and J. Renno, "Reliability Analysis of a Robotic Workcell for Transmuter Fuel Fabrication," *Proc. American Nuclear Society Winter Annual Meeting*, November, 2005.
- Student Andreas Roderburg, visiting from RWTH Aachen, completed and defended his Diploma thesis in Mechanical Engineering (January 2006). Thesis title: "Design Optimization Of Robotic Manufacturing Work Cell For Transmuter Fuel – Analysis And Simulation Of Robotic Manufacturing In A Hot Cell Environment."

Cost Function

The plant's availability is a function of each robot's failure rate and its repair rate. The annually hot cell costs result from the sum of annual investment costs and operating costs. By computing the net throughput of the production system and its capital cost, the unit costs (e.g. cost per fuel pin) can be determined by a corresponding cost function. The cost model was implemented as an interactive simulation in Matlab Simulink that permits the evaluation of multiple alternative scenarios.

Automated Vision-Based Image Acquisition and Robot Control

A remote-controlled surveillance camera (Sony EVI-D30) is operated from a computer. Image acquisition is performed by a frame grabber in the computer. The camera functions (pan, tilt, zoom, and focus) are controlled through a serial connection between camera and PC. The frame grabber transmits the image to Matlab for processing.

Object recognition is performed by identifying the object's contour, and by then matching the detected contour to those of known objects.

FUTURE WORK

Further efforts will be devoted to increasing data and knowledge regarding the cost and feasibility of automated fuel manufacture in a hot cell by analyzing candidate manufacturing processes. Artificial intelligence concepts will be developed further with respect to reliable vision-based object identification and hot cell dynamics simulations.

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Task 23

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

B.J. Das

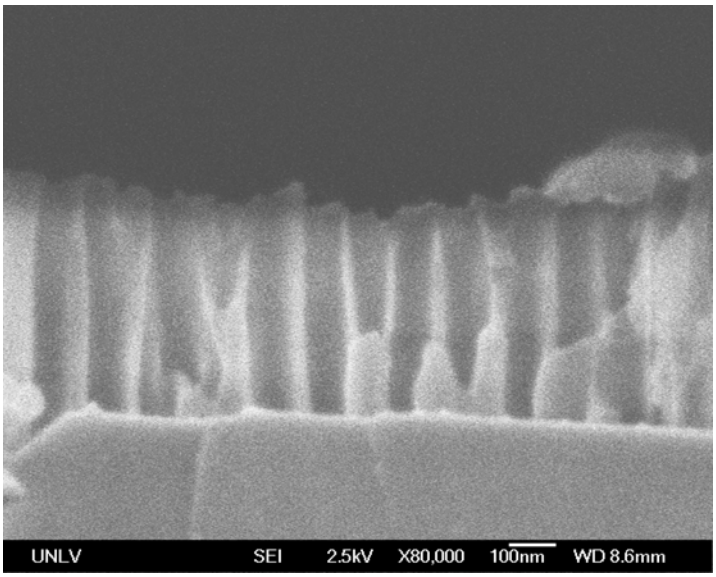
BACKGROUND

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.

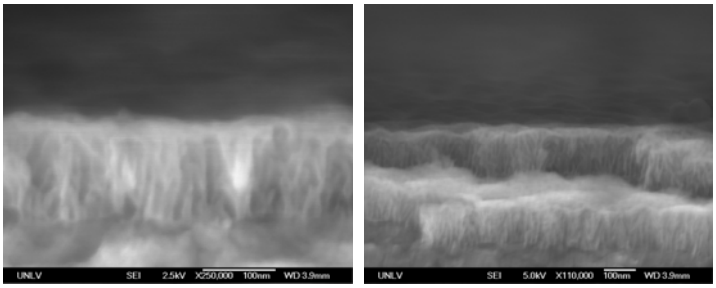
In parallel, lead bismuth eutectic (LBE) has emerged as a potential spallation target material for efficient production of neutrons, as well as a coolant in the accelerator system. While LBE has excellent properties as a nuclear coolant, it is also highly corrosive to stainless steel. The corrosion is 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.

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. 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.



Cross-sectional FESEM image of Cr nanowires inside a porous alumina template showing non-uniform distribution of nanowires.



Cross-sectional FESEM images of Ni nanowires electrochemically deposited inside nanoporous alumina for different time lengths.

Working with LANL collaborators, the stainless steel alloys HT-9 and EP-823 were chosen as the candidate materials for investigation. The 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 2 of the project (2005-2006), extensive investigation was carried out on the deposition of metal nanowires inside the pores as well as the deposition of the top dense layer of alumina. The following are the specific goals this year for the project:

- To develop the technology to deposit metal nanowires inside nanoporous alumina layers on HT-9 and EP-823 steel.
- To develop the technology to create thick dense alumina layer on metal nanowires created on steel substrates.

RESEARCH ACCOMPLISHMENTS

During Phase I of the project, a significant problem was encountered with uniformity of Cr nanowires synthesized inside the alumina pores. A systematic study was carried out to improve the

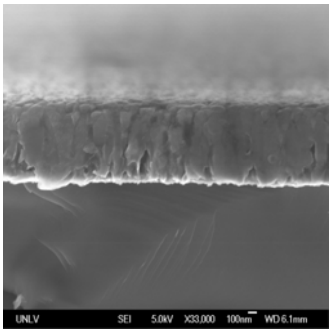
deposition uniformity; however no significant improvement could be achieved. This was a puzzling situation since a well established recipe for the deposition of Cr was used. The only explanation for the observed non-uniformity is the restricted space inside the nanopores that may not be amenable to the Cr synthesis chemistry.

As a solution to the above problem, alternative metals were looked at to form the nanowires. The purpose of the metal nanowires is to provide structural integrity to the nanoporous alumina, as well as a second defense mechanism against corrosion by oxidizing in case the top alumina layer is compromised. Nickel was selected due to its established electrochemical synthesis procedure and deposition of Ni nanowires was achieved.

In addition to the direct electrochemical deposition technique, another approach was initiated to deposit Ni inside the nanopores. This technique involves the electro-phoretic deposition of Ni nanoparticles inside the pores. A primary advantage of this technique is the improved flexibility of the Ni nanowires (consisting of nanoparticles) with thermal cycling.

Once the process parameters for the deposition of Ni nanowires were optimized, the deposition technique was transferred to steel samples. Deposition of Ni nanowires on steel substrates was achieved by using the following procedure. A new batch of steel samples were coated with metallic aluminum which were first anodized using constant current anodization. The voltage across the cathode and anode was monitored to monitor the anodization process. Since it is difficult to obtain cross-sectional images of samples created on steel samples, the filling of the nanoporous alumina pores with Ni had to be confirmed from the current-time characteristics. Based on comparison of such data with that from nanowires deposited on a silicon substrate, the Ni nanopillars deposited in the nanopores on a steel substrate are expected to have similar features as on silicon substrates.

The thick layer of dense alumina on top of the Ni nanowires provides the first layer of defense against corrosion for the steel substrates. After investigating the various techniques to deposit alumina, sputter deposition was identified as the appropriate technique for depositing thick layers of insulators. However, the insulating nature of alumina makes it a difficult task to deposit by sputtering technique. To address this problem, a pulsed DC sputtering technique was used, which is a relatively new technique for the deposition of insulators. An alumina sputter target of the appropriate dimensions was obtained for this purpose and an extensive preliminary testing was carried out to optimize the deposition process. Such preliminary experiments were carried out on silicon substrates since it allows cross-sectional imaging of the samples. The deposition rate for alumina was determined from a series of such cross-sectional images. The experimentally obtained deposition rate was used to deposit a 3 micron layer thick dense alumina layer on top of the Ni nanowires. The samples are currently being tested for thermal recycling. Effort is also continuing to deposit thicker layers of alumina, preferably up to 10 microns.



A typical cross-sectional image of dense alumina deposited on a silicon substrate by pulsed DC sputtering. Charging of the insulator prevented from getting SEM images of thicker alumina layers

ACADEMIC YEAR HIGHLIGHTS

- "Nanostructure based Corrosion-Barrier Coatings on Steel" was submitted to the *J. Nuclear Materials* (in review).

FUTURE WORK

The next phase of the project will focus on:

- extensive thermal cycling characterization of the coating layers on HT-9 and EP-823 steel at elevated temperatures,
- experimentally optimize coating parameters for maximum adhesion for thermal cycling,
- investigate and develop the deposition technique for Cr nanowires inside the alumina pores,
- evaluate the structural integrity of the coatings with Cr at elevated temperatures and under thermal cycling, and
- characterization of the coating layers in LBE.

A programmable furnace will be acquired and a specialized sample holder fabricated to perform automated thermal cycling of the coatings developed on steel samples. The samples will then be characterized by SEM and also scratch tests to evaluate the structural integrity and adhesion properties of the coatings for thermal cycling at different temperatures. The process technology will be developed for the deposition of Cr inside the alumina nanopores electrochemically to form the Cr nanowires. The nanoporous coatings on steel substrates will be subjected to elevated temperature thermal cycling, up to 500°C and 600°C. As before, the adhesion properties of the nanoporous alumina films will be evaluated using scratch tests.

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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

Simulating Spent Fuel Treatment Facility (SFTF) processes is the major focus for this project. The approach is to combine commercial process simulation software, ASPEN-Plus with the chemical separation calculation from the ANL's AMUSE code. Based on the current System Engineering Model package, TRPSEMPro (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 functionality of receiving, temporarily storing, and preparing spent nuclear fuel for leaching.

The SFTF has many individual processes that make up the overall separations process. Each individual process contains numerous operations that are responsible for the chemical separation. 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 overall goal of this project is the creation of a framework that combines all the strengths of AMUSE's complicated calculations, well-established commercial system process packages, and TRPSEMPro'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 UNLV Nevada Center for Advanced Computational Methods.

The major objectives are the following:

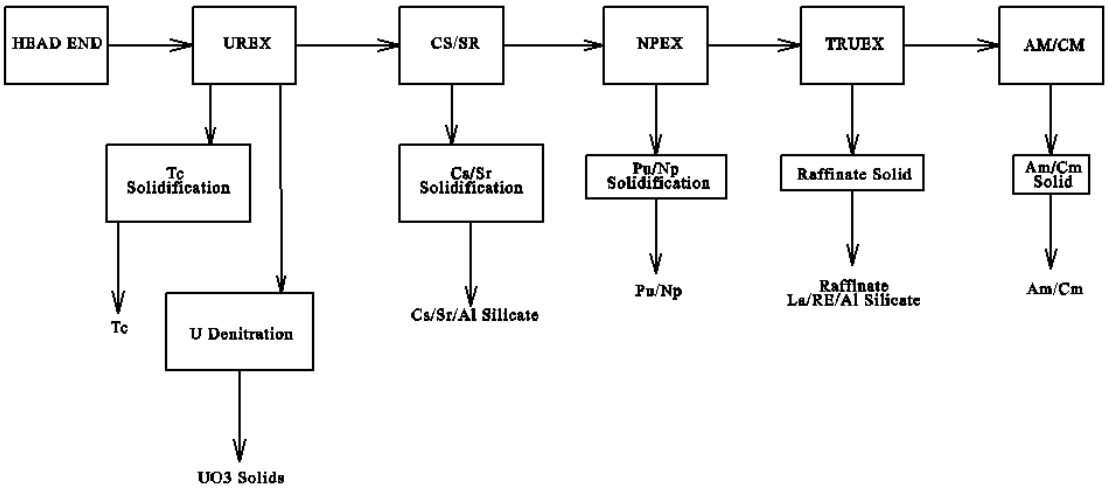
- Develop a framework for simulating the Spent Fuel Treatment Facility (SFTF) process using AMUSE code, commercial process package, such as ASPEN-PLUS, and system engineering model.
- Develop a middleware package that can communicate between the AMUSE code and any selected commercial packages.
- Extend the existing system engineering model for the optimization process that includes process simulation results.
- 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

- Completed the feasibility study of the nitric acid recycle process using the ASPEN-Plus system process package.
- Completed the "skeletal backbone" study of the NPEX process using the ASPEN-Plus system process package.
- Integrated the ASPEN-Plus process model with the TRPSEMPro system engineering modeling package, developed by the UNLV team.

<u>Process Simulation of Nitric Acid</u>

ANL is interested in understanding the feasibility of applying tower separation for nitric acid, acetic acid and water separation, with nitric acid leaving as bottoms product with a higher concentration of 4.5M from 0.6M. The purpose of the simulation is to validate the feasibility of using tower design. An arbitrarily assigned molar flow rate was chosen in an effort to test the hypothesis. Two parametric studies were conducted for this distillation simulation. The first parametric study was to observe the effects of varying the reflux ratio on the outlet flow rates while the second one examined the effect of varying the number of stages on outlet flow rate.



Overall process flow sheet.

With the temperature, pressure, feed concentration, distillate rate and number of stages held con-

stant it was desired to study how changing the reflux ratio in the column affects product flow rates. Increasing of reflux ratio gives an overall decrease of nitric acid flow rate and increase of acetic acid and water flow rate in the bottom streams. In the second parametric study, molar flow rate of nitric acid from the bottom streams continuously decreases along with the increasing of the number of stages and is gradually stabilized after number of stages larger than 6.

While the studies performed have shown that the manipulation of both reflux ratio and number of stages affects the separation of feed components, the changes are minimal and can be considered negligible. The simulation showed that it is not feasible to design a tower that removes nitric acid as a bottoms product from a feed of nitric acid, acetic acid and water. If it is desired to separate and obtain a high purity nitric acid stream; having the nitric acid leave the column as distillate is an option. Under such a circumstance, it is no longer necessary to have a rigorous separation model. ASPEN Plus can calculate the number of stages and reflux ratio based on the engineer's desired separation efficiency.

The new ASPEN Plus flow sheet for this second separation simulation will concentrate a 0.6M feed of nitric acid (in water) to a 4.5 M solution (in the tops stream). The ASPEN Plus simulation data indicates a possible optimized number of stages is around 15 with the reflux ratio of 0.60.

Process Simulation of NPEX Process

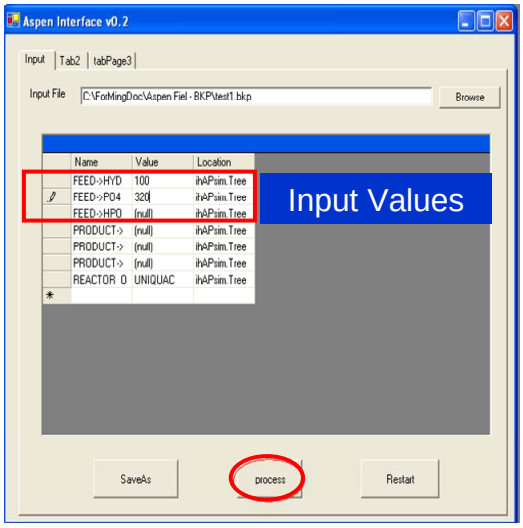
The NPEX process is used by ANL scientists to remove plutonium and neptunium from spent fuel. The work conducted in this project is the simulation of the process following the removal of the plutonium/neptunium strip product. The simulation is intended to construct a "skeletal backbone" of the plutonium metal production process due to the difficulty of acquiring the plutonium metal production process simulation parameters.

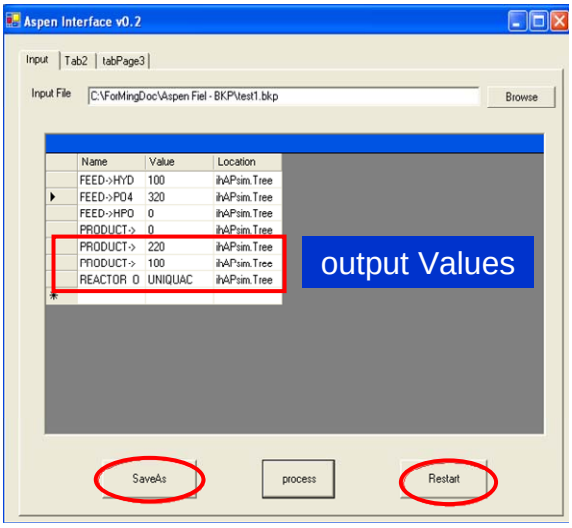
ACADEMIC YEAR HIGHLIGHTS

- "Development of Systems Engineering Model for Spent Fuel Extraction process" presented at 2005 ASME International Mechanical Engineering Congress, November 5-11, 2005, Orlando, FL.

Interface to ASPEN-Plus through the TRPSEMPro Package

To generate the middleware interface between TRPSEMPro and ASPEN Plus, element types of "Streams" and "Blocks" from ASPEN-Plus package need to be clearly identified. Streams can be further divided into input and output parts while blocks store system-related information. The currently developed interface shows the essential functions of file selection, data processing and file storage. The major role of the developed TRPSEMPro package is to perform the optimization process using both ASPEN-Plus system process engineering and chemical separation process. The data communication and result presentation from these two programs can be valuable for the SFTF design. Since the AMUSE code has been integrated with the TRPSEMPro package, the current internal database is integrated with those results generated from the ASPEN-Plus simulation. While the development of the data communication and processing tool is the major focus, optimization criteria development will be provided or developed by researchers from the ANL.





Interface for accessing ASPEN Plus package.

FUTURE WORK

- Complete the feasibility study of the nitric acid recycle process using the ASPEN-Plus system process package.
- Complete the "skeletal backbone" study of the NPEX process using the ASPEN-Plus system process package.
- Integrate the ASPEN-Plus process model with the TRPSEMPro system engineering modeling package developed by the UNLV team.

Research Staff

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Task 25

Electrochemical Separation of Curium and Americium

D.W. Hatchett and K. Czerwinski

BACKGROUND

In the AFCI 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 the lanthanides from the trivalent actinides is necessitated for 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 as 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 utilized to effectively separate actinide and lanthanide species from complex mixtures. Each chemical species has unique electrochemical properties largely based on physical properties such as ionization and chemical potential, which determine the potential for dissolution. The same thermodynamic properties identified for species dissolution from solids can be used in the deposition of these species at electrochemically controlled interfaces.

RESEARCH OBJECTIVES AND METHODS

The objective of this project is to use electrochemical techniques to develop a thermodynamic understanding of actinide and lanthanide species in aqueous solution and use this data to effectively separate species with very similar chemical properties. In consultation with a national laboratory collaborators, 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 1 examined the thermodynamic oxidation/reduction properties of actinides and lanthanides using electrochemical methods and examined how the oxidation/reduction of actinides and lanthanides change after complex formation.

Phase 2 expanded the thermodynamics studies in Phase I to include the chelation of properties Ce, Sm, and Eu at carbon, platinum and gold electrodes. It was expected that the thermodynamics of chelated species would be markedly different than the oxidation/reduction of unbound species.

Phase 3 will examine the use of conductive polymer membranes for the uptake and expulsion of complexed and uncomplexed actinide and lanthanide species and examine the uptake and 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. The potential mediated separation of single chemical species within a mixture will be the focus.

The following were specific goals for this year:

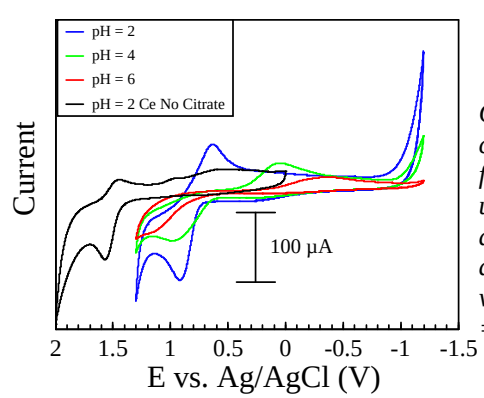
- To develop a fundamental understanding of the thermodynamic properties of actinide and lanthanide species such as Cm, Am, Ce, Nd, Eu, and Sm after complex formation.
- To examine how chelation influences the thermodynamic properties of waste form species.
- To use systematic studies to distinguish the thermodynamic signatures and ability to shift thermodynamic potentials using chelation to enhance separation properties.

RESEARCH ACCOMPLISHMENTS

The thermodynamic characterization of Ce^{3+}/Ce^{4+} redox couple and other lanthanide species has been completed in various supporting electrolytes (0.3 M $NaNO_3$, 0.5 M HNO_3, and H_2SO_4 at concentrations of 0.1 M, 1.0 M, 2.0 M, and 4.0 M). The results show that the Ce^{3+}/Ce^{4+} redox couple can be successfully resolved in aqueous environments. While the potential range was suitable for the resolution of the Ce^{3+}/Ce^{4+} redox couple it was insufficient for others. Species such as Eu and Sm were not resolved within the potential limitation of the aqueous system.

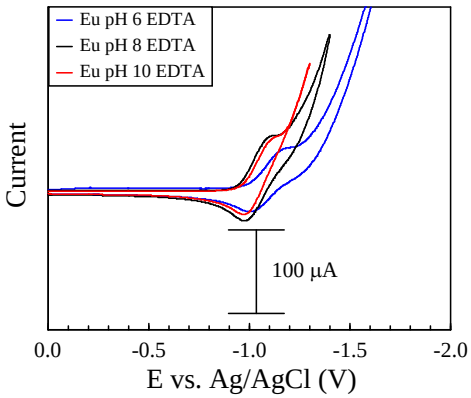
To expand the ability to resolve the electrochemical response of other species besides the Ce^{3+}/Ce^{4+} redox couple the chelation properties of ligands such as EDTA, NTA, and Citrate were utilized. The Ce^{3+}/Ce^{4+} redox couple was examined first due to the fact that the electrochemistry of the unbound species has been fully characterized.

These studies were expanded to include other chelating species with similar results including citrate. The figure below shows the chelation of Ce by citrate as a function of pH. The data for bound and unbound Ce are shifted relative to each other indicating that the thermodynamics of bound species is much different than the unbound. The difference in redox potentials for Ce bound by EDTA and Citrate indicate that chelation can be used effectively to separate species in solution. It is also apparent that the pH dramatically influences the voltammetry in citrate solutions. This is not the case for EDTA with stable redox chemistry over a pH



Electrochemistry of Ce and Ce/Citrate chelated species as a function of pH. The unbound Ce (black) and Ce/EDTA (blue) at pH = 2 are shown with Ce/EDTA at pH = 4 and pH = 6.

Electrochemistry of Eu/EDTA chelated species as a function of pH.



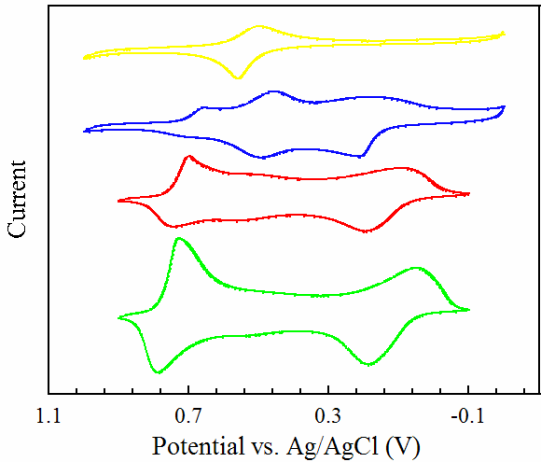
range from 2 to 12.

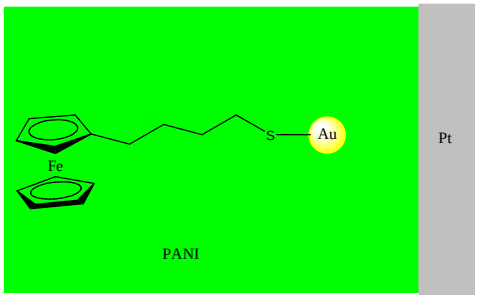
The success of shifting the redox potentials for Ce bound to species such as EDTA and citrate ion suggest that species that were not resolved when unbound may be resolved after chelation. For example, the figure above shows the voltammetric response of Eu which was not resolved when unbound, after chelation with EDTA. The redox chemistry has been shifted such that the oxidation and reduction Eu/EDTA can be resolved at very negative potentials. This species should precipitate as a hydroxide at the pH values presented in this figure. However, EDTA stabilizes the species at higher pH values allowing the electrochemistry to be resolved. The voltammetry at pH = 6 is more fully resolved than at the other pH values. However, the oxidation and reduction can be resolved at all three pH values. The redox chemistry of the Sm/EDTA species has also been successfully observed.

The last phase of this research is based on the electrochemical separation of americium and curium. The proof of principal for this experiment is shown in the figure below left. In this figure the doping of polyaniline (PANI) is shown (green) followed by the second doping (red) after the uptake and reduction of Au particles in the polymer membrane. These particles will be used to affix the chelating ligand and then the applied potential will be used to facilitate complexation and speciation. To test the ability of the Au particles interaction with thiol molecules a simple five carbon thiol with a ferrocene tail was allowed to interact with the PANI/Au membrane. The results are shown in blue in the figure with a schematic of the system to the right. For comparison the oxidation and reduction of the ferrocene thiol at a planar gold electrode is shown in yellow in the figure. The oxidation and reduction of ferrocene is clearly visible in the polymer indicating the gold particles are electroactive and can act in potential mediated chemical reactions. The ultimate goal is to use this in separation reactions using an EDTA/thiol ligand that was synthesized in the lab.

ACADEMIC YEAR HIGHLIGHTS

- S. Elkouz, K. Czerwinski, and D.W. Hatchett, "The Electrochemical Characterization of Ce at Au, Pt and Glassy Carbon Electrodes: Influence of pH and Ionic Strength," manuscript submitted, 2006.
- S. Elkouz, K. Czerwinski, and D.W. Hatchett, "The Electrochemical Characterization of Ce at Au, Pt and Glassy Carbon Electrodes: Influence of pH and Ionic Strength," 209th Electrochemical Society Meeting, Denver, CO, May 9 – 13, 2006.





Acid doping of PANI in $HClO_4$ before uptake of Au (green) and after (red). Redox properties of a PANI/Au/FcThiol membrane in $HClO_4$ (blue) and Au/FcThiol (yellow). A schematic of the PANI/Au/FcThiol is provided to the right for clarity.

FUTURE WORK

Future work will focus on the potential mediated chelation of lanthanide and actinide species using the system described above. A thorough understanding of the influence of pH and ionic strength and how these parameters influence the thermodynamics of species such as Eu, Ce, and Sm has been attained. Initially, planar Au electrodes will be used to chelate the species of interest in the absence of polymer to determine the potential for chelation for individual species. With this information the potential to control the chelation of individual species will be used. The ultimate goal is to separate individual species, thus providing highly efficient separation through potential mediation.

Research Staff

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Task 26

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

K. Czerwinski and B. Bennett

BACKGROUND

The extraction of tetravalent Pu in nitric acid solution by tributyl-phosphate (TBP) is well known and has been the basis of Pu purification for a number of decades. The extraction is based on the formation of organic phase neutral complexes. Upon reduction, the trivalent Pu species 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 AFCI.

Understanding the role of nitrate in Pu speciation is important for determining the necessary data for Pu extraction modeling. Data indicates the dinitrate complex of Pu is strong and may account for difficulties in modeling Pu extraction under some nitrate conditions. The formation of hydrolysis products may also form an extractable species that will need to be included in modeling.

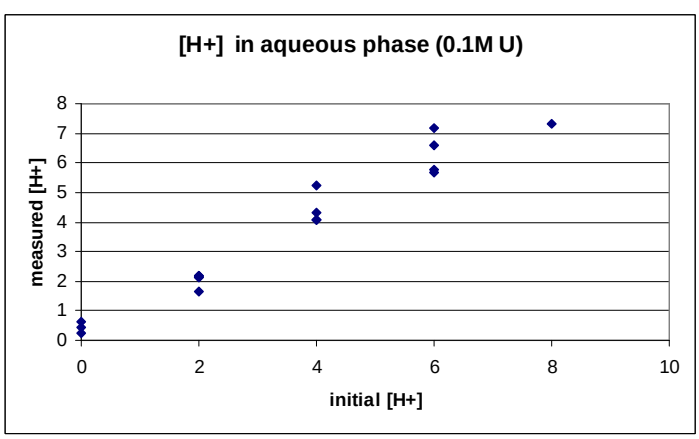
In the UREX process, acetohydroxamic acid (AHA) is expected to be used. The interaction of AHA with tetravalent Pu decreases extraction into the organic phase by either complex formation or reduction of Pu to the trivalent state. For the separation of Pu in a solvent extraction system using acetohydroxamic acid, it is necessary to determine the complexation kinetics and thermodynamics.

In addition, since Pu is a redox sensitive element, the change in speciation due to oxidation-reduction reactions upon complexation needs to be evaluated.

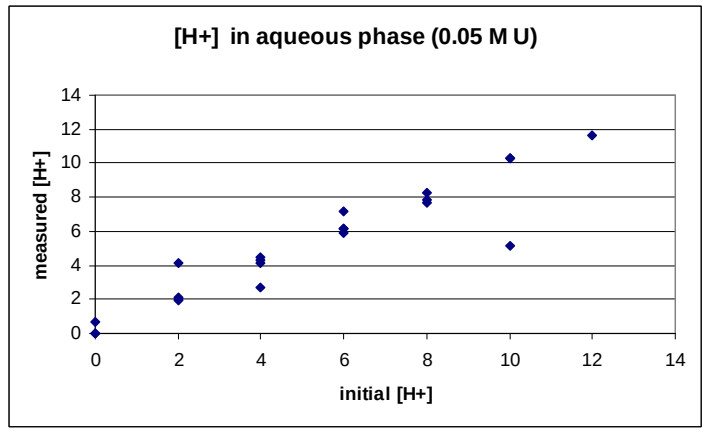
RESEARCH OBJECTIVES AND METHODS

The research objectives of this project are as follows:

- 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 (by the addition of $NaNO_3$), actinide ion concentration, temperature, and time.



Measured aqueous acid concentration with varied initial acid.



Measured aqueous acid concentration with varied initial acid.

- 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. Experiments will initially examine the aqueous phase then examine the two phase system.
- To incorporate thermodynamic and kinetic data into existing modeling codes.

The following experimental techniques are used in the evaluation of U and Pu speciation: UV-Visible spectroscopy, Time resolved laser fluorescence spectroscopy, NMR spectroscopy, IR spectroscopy, Raman spectroscopy, Titrations, ICP-MS, ICP-AES, XAFS, and Electrochemical. Initial experiments are performed with UO_2^{2+}. The initial results obtained with UO_2^{2+} are the basis for further experiments with Pu.

RESEARCH ACCOMPLISHMENTS

Efforts focused on methods for the determination of nitrate concentration in the experimental system. Ion Chromatography (IC) was examined as a method for nitrate determination and was found to be suitable.

Analysis of XAFS data was completed during year. Different hypotheses were proposed in the literature concerning the nature of the U species in the heavy organic phase examined:

i) formation of the compound $HUO_2(NO_3)_3$.xTBP
ii) formation of U(VI) polymer
iii) modification of nitrate bounding and formation of hydrogen bond with water or acid nitric present in the third phase

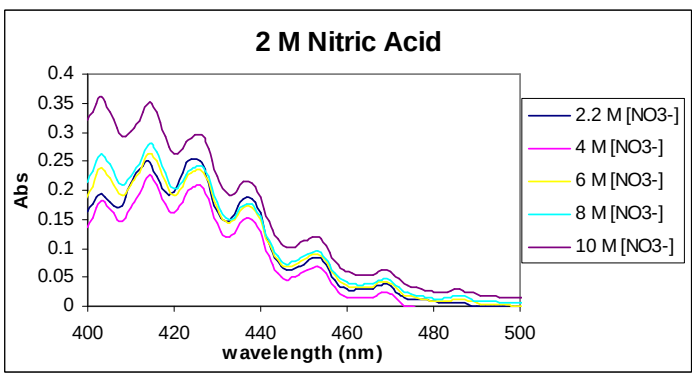
According to EXAFS result obtained in this study the following was found for the different theories. Hypothesis (i) was rejected since the formation of an eventual $HUO_2(NO_3)_3$.xTBP will lead 6

O(N) atom at 2.50 Å, and this was not found. Hypothesis (ii) cannot be completely rejected, and it might be possible that $[UO_2(NO_3)_2.2TBP]_2$ and $UO_2(NO_3)_2.2TBP$ are simultaneously extracted in the heavy third phase. Hypothesis (iii) corroborates the observation from 15 M HNO_3 media but is not verified in 8M and 12 M HNO_3 media.

Extraction studies on samples containing two different uranium concentrations were performed. The organic phase of each sample consisted of a pre-equilibrated solution of 30% TBP (tributylphosphate) in dodecane. The aqueous phase consisted of nitric acid (0-12M), lithium nitrate (0-12M), uranyl nitrate (0.1 and 0.05M) and water. After contact the phases were separated and analyzed for nitrate and uranium concentrations by IC (ion chromatography) and LSC (liquid scintillation counting), respectively. The amount of nitrate extracted into the organic phase was surveyed. The data shows a slightly increasing trend as nitric acid and total nitrate increase though, generally the amount of nitrate extracted stays between 0.5 M and 1.5 M regardless of the varying initial nitrate, acid or uranium concentrations. The distribution ratio for uranium has shown a general decrease with increasing acid concentration and an increasing trend with increasing nitrate concentration. Both of these effects seem to level of around a K_d value of 10 which occurs around 10 M acid and nitrate.

The acid concentrations of the samples were determined by titration in order to have more complete information about the phases. Also UV-Vis spectroscopy was done on the organic phases of the samples.

The organic phases of the samples were examined with UV-Visible spectroscopy. There are not noticeable peak shifts as the nitrate increases, but the relative peak heights do change. The peak around 403nm gets larger while the peak at 425nm gets smaller. The trends in this spectrum are very similar to the other spectra taken when holding acid concentration constant. Similar effects are not seen when holding total nitrate concentration constant. This suggests that as nitrate concentration increases there may be a difference in the bonding around uranium with a chance in speciation to the nitrato form.



Uranium absorbance with varied nitrate.

ACADEMIC YEAR HIGHLIGHTS

- J. Plaue, S. Goeury, J. Petchsaiprasert, M. Draye, J. Foos, and K. Czerwinski, "Comparison of Uranyl Third-Phase Formation in 30 % TBP-Nitric Acid in Dodecane and HPT using UV-Visible Spectroscopy," *ACS Symposium Series 933, Separations for the Nuclear Fuel Cycle in the 21st Century*, Gregg Lumetta et al. editors, 119-134 (2006).
- J. Plaue, A. Gelis, and K. Czerwinski, "Actinide Third Phase Formation in 1.1 M TBP/Nitric Acid/Alkane Diluent Systems," *Sep. Sci. and Techn*, 41, 1–10 (2006).
- J. Plaue, A. Gelis, K. Czerwinski, P. Thiyagarajan, and R. Chiarizia, "Small-angle neutron scattering study of plutonium third phase formation in 30% TBP/HNO3/alkane diluent systems," *Solv. Extr. Ion Exch.* 24(3), 283-298, (2006).
- J. Plaue, A. Gelis, and K. Czerwinski, "Plutonium third phase formation in the 30% TBP/nitric acid/hydrogenated polypropylene tetramer system," *Solv. Extr. Ion Exch.*, 24(3), 271-282 (2006).

The interaction of uranium with AHA was reinvestigated. The ionic strength was held constant at 1.003 M using $NaClO_4$ with a constant 4:1 ratio AHA to uranium and the pH varied from approximately 0 to 10. There was a noticeable optical variation with pH and an accompanying change in absorbance. Further experiments were performed at pH 5 with a constant uranium concentration and the AHA varied. Kinetic experiments were also performed and showed rapid complexation of uranium to AHA.

FUTURE WORK

The influence of nitrate and pertechnetate on the speciation of U and Pu in the TBP-dodecane-nitric acid system will be examined. The nitrate research is a continuation of previous studies. The pertechnetate studies will included experiments with perhenates. The speciation of U and Pu with AHA in the presence and absence of TBP-dodecane organic phase will be continued, with an emphasis on the impact of the organic system.

Research Staff

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Task 27

Reactor Physics Studies for the AFCI Reactor-Accelerator Coupling Experiments (RACE) Project

D. Beller

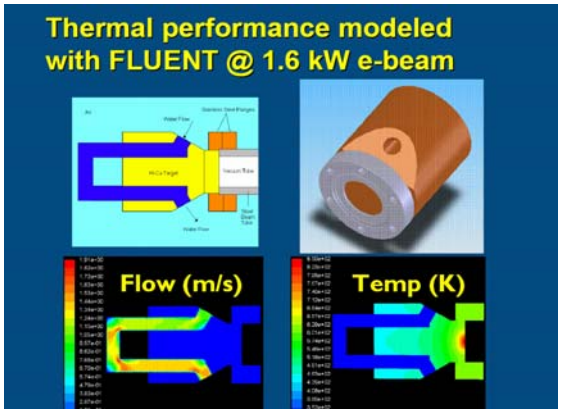
BACKGROUND

In the RACE Project of the Advanced Fuel Cycle Initiative, a series of accelerator-driven subcritical systems (ADSS) experiments were 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 x 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. 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.

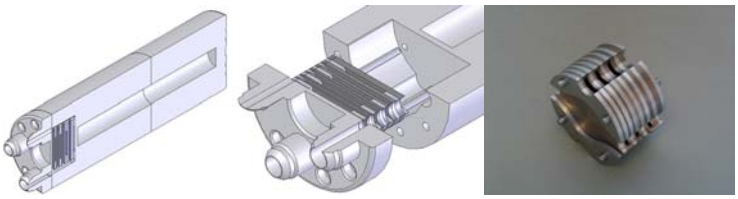
The RACE Project is an important intermediate step between the recent European program MUSE and a future near full-scale demo. For design of full scale ADSS, a complete knowledge of the effects of the driving neutron source is essential. This will ultimately require spectral, temporal, directional, and 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 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.

RESEARCH OBJECTIVES AND METHODS

The specific research objective of this three-year project is to design and conduct an accelerator driven experiment. This experiment 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.



Modeling of the Texas RACE target with FLUENT computational fluid dynamics code.



High-power RACE Target. The left is a cutaway drawing of the full assembly as assembled showing the target, water cooling channels, and electron-to-photon converter plates. The middle picture is a close-up of the plate assembly and water cooling channels. At the right is a photograph of tungsten-copper converter plates and spacer assembly with alignment pins.

RESEARCH ACCOMPLISHMENTS

Modeling for Texas RACE

UNLV examined the thermal performance of the accelerator target for experiments to be conducted at UT-Austin with their TRIGA reactor. A MCNPX (LANL radiation transport code) model was developed to produce energy deposition data for thermal analysis of the Texas RACE target. FLUENT, a computational fluid dynamics code, was then used to predict the thermal performance of the target.

High-power Target Design

A new high-power, uranium-containing water-cooled target for the RACE Project was designed, constructed and tested. The design included a tungsten electron-photon converter, an aluminum cooling shroud, and aluminum-clad natural uranium photon-neutron converter. After analyzing and constructing a prototype of a compact version of the Cooled Electron Target — Optimized for Neutron production (CETON), it was determined that a design change was needed. The new design includes a multiple plate tungsten electron-photon converter, an aluminum cooling shroud, and a cavity for inserting an aluminum-clad natural uranium photon-neutron converter. The CETON was assembled in Nevada and successfully leak tested with high-pressure water. The finished High-Power RACE (CETON) Target was then assembled and tested at the Idaho Accelerator Center with lead beads substituted for the uranium rod. Thermal and neutron production performance with an electron linac were measured.

As a result of their design, acquisition, fabrication, and construc-

tion, the students won the UNLV Mechanical Engineering Senior Design Competition for their design of the High-Power RACE Target.

Reactor Physics Studies

A variety of code systems for modeling neutron generation and transport and thermal feedback effects in accelerator-driven TRIGA as well as other reactors were evaluated. Code systems considered were ERANOS, RELAP, PARCS, and APOLLO. Modeling with MCNPX was initiated in support of subcritical experiments at the Idaho Accelerator Center and of target design studies for Texas RACE. Electron beam/target interactions were studied for maximizing and characterizing photoneutron production from high-energy electrons.

Experiments

UNLV collaborated with ISU and CEA in a series of accelerator-driven subcritical (ADS) experiments at the Idaho Accelerator Center. A fuel loading/criticality measurement experiment was conducted in the ISU RACE Subcritical Assembly (SCA). This measurement was followed by a series of ADS experiments using a low-power, 20-MeV electron accelerator coupled to the SCA with a tungsten-copper neutron generating target. Results are being analyzed.

Components of the CETON (Cooled Electron Target — Optimized for Neutron production) excluding tungsten-copper disks for converting electrons to photons. The W-Cu disks fit in the cavity at the upper left. In addition, the body is bored to accept a 10" aluminum-clad uranium photo-neutron generator.

ACADEMIC YEAR HIGHLIGHTS

- D. Beller, F. Harmon, T. Ward, and F. Goldner, "Update on the AFCI Reactor-Accelerator Coupling Experiments (RACE) Project," *Proceedings of the Nuclear Criticality Safety Division 2005 Conference*, Knoxville, TN, Sept 21, 2005.
- D. Beller and J. Knebel, "Phase IV of the RACE Project: European Collaborations," *Transactions of the American Nuclear Society, 93*, Washington, DC, pp. 901-902 (2005).
- D. S. O'Kelly, D. Beller, and W. S. Charlton, "Accelerator Driven Subcritical System Experiments at The University of Texas," *Transactions of the American Nuclear Society, 93*, Washington, DC, p. 903 (2005).
- V. K. Taraknath Woddi, S. OKelly, T. Green, and D. Beller, "Reactor-Accelerator Coupling Experiments (RACE): Heat Generation Rates Using W-Cu and U Targets, W. S. Charlton," *Transactions of the American Nuclear Society, 93*, Washington, DC, pp. 904-906 (2005).
- J. Chen, D. Beller, F. Harmon, and K. Sabourov, "ISU Accelerator-Driven Sub-critical System Characterization," *Transactions of the American Nuclear Society, 93*, Washington, DC, pp. 907-908 (2005).
- D. Beller, Overview of the AFCI Reactor-Accelerator Coupling Experiments (RACE) Project, *Proceedings of the Eighth Information Exchange Meeting on Actinide and Fission Product Partitioning & Transmutation*, OECD/NEA, Paris, France, pp 495-504 (2005).
- D. Beller, A. Hunt, J. Bennion, M. Reda, K. Sabourov, R. Spaulding, and K. Folkman, Initial Results from the AFCI Reactor-Accelerator Coupling Experiments (RACE) Project, *Proceedings of the Eighth Information Exchange Meeting on Actinide and Fission Product Partitioning & Transmutation*, OECD/NEA, Paris, France, pp 699-710 (2005).
- T. Beller, B. Howard, R. LeCounte, and D. Beller, "High-Power Accelerator Target Design for the AFCI RACE Project," *Proceedings of the 2006 International High Level Radioactive Waste Management Conference*, 2006.

FUTURE WORK

UNLV will focus on conducting subcritical experiments at ISU and completing the evaluation of the CETON high-power RACE target. The ADSS experiments will focus on increasing the level of subcriticality of the ISU RACE assembly, evaluation of results, and comparison to Monte Carlo modeling. The target work will include further testing at the Idaho Accelerator Center and analysis of results using MCNPX and FLUENT.

Research Staff

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Shruti Patil, Graduate Student, Department of Electrical and Computer Engineering
Timothy Beller, Brice Howard and Ryan LeCounte, Undergraduate Students, Department of Mechanical Engineering

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William Charlton, Texas A&M University
Sean O'kelly, University of Texas at Austin
John C. Lee, University of Michigan

Task 28

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

T. Hartmann

BACKGROUND

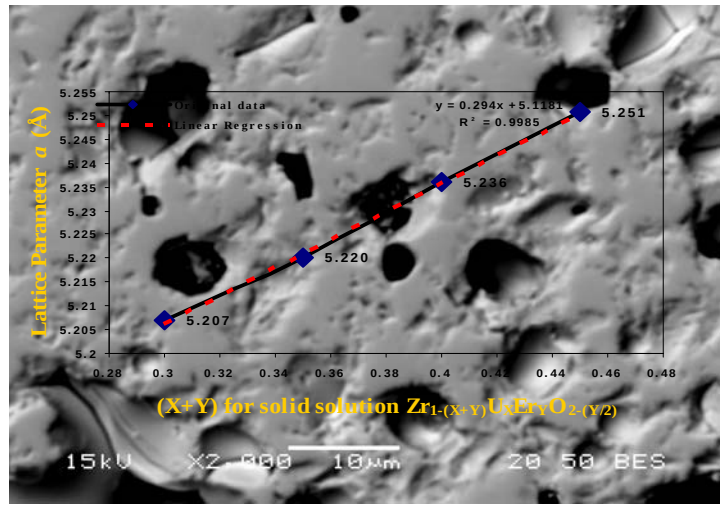
Advanced Fuel Cycle Initiative research on transmutation fuels includes mono-nitride ceramic fuel forms, and consists of closely coordinated "hot" actinide and "cold" inert and surrogate fuels work. Matrix and surrogate materials work involves three major components: (1) fuel matrix synthesis and fabrication, (2) fuel performance, and (3) fuel materials modeling. The synthesis and fabrication component supports basic material studies, as well as actinide fuel fabrication work through fuel fabrication process development. Fuel performance studies are examining the tolerance of nitride-type fuel to heavy irradiation damage. The fuel materials simulation work involves both atomistic and continuum scale modeling employing first principles, molecular dynamics, and thermo-chemical calculations. This modeling work is closely integrated with fuel design and experimental work where it provides prediction of phase transformation and stability, reaction kinetics, radiation damage mechanism and tolerance, and fission product retention. Results for fuel fabrication and radiation tolerance studies based on the proposed ZrN fuel matrix material will be reviewed as well as experimental surrogate studies for volatilization and phase stability. The actinide fuel effort at LANL emphasizes synthesis and fabrication of actinide-bearing nitride fuel pellets. These pellets are designed to be inserted into the Advanced Test Reactor and contain varying amounts of Pu, Am, Cm, and Np.

Presently, fuel materials simulation work which involves atomistic and continuum scale modeling, molecular dynamics, and thermo-chemical calculations are based on a theoretical understanding of crystal structure and microstructure of inert matrix fuels. This task's contribution is to provide real structural data on surrogate and radioactive fuels. Crystallographic properties are being determined and nano structures of oxide-based and nitride-based fuels, as considered for next generation reactor fuels, are being imaged after applying different synthesis routes. The chemical behavior of the ceramics under repository, reprocessing, and reactor conditions will be examined. Two fully equipped sample preparation laboratories can be taken advantage of, one for the preparation of surrogate fuel, and one for the preparation of radioactive fuel specimens.

RESEARCH OBJECTIVES AND METHODS

The research objectives are:

- Installation of sample preparation equipment for radioactive fuel samples to allow the manufacture of high quality polished microscopy samples and electron transparent TEM specimens.
- Literature research on Inert Fuel Matrix (IMF) fuels.
- Optimized synthesis of oxide fuels in the system ZrO2 – Er2O3 – UO2.



Oxide fuel sample in the system Zr-U-Er-O by Scanning Electron Microscopy, BES, 2,000 times magnified. The oxide fuels do not contain domains or impurities. The lattice parameter a in the solid-solution phases $Zr_{1-(X+Y)}U_XEr_YO_{2-(Y/2)}$ increases linearly with the substitution of uranium and erbium for zirconium.

- Synthesis of nitride fuels in the system ZrN-ErN-UN by carbothermic reduction / nitridization.

RESEARCH ACCOMPLISHMENTS

Zirconia-based Ceramic Fuel in the System ZrO_2-$ErO_{1.5}$-UO_2

Oxide fuels have been successfully synthesized in the system ZrO_2-UO_2-$ErO_{1.5}$ as phase-pure solid-solution phases of $Zr_{1-(x+y)}U_xEr_yO_{2-(y/2)}$ for $0.3<(x+y)<0.45$. The oxide phase $Zr_{1-(x+y)}U_xEr_yO_{2-(y/2)}$ is showing a linear increase in the lattice parameter as the substitution of U+Er for Zr progresses and the lattice parameter *a* increases from 5.2070(3) Å for (x+y)=0.3 to 5.2507(3) Å for (x+y)=0.45.

Prototype Zirconia-based ceramic fuel in the System ZrO_2-$ErO_{1.5}$-UO_2 was produced through dry chemical processing. The synthesis was completed after annealing at 1700°C for 24 hrs to 48 hrs in inert/reducing atmosphere.

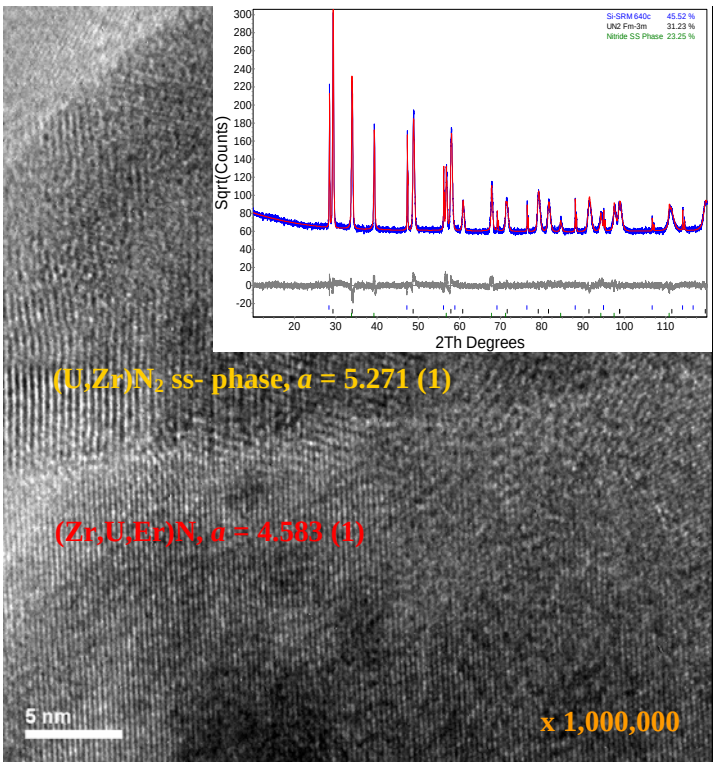
Ceramic Nitride Fuel in the System ZrN-ErN-UN

The synthesis of radioactive nitride fuel in the system ZrN-ErN-UN through carbothermic reduction/nitridization led to the formation of a ZrN-based solid solution phase and UN_2-based solid solution phase, indicating different affinities of zirconium and uranium to nitrogen. An electron-transparent TEM specimen was prepared and the structure of the ceramics could be imaged with highest resolution. Ceramic ZrN surrogate fuel samples (provided by LANL) were analyzed by TGA/DSC thermal analysis in the temperature range of 25°C to 1400°C in N_2 atmosphere, and

changes in phase constitution and crystal structure were analyzed by XRD-Rietveld analysis and by TEM. One of three ZrN samples exhibited an exothermal reaction at about 1169°C while all samples gain about 1% in weight associated with the formation of Zr_2ON_2 and increased cubic zirconia contents.

Ceramic Nitride Fuel in the System ZrN-ErN

The carbothermic reduction / nitridization of $Zr_{0.7}Er_{0.3}O_{1.85}$ lead to the formation of $Zr_{1-x}Er_xN$ (lattice parameter a = 4.6085(3) Å) and $(Zr_{1-x}Er_x)_2(N,O)_3$ (lattice parameter a = 10.940(1) Å). As a result, the solubility e.g. of rare earth elements in nitrides is significantly lower than in the precursor oxide system, which can result in phase separation while applying carbothermic reduction / nitridization. In order to closer study and to quantify these phenomena focus was placed on solubility limits of erbium (a designated neutron poison) in zirconium nitrides. The solubility limit of erbium in zirconium-mononitride surrogate fuel at 1700°C was determined. Therefore a mono-phase $Zr_{0.7}Er_{0.3}O_{1.85}$ precursor oxide-solid solution was synthesized and treated at 1700°C for 20h in purified nitrogen atmosphere. The phase constitution and the phase compositions of the equilibrium phases were determined quantitatively using XRD/Rietveld analysis and especially electron microprobe analysis. The impact of erbium solubility on the crystallographic parameter of ZrO_2 and ZrN was determined. Four samples of the solid-solution phase $Zr_{1-x}Er_xO_{2-x/2}$ for $0.02<x<0.12$ were synthesized and their lattice parameter were determined by XRD/Rietveld analysis. The solid solution phases in the system $Zr_{1-x}Er_xO_{2-x/2}$ were treated by carbothermic reduction/nitridization to further determine the impact of erbium solubility on the crystallographic parameter in ZrN-based mononitrides. The phase constitution of the mononitride system $Zr_{1-x}Er_xN$ was determined. The solubility limit for erbium in the system $Zr_{1-x}Er_xN$ was measured to be $0.07<x<0.10$.



High resolution image of Zr-Er-U-N ceramic nitride fuel after carbothermic reduction/nitridization of an oxide solid solution. An interface between two solid solution phases can be observed. The radioactive ceramic TEM sample was prepared using an ultra-microtome. The phase constitution was confirmed by XRD/ Rietveld Analysis and the crystallographic parameter refined. The image is 1,000,000 times magnified.

ACADEMIC YEAR HIGHLIGHTS

- G.W.C. Silva, T. Hartmann, K. Czerwinski, "Synthesis and characterization of GEN IV reactor fuels," 231st ACS National Meeting, Atlanta, GA, March 26-30, 2006.
- K.S. Holiday, T. Hartmann, K. Czerwinski, "Zirconium-Magnesium oxides as inert matrix fuels," 231st ACS National Meeting, Atlanta, GA, March 26-30, 2006.
- S.L. Voit, K.J. McClellan, C.R. Stanek, J.T. Dunwoody, T. Hartmann, S.A. Malloy, S.P. Willson, G.E. Egeland, R.W. Margevicius, H.T Hawkins, "The Design and Production of Nitride Fuels for the AFCI Program," *Proceedings of Global 2005*, Tsukuba, Japan, October 9-13, 2005.
- C.R. Stank, K.J. McClellan, J.T. Dunwoody, R.W. Margevicius, T. Hartmann, "Optimization of Nitride Fuel Processing through Surrogate Experiments," Global 2005, Tsukuba, Japan, October 9-13, 2005.

Production of TRISO-type fuel kernels by Sol-Gel Method

The first spherical precursors for the potential production of TRISO-type kernels could be produced and - after calcination - kernel sizes between 400 mm and 320 mm were measured. For now the spheres show poor isotropy. Some kernels are hollow and the overall kernel quality has to be improved much further.

FUTURE WORK

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

- Determine solubilities and phase constitution in the system ZrN-ErN-UN.
- Optimize TEM sample preparation to be able to perform PEELS spectroscopy.
- Improve fuel synthesis applying wet-chemical processing (including particle fuel).
- Study fuel corrosion under different scenarios.
- Determine impact of heavy ion-irradiation to fuel properties.

Research Staff
Thomas Hartmann, Principal Investigator, Research Scientist, Harry Reid Center
Ken Czerwinski, Principal Investigator, Associate Professor, Department of Chemistry

Students
Chinthaka Silva, PhD Student, Department of Chemistry

Task 29

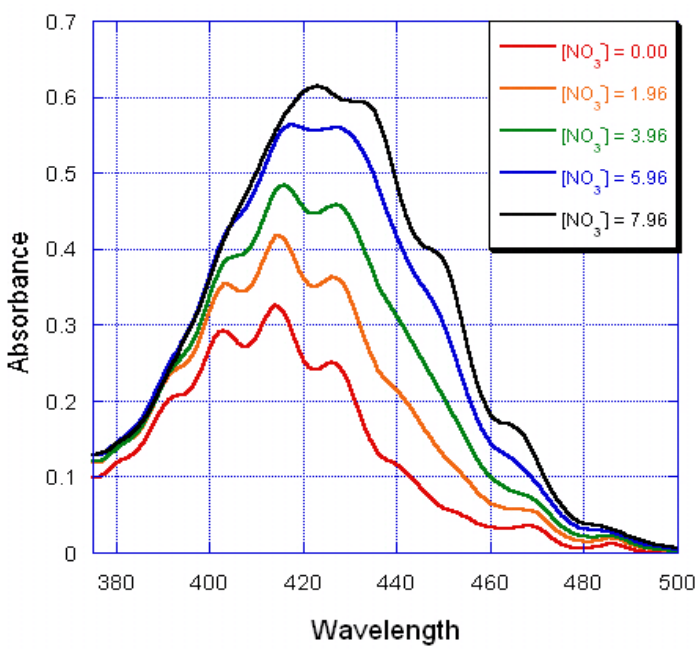
Investigation of Optical Spectroscopy Techniques for On-Line Materials Accountability in the Solvent Extraction Process

G. Cerefice and K. Czerwinski

BACKGROUND

One of the primary challenges facing any advanced fuel cycle is the proliferation resistance of that fuel cycle, especially the potential for illicitly diverting nuclear material from the fuel cycle for other purposes. The key step in almost all of the fuel cycles currently under evaluation in the Advanced Fuel Cycle Initiative is the chemical separation and partitioning of used nuclear fuel, either as the starting point for treating existing used fuel, or as a key step in the recycling and destruction of the higher actinides. Any partitioning of the actinides has the potential for decreasing the proliferation resistance of the fuel cycle unless the process or plant can be designed to prevent, or at least detect, the diversion of nuclear material from the process. To address this concern, the AFCI has proposed that any new separations plant include in its design an integral system capable of providing materials accountability for the actinide elements to minimize the potential for undetected diversion of material.

Optical spectroscopic techniques, such as Ultraviolet-Visible Spectroscopy (UV/Vis) and Laser Fluorescence Spectroscopy (LFS), allow for the on-line, real-time analysis of the actinide elements for a solvent extraction process. UV/Vis and LFS are quantitative analytical techniques that have been used for measuring the concentration of the actinides under laboratory conditions, and are easily adaptable to multiple sampling geometries, such as dip probes, fiber-optic sample cells, and flow-through cell geometries. 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. In addition to the potential materials accountability applications, UV-Vis Spectroscopy and LFS can provide information regarding the speciation of the actinides in the process stream (oxidation state, complex formation, etc.). This information will help elucidate the behavior of the actinides under process conditions, improving the understanding of the chemical interactions underlying these separations processes.



Effect of increasing nitrate concentration on uranyl spectra.
$[UO_2^{2+}] = 0.047$ M, $[H^+] = 2.0$ M

RESEARCH OBJECTIVES AND METHODS

The long-term goal of this project is the evaluation of optical spectroscopy-based techniques for the on-line, real-time determination of actinide element concentrations in fuel recycling plant process streams. To generate the information necessary to evaluate the potential of these systems, initial experiments will focus on determining the detection limits for UV/Vis and LFS will be measured for the actinide elements under chemical conditions representative of the process streams for the UREX+ process. The system will then be systematically explored to examine the impact of acid concentration, nitrate concentration, redox potential, diluent concentration, ligand concentration, and contaminant/fission product concentration on the sensitivity of these techniques. The potential for interferences will also be examined.

The research objectives are:

- To evaluate the potential for utilizing UV-Visible and laser fluorescence spectroscopy to determine actinide concentrations under process conditions.
- To examine the impact of process environment on the sensitivity of UV-Visible and laser fluorescence spectroscopy to the actinides, including the impact of acid concentration, solvent concentration, ligand concentration (TBP, AHA), coloring agents (iron, fission products, etc.), competing actinide elements.

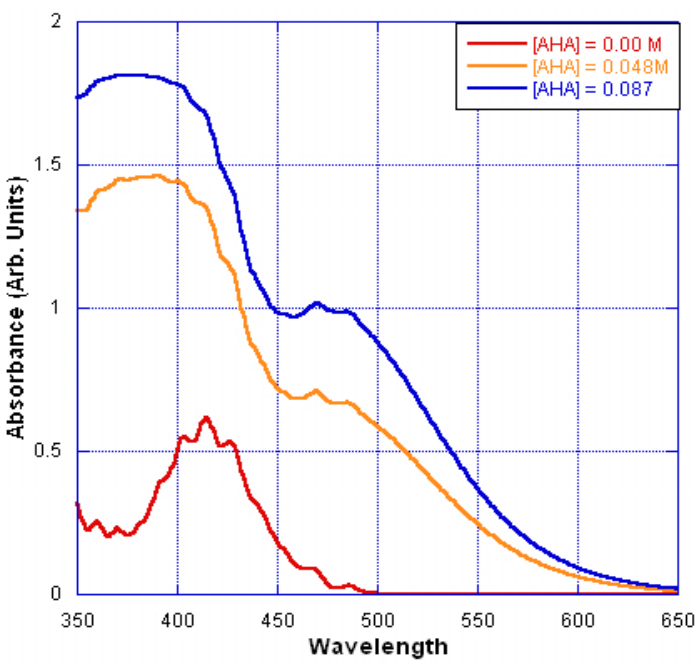
RESEARCH ACCOMPLISHMENTS

To evaluate the potential application of UV/Visible spectroscopy for the determination of uranium in the aqueous process streams of the UREX process the impact of process chemical conditions on the absorbance behavior of the uranyl ion was examined. The process streams of interest are distinguished by three main vari-

ables in the aqueous system: the metal ion concentration, the acid concentration, and ligand concentration (NO_3^-, AHA). General trends were observed in the molar absorptivity constants as conditions were varied. The most noticeable changes occurred as the nitrate concentration was increased. The figure on the opposite page shows the effect of increasing nitrate concentration at constant metal and acid concentrations. There is a large change in the molar absorptivity constant as the concentration of the free uranyl ion is decreased and two or more uranyl nitrate solution complexes become dominant. An accompanying shift in the uranium spectrum, as well as a wavelength shift at the peak intensity was observed as the nitrate concentration was increased from 2 M to 8 M.

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, which will require either the reduction of the path length or the dilution of the feed prior to analysis. In designing the equipment train for the recycling plant, a slip stream could be extracted from the feed or uranium product streams for analysis. This slip stream could easily be mixed in a controlled mass ratio with a diluent stream of nitric acid or passed through a reduced diameter section to provide a significant reduction in path length.

The raffinate and technetium streams are expected to have significantly lower concentrations of uranium. The primary differences in these streams are the nitric acid concentrations and the presence of AHA in the raffinate stream. In these streams, the expected concentrations will likely fall below the detection limits observed for a 1 cm optical path.



Effect of increasing AHA concentration on uranyl spectra at pH=2. $[UO_2^{2+}]$ = 0.094 M, $[NO_3^+]$ = 1.2 M

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 from the 47th Annual Institute For Nuclear Materials Management Annual Meeting*. July 16 – 20, 2006. (IN PRESS)
- N.A. Smith, G.S. Cerefice, and K.R. Czerwinski, "Optical techniques for improved materials accountability in the UREX+ process," Oral Presentation, American Chemical Society National Meeting, Atlanta, GA, March 30, 2006.

In addition to the potential applications for direct, on-line concentration measurements, UV/Visible spectroscopy may also provide analysts with the ability to directly observe process chemistry. From a proliferation resistance point-of-view, two observations show immediate promise. By examining the absorbance spectrum, it should be possible to detect the conversion of a recycling plant from the UREX process, which does not separate plutonium, to the PUREX process, which does result in a purified plutonium product due to the associated increase in molar absorptivity along with a change in peak shape. The spectrum loses individual peaks and is replaced by one broad, flat peak. This change in process chemistry could also be detected in the raffinate stream. The presence, or absence, of AHA in the raffinate stream becomes significantly more pronounced as the pH of the analyzed stream is increased. By titrating a slip stream from the raffinate product stream to higher pH, and comparing the observed spectrum to one from a second, unaltered slip stream, the presence of AHA in the raffinate can be confirmed.

FUTURE WORK

For the remainder of the first project year, work will focus on the evaluation of laser fluorescence for the determination of uranium concentration in the aqueous streams of the UREX+ process. In the second year of the project, work will expand along two fronts. The current work examining the determination of uranium concentrations in the aqueous system will be expanded to examine the determination of the higher actinide concentrations in these process streams. In a parallel effort, the evaluation of uranium concentration measurement by optical spectroscopy techniques in the organic process streams of the UREX+ separations process will begin.

Research Staff

Gary Cerefice (PI), Asst. Research Professor, UNLV Radiochemistry Ph.D. Program
Ken Czerwinski, Assc. Professor, UNLV Chemistry Department, Director – UNLV Radiochemistry Ph.D. Program

Students

Nicholas Smith, Graduate Student, UNLV Radiochemistry Ph.D. Program

Collaborators

George Vandergrift, Argonne National Laboratory

Task 30

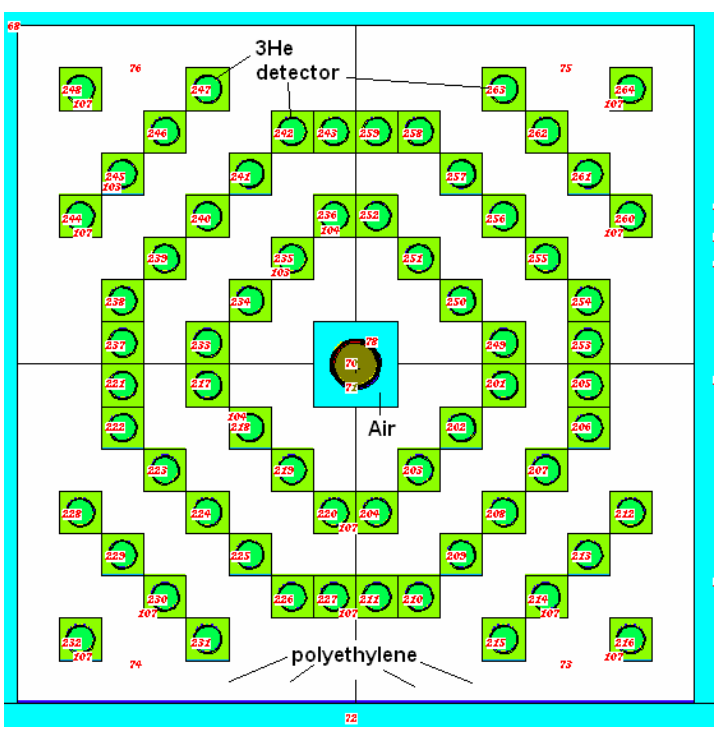
Combined Radiation Detection Methods for Assay of Higher Actinides in Separation Processes (AFCI)

D. Beller and W. Kernan

BACKGROUND

Monitoring of higher actinides (HA, includes neptunium, plutonium, americium, and curium) during the separation of used nuclear fuel has been identified as a critical research area in the Advanced Fuel Cycle Initiative. Recycling of used fuel by chemically separating it into uranium, fission products, and HA 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. The objective of this MPAC project is to develop technology to detect and accurately measure quantities of higher actinides in used fuel assemblies and processing systems without taking frequent samples. Process systems may include separations batches, pipelines, storage tanks, and fuel fabrication equipment. A variety of measurements may be combined to calculate flow rates of actinide elements with a to-be-determined precision.

In this MPAC project, faculty and students will investigate 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 (IAC) at Idaho State University (ISU) to use electron linear accelerators for producing photoneutrons in situ, for photon activation of HA, or for stimulating emissions processes (e.g. x-ray fluorescence).



Cross section of NMDS surrounding a steel pipe containing higher actinides in solution.

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 years 2 and 3 are to be determined, but may include small quantities of radioactive actinides at UNLV in addition to accelerator-coupled experiments at ISU.

RESEARCH ACCOMPLISHMENTS

To initiate the AFCI MPAC Project, a kick-off meeting was held that included representatives and technical staff from the DOE, LANL, INL, ANL, PNNL, UNLV, ISU, and others. A collaboration with Los Alamos, which supplied safeguards monitoring equipment for the Rokkasho reprocessing plant in Japan, was initiated. UNLV faculty met with group leaders and technical staff at LANL in conjunction with the MPAC PI and others from Idaho State University to develop collaborations for monitoring systems development. They also met with N-1 Safeguards Science & Technology Group and N-2 Advanced Nuclear Technology Group. In addition, technical staff from N-1, N-2, and N-4 Safeguards Systems Group visited UNLV to discuss ongoing and potential MPAC projects, to tour labs, and to meet with students.

One technique that has been used in a variety of MPAC applications is neutron multiplicity measurement. This is the coincidence measurement of multiple neutrons that are emitted in individual fission events. A Neutron Multiplicity Detector System (NMDS) was previously built in collaboration with the V. G. Khlopin Radium Institute (KRI) in St. Petersburg, Russia (see Task 6 on

pages 16 and 17). The system has since been extensively tested at UNLV and ISU. The NMDS is a modular system consisting of 64 ^{3}He detectors (tubes), electronics, and lead and polyethylene bricks. The modular nature of the system allows it to be used in a variety of configurations and for a variety of purposes. Examples are measurement of neutron multiplicity from high-power, high-energy spallation targets, detection of fissile materials in cargo systems or luggage, and assay of actinides in fuel or storage containers. Count rate and data acquisition capabilities of the NMDS were expanded in TRP Task 6, "Neutron Multiplicity Measurements for the AFCI Program." As part of Task 30, a new connector board was acquired to interface the remaining 32 detectors to the field programmable gate array (FPGA) board, such that the entire NMDS can now be operated with either the Russian DAQ or the new high-rate UNLV DAQ. Comparison testing is ongoing.

Data required for studying detection concepts includes elemental and isotopic constituents of discharged reactor fuel rods or assemblies, separations processes, storage systems, and fuel and waste-form fabrication systems. The RADDB code system, which is a user-friendly SCALE/ORIGEN-based code, was initially used to generate isotopic fractions for the higher actinides for initial scoping studies, in which the MCNPX radiation transport code system was used with the latest data libraries to model the NMDS. Elemental constituents of process flows and flow rates were later obtained from a detailed UREX+ flow sheet from ANL for use in designing conceptual detector systems. This information was then used in MCNP modeling. In one of these studies, the system was configured to surround a separations processing pipe to measure mixed transuranics. In addition, the effects of isotopic concentration on neutron multiplicity counting was studied. The NMDS model in MCNPX was reconfigured to surround a 2-inch process pipe containing actinides in solution (see the figure on the opposite page. Physical models were also assembled to ensure that there would be sufficient materials (e.g. polyethylene).

In addition to the NMDS, modeling of a germanium detector with MCNPX was initiated based on a report of similar work from Sandia National Laboratories. In addition, concepts for combined neutron-gamma and passive-active interrogation systems using the NMDS were developed.

ACADEMIC YEAR HIGHLIGHTS

- 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*, OECD/NEA, Paris, France, pp 687-698 (2005).
- 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," invited, accepted for oral presentation at the 47th Annual Meeting of the Institute of Nuclear Materials Management, Nashville, TN, July 16-20, 2006.

FUTURE WORK

In the following year modeling will be completed, the NMDS will be tested further, and it will be employed in two separate projects. One is to develop a lead neutron slowing down spectrometer (SDS) to assay fuel assemblies upon receipt for separations, and the other is to assay a process pipe containing separated higher actinides. Both projects will involve testing using the NMDS. For fuel assembly assays, the use of a lead SDS (LSDS) will be investigated, and testing will involve a carbon (graphite) SDS (CSDS). The CSDS has been constructed at the Idaho Accelerator Center. Actinides for the pipe assay experiments are available at UNLV.

Research Staff

Dr. Denis Beller, Principal Investigator, Research Professor, Mechanical Engineering Department
Dr. Warnick Kernan, UNLV Instructor, Physics Department; Principal Scientist, Remote Sensing Laboratory (RSL)

Students

Quinten Newell and Lawrence Lakeotes, Graduate Students, Mechanical Engineering Department
Pavan Kumar Attur and Shruti Patil, Graduate Students, Electrical and Computer Engineering Department
Timothy Beller and Brice Howard, Undergraduate Students, Mechanical Engineering Department

Collaborators

Dr. Mark Schanfein, Safeguards and Security Group, Los Alamos National Laboratory
Dr. James Laidler, National Technical Director for Separations and Waste, Argonne National Laboratory
Dr. Thomas Ward, UNLV Science Adviser for Russian Collaborations, TechSource, Inc.

Materials and Nuclear Engineering Masters of Science Program

To support graduate research in nuclear energy and recycling of used nuclear fuel at UNLV, a new degree program was approved in 2004. The UNLV Masters of Science in Materials and Nuclear Engineering (M&NE) degree program was formed to recognize the education and research of students who are focused on the nuclear physics and nuclear materials aspects of these technologies in the Department of Mechanical Engineering. To facilitate this program, Research Professor Denis Beller was appointed M.S. M&NE program coordinator and was supported by the Transmutation Research Project to develop curricula, to "market" the program, to recruit graduate students, to enlist part-time faculty to teach courses, to coordinate research assistantships for graduate students enrolled in the program, and to conduct other administrative duties. These include advising the UNLV Student Section of the American Nuclear Society and representing UNLV on the Nuclear Engineering Department Heads Organization (NEDHO) and on the Western Nuclear Science Alliance (WNSA).

Highlights

- Three students enrolled in the Nuclear Engineering program and completed courses. They were Daniel Lowe, Robert O'Brien, and Lawrence Lakeotes.
- UNLV graduated its first nuclear engineer in May. Daniel Lowe was graduated with the degree of M.S. in Materials and Nuclear Engineering.
- Two courses were taught by adjunct professors who were supported by the TRP: MENG 455/655 Radioactive Waste Management and MENG 495/695 Introductory Nuclear Reactor Physics.
- The MS M&NE program coordinator represented UNLV at NEDHO, DOE, and other meetings as well as at General Atomics' Academic Advisory Committee meeting.
- UNLV hosted a semi-annual WNSA Academic Advisory Committee meeting, of which UNLV is now a member. The meeting included a tour of the Nevada Test Site including the new Critical Experiments Facility for some participants and a tour of the Yucca Mountain Project for others.

Radiochemistry Ph.D. Program

The second program developed to support the student research activities at UNLV, including those within the UNLV Transmutation Research Program, was the Radiochemistry Doctorate of Philosophy program. Initiated as a joint program between the Health Physics and Chemistry departments, the Radiochemistry Ph.D. program also opened its doors Fall term in 2004.

Radiochemistry is the discipline dedicated to the study of the chemical and physical properties of radioactive elements. Through the development of a fundamental understanding of the behavior and properties of these elements and compounds,

students endeavor to address technical needs in many technical areas, such as the fate and transport of radionuclides in the environment, the separation and recycling of the actinide elements from used nuclear fuel, and the incorporation of radionuclides into ceramic fuel and waste forms. Students supplement a core of nuclear and chemical fundamentals with higher level electives in their specialties, tied together by their thesis work, to gain experience in the field.

The Radiochemistry Ph.D. program currently serves as the home department for students on a number of Transmutation Research Program Tasks:

- Dissolution, Reactor, and Environmental Behavior of ZrO_2MgO Inert Fuel Matrix (Task 19)
- Fundamental Chemistry of U and Pu in the TBP-Dodecane-Nitric Acid System (Task 26)
- Impact of the Synthesis Process on Structure Properties for AFCI Fuel Candidates (Task 28)
- Investigation of Optical Spectroscopy Techniques for On-Line Materials Accountability in the Solvent Extraction Process (Task 29)

in addition to supporting students working on research projects supporting other programs.

UNLV TRP EVENTS

July 22, 2005
UNLV local television station interviewed faculty and students regarding the transmutation research program.

August 19, 2005
The World Nuclear University Summer Institute session on Nevada nuclear politics, perception, and UNLV nuclear programs was held in Las Vegas, NV.

September 1, 2005
Al Sattelberger, a Senior Laboratory Fellow at LANL, joined the UNLV Radiochemistry Program as a Visiting Professor.

September 9-23, 2006
Six Russian visiting scientists from the Institute for Physics and Power Engineering (IPPE, Obninsk, Russia) assisted in the final installation of the ISTC TC-1 Loop.

September 21-23, 2006
Twenty posters from UNLV TRP tasks were on display at the AFCI Semiannual Review in Crystal City, VA.

September 23, 2005
Susan Eisenhower (granddaughter of President Dwight D. Eisenhower) gave a seminar at UNLV entitled "Nuclear Energy, International Cooperation, and Leadership."

October 1-2, 2005
Students and faculty staffed a nuclear educational and informational booth at the Town of Pahrump Fall Festival.

October 5, 2005
Darlene Hoffman visited UNLV and met with the Radiochemistry program students and faculty.

October 7, 2005
The Transmission Electron Microscopy User Facility ceremonial grand opening was held.

November 3, 2005
Ralf Sudowe, Lawrence Berkeley National Laboratory, gave a seminar at UNLV entitled "Radiochemical Separation Techniques for the Study of the Heaviest Elements."

November 16, 2006
Gordon Jarvinen, LANL, gave a seminar at UNLV entitled "Separations Technology for Advanced Fuel Cycles."

December 13, 2005
Steven Bakhtiar, Lawrence Berkeley National Laboratory, Radiochemistry Society President, gave a seminar at UNLV entitled "Sequential Isotopic Determination of Actinides in Low Level Samples."

January 9-13, 2006
UNLV hosted an MCNPX training course.

January 18, 2006
Four speakers from LANL gave seminars: Douglas Reilly, Mark Schanfein, J.D. Doak, and David Loaiza.

January 26, 2006
Steven Conradson, LANL, presented a lecture on EXAFS analysis.

February 21, 2006
Raymond Teller, ANL, presented a lecture entitled "Condensed Matter Research at the Intense Pulsed Neutron Source."

February 21 & 23, 2006
Glenn Knoll, University of Michigan, presented two lectures on the fundamentals of nuclear radiation detection.

February 22, 2006
Stephen Agnew, Nuclear Waste Consulting, presented a lecture entitled "Molten Salt Processing of High Level Waste."

February 28, 2006
UNLV participated in the Nuclear Energy Institute's Nuclear Energy R&D Summit meeting in Washington, DC, which included visits to Congressional energy staffers as NEDHO representatives.

March 3, 2006
UNLV hosted three administrators from the Japan Science and Technology Agency to discuss innovative nuclear research and development programs.

March 26-30, 2006
Nine graduate students attended the Nuclear Chemistry Student Forum of the American Chemical Society meeting in Atlanta, GA.

March 30-April 1, 2006
Six graduate students from UNLV attended the American Nuclear Society Student Conference at RPI in Troy, NY and staffed a promotional booth for UNLV.

April 27-28, 2006
UNLV hosted the academic advisory committee meeting of the Western Nuclear Science Alliance including a tour of the Yucca Mountain Project and the Nevada Test Site.

May 2006
Daniel Lowe was the first student to graduate under the new M.S. program in Nuclear Engineering at UNLV.

May 4, 2006
Bernhard Kienzler, FZK, Karlsruhe, Germany, presented a lecture entitled "Safety Research for Nuclear Waste Disposal at INE."

May 5, 2006
Anthony Hechanova, UNLV, gave a lecture on "Advanced Nuclear Fuel Cycles" as part of a panel on The Future of Nuclear Energy Worldwide and Potential Benefits to Nevada at the Sun City Summerlin Nuclear Science Club Colloquium.

Transmutation Research Program Financial Statement

Program Administration	FY01	FY02	FY03	FY04	FY05	TOTAL
Program Support						
Labor	$187,305	$348,324	$564,755	$452,274	$508,401	$2,061,059
Other Costs	$121,779	$72,336	$115,047	$104,888	$129,336	$543,386
LANL Subcontract	$150,000	$162,500	$0	$0	$0	$312,500
SRNL Subcontract	$0	$0	$0	$0	$20,250	$20,250
Infrastructure Augmentation						
New Hires	$112,692	$240,648	$433,832	$391,000	$646,210	$1,824,382
Facilities	$1,492,446	$799,837	$838,661	$606,034	$499,143	$4,236,121
Academic	$0	$0	$0	$181,200	$242,022	$423,222
International Collaboration	$144,973	$377,175	$155,200	$121,700	$26,500	$825,548
Subtotal	**$2,209,195**	**$2,000,820**	**$2,107,495**	**$1,857,096**	**$2,071,862**	**$10,246,468**
Student Research Tasks Totals	**$790,805**	**$2,499,180**	**$1,752,505**	**$1,642,904**	**$1,896,138**	**$8,581,532**
Totals	**$3,000,000**	**$4,500,000**	**$3,860,000**	**$3,500,000**	**$3,968,000**	**$18,828,000**

Student Research Task by Task

	FY01	FY02	FY03	FY04	FY05	TOTAL		FY04	FY05	TOTAL
Task 1	$97,379	$185,495	$141,417	$0	$0	$424,291	Task 17	$165,253	$156,770	$322,023
Task 2	$127,146	$195,148	$161,067	$0	$0	$483,361	Task 18	$149,704	$194,267	$343,971
Task 3	$98,896	$285,346	$192,321	$0	$0	$576,563	Task 19	$140,865	$109,349	$250,214
Task 4	$108,615	$179,270	$144,794	$0	$0	$432,679	Task 20	$103,587	$177,101	$280,688
Task 5	$40,655	$142,081	$89,214	$3,044	$0	$274,994	Task 21	$106,290	$142,928	$249,218
Task 6	$58,952	$219,403	$90,863	$0	$0	$369,218	Task 22	$56,921	$91,522	$148,443
Task 7	$55,565	$201,791	$160,324	$32,283	$3,425	$453,388	Task 23	$79,941	$135,153	$215,094
Task 8	$57,700	$206,215	$86,441	-$266	$0	$350,090	Task 24	$124,228	$71,195	$195,423
Task 9	$21,609	$109,376	$71,167	$18,850	$0	$221,002	Task 25	$91,545	$133,114	$224,659
Task 10	$57,175	$112,610	$73,586	$0	$0	$243,371	Task 26	$135,776	$117,525	$253,301
Task 11	$41,308	$68,815	$69,110	$1,786	$0	$181,019	Task 27	$79,950	$120,944	$200,894
Task 12	$25,805	$146,974	$81,792	$27,404	$0	$281,975	Task 28	$0	$119,694	$119,694
Task 13	$0	$146,048	$172,502	$105,697	$0	$424,247	Task 29	$0	$151,217	$151,217
Task 14	$0	$120,438	$107,073	$82,491	$3,996	$313,998	Task 30	$0	$144,201	$144,201
Task 15	$0	$74,050	$64,833	$63,389	$0	$202,272				
Task 16	$0	$106,120	$46,001	$74,166	$23,737	$250,024				
Totals	**$790,805**	**$2,499,180**	**$1,752,505**					**$1,642,904**	**$1,896,138**	**$8,581,532**

Infrastructure Facilities Augmentation

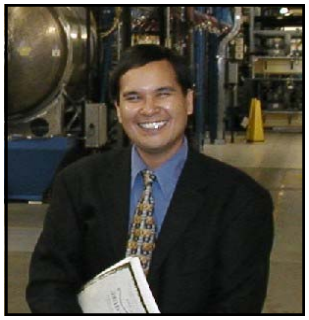
	FY01	FY02	FY03	FY04	FY 05	Total
Electron Microanalysis and Imaging Laboratory	$42,313	$63,000	$63,000	$63,000	$63,000	$294,313
Materials Performance Laboratory	$150,133	$77,360	$0	$0	$0	$227,493
Transmission Electron Microscope	$1,300,000	$159,369	$321,582	$150,000	$200,000	$2,130,951
ICP – Atomic Emission Spectrometer	$0	$100,163	$0	$0	$0	$100,163
Lead-Bismuth and Other Molten Materials Facilities	$0	$234,198	$121,579	$218,300	$158,156	$732,233
Machining System and Equipment	$0	$72,619	$22,500	$934	$0	$96,053
Flow Visualization System (Task 2)	$0	$22,207	$0	$0	$0	$22,207
Pyrolizer, Baths, and Controller (Task 15)	$0	$20,921	$0	$0	$0	$20,921
Prof. B.J. Das Startup Package Equipment	$0	$50,000	$50,000	$0	$0	$100,000
Actinide Chemistry Laboratory	$0	$0	$260,000	$123,800	$77,987	$461,787
Oxygen in LBE Control System	$0	$0	$0	$50,000	$0	$50,000
Totals	**$1,492,446**	**$799,837**	**$838,661**	**$606,034**	**$499,143**	**$4,236,121**

International Collaboration

Khlopin Radium Institute Contracts	$113,050	$229,500	$23,950	$0	$0	$366,500
International Science and Technology Center		$87,500	$98,250	$51,700	$12,500	$249,950
International Collaboration Program Coordination	$31,923	$60,175	$33,000	$70,000	$14,000	$209,098
Totals	**$144,973**	**$377,175**	**$155,200**	**$121,700**	**$26,500**	**$825,548**

Photo Gallery

Transmutation Research Program Administration



HRC Director
Anthony E. Hechanova

HRC Deputy Director
Gary S. Cerefice

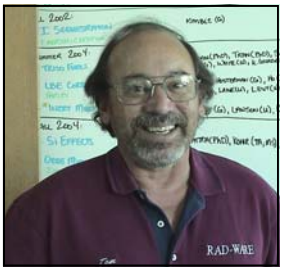
HRC Finance Director
Patricia Rugeiro

TRP Finance Director
Leisa Rodriguez

Finance Assistance
Hallie Lyons

Project Assistance
Kathy Lauckner

Laboratory Manager
Jeanette Daniels



Laboratory Manager
Thomas O'Dou

Webmaster
John Knoten

HRC Network Admin
Kris Davidson

HRC Travel Coordinator
Joseph Zimmerman

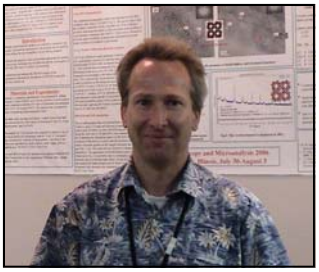
Assistant/Coordinator
Rebecca Arbour

International Programs
Coordinator
Ning Li (LANL)

Not pictured:
Ruby Bynum
Karen Bukowski
Monica McVey
Cristalyne Estella

International Programs
Adviser
Thomas Ward

Transmutation Research Program Staff, Faculty Researchers and Students

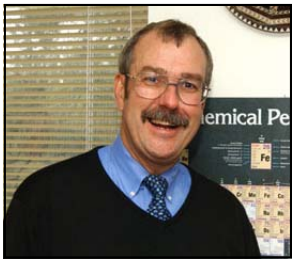


Group Leader
Structure & Solid Phase Analysis
Thomas Hartmann

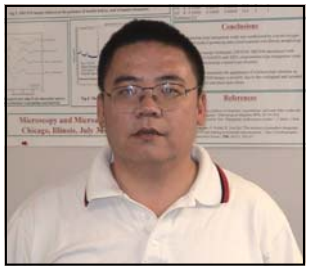
Group Leader
Radiochemistry
Ken Czerwinski

Group Leader
Molten Materials Research
Jian Ma

Detector Development
Frank Avignone



Visiting Professor
Radiochemistry
Al Sattelberger



Research Professor
Materials
Longzou Ma

Research Technician
Valery Ponyavin

Post Doctoral Researcher
Cynthia Gong

Post Doctoral Researcher
Frederic Poineau

Post Doctoral Researcher
Tyler Sullens

Not pictured:

Charles Yeamans	Graduate Student
Julie Gostic	Graduate Student
Dusty Crawford	Undergraduate Student
Xiuju Tan	Graduate Student
Richard Robinson	Graduate Student

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

Yulien Chen
Paul Lawson

Not pictured

Xiaolong Wu

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

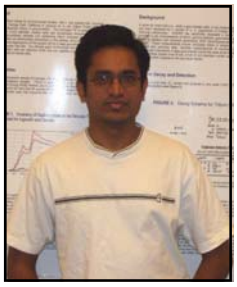
Chris Harland

Stacy Sidle

Task 4:

Ajit Roy
Associate Professor
Department of Mechanical Engineering

Mohammad Hossain



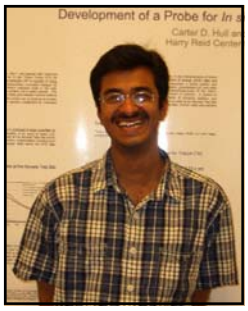
Sudheer Sama

Venkataramakrishnan Selvaraj

Nikata Agarwal
Aaron Tippets

Not pictured

Ramprashad Prabhakaran



Phandi Gudipati

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

Steve Curtis Not pictured

Timothy Beller

Brice Howard

Dean Curtis

Shruti Patil

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

Darrell W. Pepper
Professor
Mechanical Engineering Department
Director, NCACM

Sushma Gujjula
Sridhar Munaga

Not pictured

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
Associate Professor
Department of Mechanical Engineering

Brendan O'Toole
Associate Professor
Department of Mechanical Engineering

Venkata Potluri

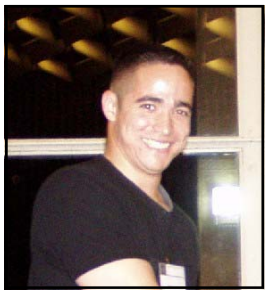
Srinivas Kukatla

Prad Koppula
Raymond Kozak

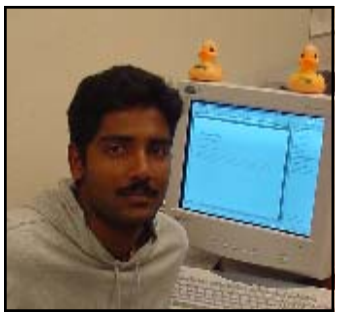
Not pictured

Mark Jones

John Motaka



Martin Lewis



Bhagath Yarlagadda

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

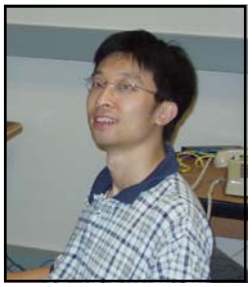
Suresh Sadineni

Trevor Wilcox

Daniel Lowe

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
Post-Doctoral Research Associate
Department of Mechanical Engineering

Xiaolong Wu

Task 14:

Ajit Roy
Associate Professor
Department of Mechanical Engineering

Subhra Bandyopadhyay

Silpa Budugur

Srinivas Chanda

Task 15:

Spencer Steinberg
Professor
Department of Chemistry

Gary Cerefice
Research Scientist
Harry Reid Center

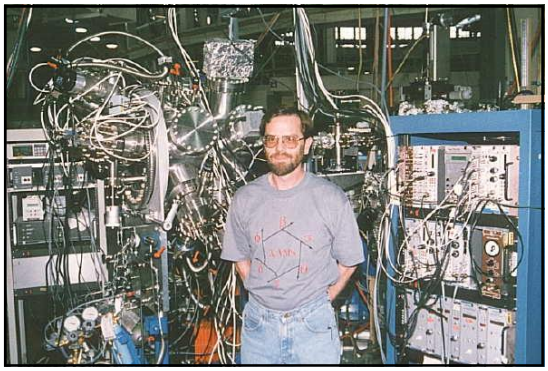
Ginger Kimble

David Emerson
Emeritus Professor
Department of Chemistry

James Dorman

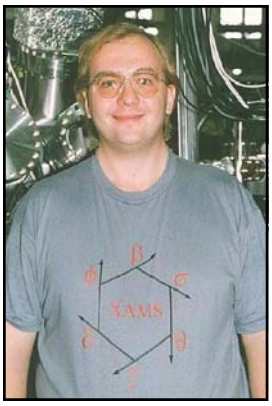
Gregg Schmett

Task 16:



Dennis Lindle
Professor
Department of Chemistry

Dale Perry
Adjunct Professor
Department of Physics



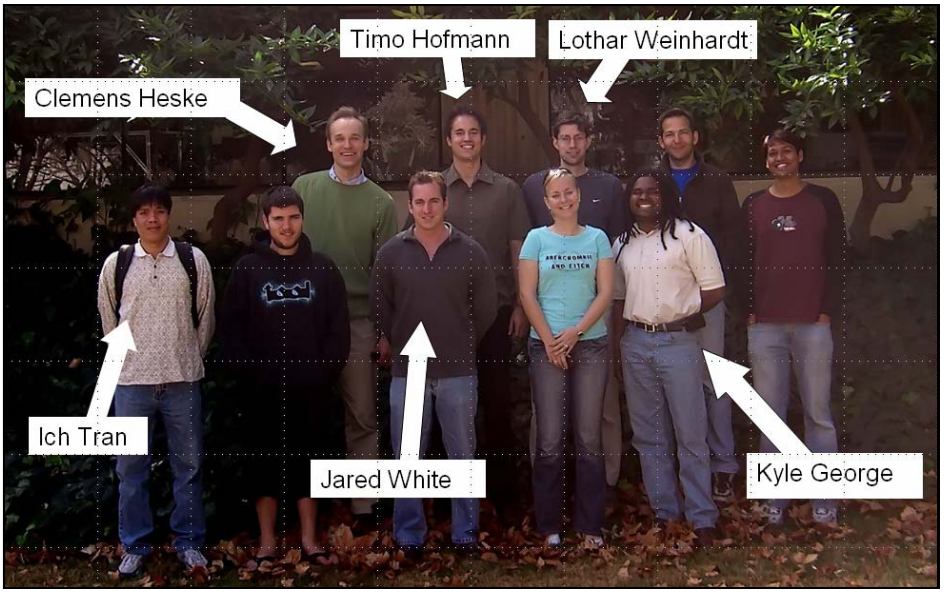
Oliver Hemmers
Assistant Research Professor
Department of Chemistry

Chinthaka Silva

Chirantha Rodrigo

Task 17:

Clemens Heske
Associate Professor
Department of Chemistry

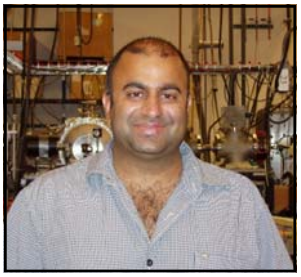


Goverdhan Gajjala

Varun Marepally | Not pictured

Task 18:

John Farley
Professor
Department of Physics

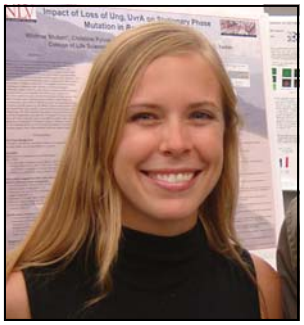


Umar Younas

Thao Trung Ho

Allen Johnson
Assistant Professor
Department of Chemistry

Dan Koury



Jenny Welch

Timothy Lane

Brian Hostermann

Task 19:

Ken Czerwinksi
Associate Professor
Department of Chemistry

Thomas Hartmann
Staff Scientist
Harry Reid Center

Wendy Pemberton
Deborah Callway

Not pictured

Emil Fridman

Earl Wolfram

Frederic Poineau

Kiel Holliday

Sergei Kolesnikov

Task 20:

Ajit Roy
Associate Professor
Department of Mechanical Engineering

Pankaj Kumar

Sreenivas Kohir

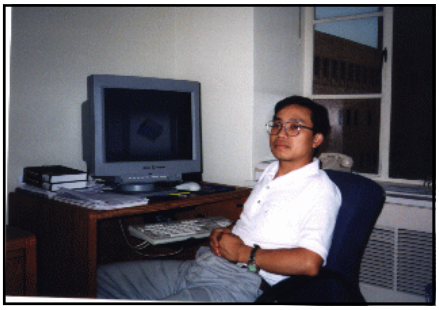
Harish Krishnamurthy

Debajyoti Maitra

Task 21:

Yitung Chen
Associate Professor
Department of Mechanical Engineering

Jichun Li
Assistant Professor
Department of Mathematics



Huajun Chen
Postdoctoral Researcher
Department of Mechanical Engineering

Xianfang Tan

Taide Tan

Task 22:

Georg Mauer
Professor
Department of Mechanical Engineering

Kamalakar Aluri — Not pictured

Douglas Wettekin

Koushik Damera

Jamil Renno

Andreas Roderburg

Task 23:

Biswajit Das
Associate Professor
Department of Electrical and Computer Engineering

Michael Sadowitz
Saurabh Mookerjea
Karina Diestra
Not pictured

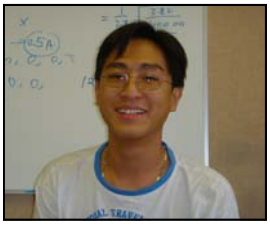
Pavan Singaraju

Jonathan Ross

Task 24:

Yitung Chen
Associate Professor
Department of Mechanical Engineering

Sean Hisieh
Research Associate Professor
Mechanical Engineering Department



Ming Chang

Ling Kwan

Matthew Hodges

Ruilong Li

Task 25:

David Hatchett
Assistant Professor
Department of Chemistry

Ken Czerwinski
Associate Professor
Department of Chemistry

Sujanie Gamage
Moustapha Eid Moustapha
Patrick Houlihan

Not pictured

Sandra Elkouz

Task 26:

Ken Czerwinski
Associate Professor
Department of Chemistry

Amber Wright

Jade Morgan
Wendy Pemberton
Trent Ohman
Byron Bennett
Lena Wright

Not pictured

Cynthia Gong

Frederic Poineau

Jeanette Daniels

Task 27:

Ryan LeCounte, Tim Beller, Brice Howard, Dr. Denis Beller with the High-Power RACE Target.

Denis Beller
Research Professor
Department of Mechanical Engineering

Shruti Patil

Evgeny Stankovskiy

Task 28:

Thomas Hartmann
Staff Scientist
Harry Reid Center

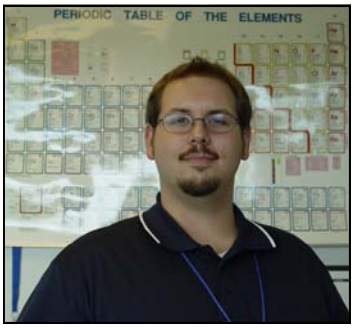
Ken Czerwinski
Associate Professor
Department of Chemistry

Chinthaka Silva

Task 29:

Gary Cerefice
Research Scientist
Harry Reid Center

Ken Czerwinski
Associate Professor
Department of Chemistry



Nicholas Smith

Task 30:

Denis Beller
Research Professor
Department of Mechanical Engineering

Warnick Kernan
Lawrence Lakeotes
Pavan Attur

Not pictured

Shruti Patil

Timothy Beller

Quinten Newell

Brice Howard

Acronyms

ADS	Accelerator-driven transmutation systems
ADSS	Accelerator-driven sub critical systems
ADTTA	Accelerator-Driven Transmutation Technologies and Applications
AECL	Atomic Energy Canada, Ltd.
AES	Auger electron spectroscopy
AFCI	Advanced Fuel Cycle Initiative
AHA	Acetohydroxamic acid
AI	Artificial intelligence
ALI	Annual limit on intake
ALS	Advanced Light Source facility in Berkeley, CA
AMUSE	Argonne Model for Universal Solvent Extraction
ANL	Argonne National Laboratory
ANS	American Nuclear Society
ASM	American Society of Metals
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
CAD	Computer aided design
CAINE	Computer Applications in Industry and Engineering
CEA	French Atomic Energy Commission
CETON	Coded Electron Target Optimized for Neutron Production
CFD	Computational fluid dynamics
CL	Constant load
CPP	Cyclic potentiodynamic polarization
CR	Cold-reduction
CSDS	Carbon (Graphite) Slowing Down Spectrometer
CTD	Chemical Technology Division
CW	Cold-worked
DAC	Derived air concentration
DAQ	Data Acquisition
DC	Dose coefficient
DCAL	Dose and risk calculation software
DELTA	Development of Lead-Bismuth Target Applications (test loop at LANL)
DHS	U.S. Department of Homeland Security
DOE	U.S. Department of Energy
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
ECATS	Experimental Activities on the Coupling of an Accelerator, a spallation Target and a Sub-critical blanket project
ECS	Electrochemical Society
EDAX	Energy dispersive x-ray spectroscopy
EDS	Energy dispersive spectrometry
EDTA	Ethylene Diamine Tetra-acetate
EELS	Electron energy loss spectrometry
EFTEM	Energy-filtered electron microscopy
%El	Percent elongation
EMIL	Electron Microanalysis and Imaging Laboratory
ENEA	Italian Agency for New Technologies, Energy, and the Environment
ENSDF	Evaluated nuclear structure data file
EPMA	Electron microprobe analyzer
EUROTRANS	European research program for the transmutation of high level nuclear waste in an accelerator driven system
EXAFS	Extended X-ray Absorption Fine Structure
FCC	Fullerene containing carbon
FEM	Finite Element Method
FESEM	Field Emission Scanning Electron Microscopy
FGR	Federal Guidance Report
FLEX	Fluoride extraction process
FLUENT	Computational Fluid Dynamics Code
FPGA	Field Programmable Gate Array
FY	Fiscal year
FZK	Forschungszentrum Karlsruhe, Germany
GUI	Graphical user interface
HA	Higher Actinides
HE	Hydrogen embrittlement
HEPA	High efficiency particulate air
HRC	Harry Reid Center for Environmental Studies, UNLV
HTGR	High Temperature Gas-Cooled Reactor
HTMEF	High Temperature Materials Experiments Facility, UNLV
IAC	Idaho Accelerator Center, Idaho State University
IC	Ion Chromatography
ICP	Inductively coupled plasma
ICP-AES	Inductively coupled plasma—atomic emission spectrometer
ICP-MS	Inductively coupled plasma mass spectrometer
ICRACM	International Conference on Advanced Composite Material
ICRP	International Commission on Radiological Protection
IEEE	Institute of Electrical and Electronics Engineers, Inc.
IFM	Inert Fuel Matrix
INL	Idaho National Laboratory
IPES	Inverse Photoelectron Spectroscopy
IPPE	Institute for Physics and Power Engineering
IR	Infrared
ISM	Induction skull melter
ISTC	International Science and Technology Center
ISU	Idaho State University
IYNC	International Youth Nuclear Congress
KRI	Khlopin Radium Institute, St. Petersburg, Russia
KRI-KRISI	Khlopin Radium Institute Research Industrial Enterprise, St. Petersburg, Russia
LANL	Los Alamos National Laboratory

LANSCE	Los Alamos Neutron Science Center
LBE	Lead bismuth eutectic
LEED	Low-energy electron diffraction
LFS	Laser Fluorescence Spectroscopy
LLW	Low-level waste
LMCE	Liquid Metal Corrosion Experiment
LSC	Liquid Scintillation Counting
LSDS	Lead Slowing Down Spectrometer
LWR	Light water reactor
MATLAB	A software system integrating mathematical computing and visualization
MCNP	Monte Carlo n-particles code
MCNPX	Monte Carlo n-particles code, extremely high-energy version
MIT	Massachusetts Institute of Technology
M&NE	Materials and Nuclear Engineering
MOX	Mixed oxide
MPAC	Materials Protection, Accounting, and Control
MPI	Message passing interface
MS SQL	Microsoft Standard Query Language
MS VB	Microsoft Visual Basic
MSZ	Magnesia Stabilized Zirconia
MTS	Materials Testing System
MUSE	Multiplication avec Source Externe project, Cadarache, France
NACE	National Association of Corrosion Engineers
NCACM	Nevada Center for Advanced Computational Methods, UNLV
ND	Neutron diffraction
NE	Nuclear Energy, Science and Technology
NEDHO	Nuclear Engineering Department Heads Organization
NICEST	Neutrons in Solid-State Chemistry and the Earth Sciences Today and Tomorrow
NMDS	Neutron multiplicity detector system
NMR	Nuclear Magnetic Resonance
NOM	Natural organic matter
NPEX	Neptunium Extraction
NTA	Nitrilotriacetic Acid
NTS	Nevada Test Site
NUBASE	A nuclear properties database
OCS	Oxygen Control System
OM	Organic matter / Optical Microscopy
ORNL	Oak Ridge National Laboratory
OTA	Oxygen Thermodynamic Activity
PANI	Polyaniline
PAS	Positron annihilation spectroscopy
PC	Personal computer
PEELS	Parallel energy loss spectroscopy
PNNL	Pacific Northwest National Laboratories
PUREX	Plutonium extraction process
PVM	Parallel virtual machine
PWR	Pressurized water reactor
PWTT	Post-weld-thermal-treatments
%RA	Percent reduction in area
RACE	Reactor-accelerator coupled experiment
RADDB	Radiological Data Base
RC	Ring-core
R&D	Research and Development
RELAP	Plant Safety Modeling Code
RGA	Residual gas analyzer
RPI	Rensselaer Polytechnic Institute
RSL	Remote Sensing Laboratory
SCA	Sub Critical Assembly
SCALE	Standardized Computer Analyses for Licensing Evaluation code
SCC	Stress corrosion cracking
SDP	Sputter Depth Profiling
SDS	Slowing Down Spectrometer
SEE	Secondary electron emission
SEM	Scanning electron microscope
SFTF	Spent Fuel Treatment Facility
SIMS-TOF	Time of Flight Secondary Ion Mass Spectrometer
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
TAMU	Texas A&M University
TBP	Tributylphosphate
TC-1	Target Complex 1
TEM	Transmission electron microscope
TRADE	TRIGA Accelerator Driven Experiment
TRIGA	Training, Research, Isotopes, General Atomics
TRISO	A silicon carbide and pyrocarbon composite coating
TRP	UNLV Transmutation Research Program
TRPSEMPro	TRP System Engineering Model Program
TRU	Transuranic actinides
TRUEX	TRU extraction
TTF	Time-to-failure
UHV	Ultra High Vacuum
UNLV	University of Nevada, Las Vegas
UPS	UV photoelectron spectroscopy
UREX	Uranium extraction process
UREX+	Uranium extraction process plus
UT	University of Texas
UTS	Ultimate tensile strength
UV	Ultra-violet
VIM	Vacuum induction melting
WIPP	Waste Isolation Pilot Plant, Carlsbad, NM
WNSA	Western Nuclear Science Alliance
XAES	X-ray auger electron spectroscopy
XAFS	X-ray absorption fine-structure spectroscopy
XANES	X-ray Absorption Near Edge Structure
XML	Extensible markup language
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
YS	Yield strength
YSZ	Yttria-stabilized zirconia

References

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

http://aaa.nevada.edu

Credits

The University of Nevada, Las Vegas Transmutation Research Program is administered by the Harry Reid Center for Environmental Studies under the auspices of the U.S. Department of Energy (Grant No. DE-FG07-2001AL67358).

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