AFCI Quarterly Input – UNLV January 1 through March 31, 2006

Harry Reid Center for Environmental Studies. Nuclear Science and Technology Division

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UNLV Transmutation Research Program. The University of Nevada, Las Vegas supports the AFCI through research and development of technologies for economic and environmentally sound refinement of spent nuclear fuel. The UNLV program has four components: infrastructure, international collaboration, student-based research, and management and program support. Management and program support highlights are the following:

- Coordination of administrative and financial management of the UNLV Transmutation Research Program.
- Coordination of the next academic advisory committee meeting of the Western Nuclear Science Alliance, which will take place at UNLV April 28. In conjunction with the WNSA meeting, UNLV TRP administrators are planning a visit to the Atomic Testing Museum and a tour of the Nevada Test Site including the new Critical Experiments Facility for WNSA members and advisors.
- UNLV hosted a MCNPX training course January 9 – 13.
- Four speakers from Los Alamos National Laboratory gave seminars on January 18: Douglas Reilly (Detectors for Nuclear Safeguards), Mark Schanfein (IAEA Unattended Monitoring Systems: A Brief Overview), J.D. Doak (Improving Near Real Time Accounting at the Japanese Mixed Oxide Fuel Fabrication Facility), David Loaiza (Critical Experiments Facilities).
- Steven Conradson, Los Alamos National Laboratory, presented a lecture on January 26 on EXAFS analysis.
- Raymond Teller, Argonne National Laboratory, presented a lecture on February 21 entitled “Condensed Matter Research at the Intense Pulsed Neutron Source.”
- Glenn Knoll, University of Michigan, presented two lectures on the fundamentals of nuclear radiation detection February 21 and 23.
- Program representatives from DOE, LANL, UNLV, IAC, and UNR met in Reno on February 22 to discuss the establishment of a new university consortium for the purpose of communications and potential collaborations. The group agreed to move forward with the concept.
- Stephen Agnew, Nuclear Waste Consulting, presented a lecture on February 22 entitled “Molten Salt Processing of High Level Waste.”
- UNLV participated in a meeting of the Nuclear Engineering Department Heads Organization in Washington, DC, February 27, 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 February 28, 2006.
- Three faculty members attended the Materials Working Group and provided presentations on current research on March 1 and 2.
UNLV hosted three administrators from the Japan Science and Technology Agency on March 3 to discuss innovative nuclear research and development programs.
The UNLV TRP Director met with the DOE Idaho Office university liaison Jihad Aljayoushi on March 10 to discuss the new UNLV Cooperative Agreement at Idaho Falls, ID.
Program directors from UNLV and ISU/IAC met in Pocatello, ID on March 10 to discuss AFCI university consortium. A draft Memorandum of Understanding was developed.
Nine graduate students attended the Nuclear Chemistry Student Forum of the American Chemical Society meeting March 26-30 in Atlanta, GA.
Six graduate students from UNLV attended the American Nuclear Society Student Conference at RPI in Troy, NY, March 30-April 1 and staffed a promotional booth for UNLV.

1.1 Infrastructure Augmentation

1.1.1 Infrastructure Augmentation Scope
The infrastructure augmentation component of the UNLV Transmutation Research Program enhances UNLV’s research staff, facilities, and academic programs to increase the ability of the university to perform AFCI research.

1.1.2 Infrastructure Augmentation Highlights
- Initiation of the development of a Ph.D. Nuclear Engineering program.
- Renovation of CHE 212C for the High Temperature Materials Experimental Facility: power was installed, electrical and heating, ventilation, and air conditioning (HVAC) renovation was completed. Gas phase experiments at the facility are now moving ahead.
- A location at UNLV for the LANL-built Lead Correlation Stand (LCS) was investigated and no interim location could be identified before the new UNLV Science and Technology building is completed in 2007/2008. Therefore, the apparatus may have to be operated initially at LANL.
- A test section apparatus was designed for the TC-1 loop to enable corrosion and other experiments using flowing lead-bismuth. The design is being discussed with the UNLV Risk Management and Safety Office; Planning and Construction Office; and, Facilities and Maintenance Office to ensure all appropriate authorities are consulted before actions are taken to modify the TC-1 loop.

1.2 International Collaboration

1.2.1 International Collaboration Scope
The international collaboration component of the UNLV Transmutation Research Program enhances UNLV’s breadth of scientific and scholastic experience. University collaboration is also an efficient conduit for international collaboration that benefits the national AFCI program. UNLV has ongoing relationships with the International Science and Technology Center (ISTC) who manages contracts with the Institute for Physics and Power Engineering (IPPE) in Obninsk, Russia for the TC-1 lead bismuth target loop and the Research Coordinative Center on the Problem of Muon Catalyzed Fusion and Exotic Quantum Systems (MUCATEX) in Moscow,
Russia for the project entitled “Preparatory Work for the Systematic Measurements and Evaluation of Minor Actinide Nuclear Data.” UNLV also has ongoing collaboration with the Ben Gurion University of the Negev in Beer Sheva, Israel (Task 19).

1.2.2 International Collaboration Highlights

- Two new projects were started regarding the TC-1 loop in consultation with Russian collaborators: (1) electro-magnetic pump efficiency studies and (2) improvement to the heating control algorithm.
- The new ISTC contract for the project “Preparatory Work for the Systematic Measurements and Evaluation of Minor Actinide Nuclear Data” was implemented.

1.3 Student Research

1.3.1 Student Research Scope

The Student Research component is the core of the UNLV Transmutation Research Program. The milestones, schedules, and deliverables of the student research projects are detailed in the individual research proposals. UNLV has 16 active student research tasks and 14 tasks that have concluded. The tasks are divided below in terms of their research area: fuels, separations, and transmutation sciences.

1.3.2 Student Research Highlights

FUELS TECHNOLOGY

Interaction between Metal Fission Products and TRISO Coating Materials (Task 17) Highlights.

- Goverdhan Gajjala successfully prepared and defended his M.S. thesis entitled “Interaction Between Pd and SiC: A Study for TRISO Nuclear Fuel” under the UNLV Department of Electrical Engineering
- A new Cs evaporator was constructed for the Cs/SiC experimental campaign.
- A four-chamber UHV instrument was reactivated after a Chemistry department asbestos abatement shutdown. The central oil-diffusion pumps were replaced by turbomolecular pumps to lower operating costs.

Dissolution, Reactor, and Environmental Behavior of ZrO2-MgO Inert Fuel Matrix (Task 19) Highlights.

- Acid dissolution studies with Ce show that H2SO4 could be a viable alternative if leaching U from the ceramic with HNO3 is unsuccessful.
- X-ray diffraction patterns have been analyzed using Rietveld structure refinement to quantify the phases present at all concentrations of Mg.
- A microprobe was used to measure elemental concentrations in the phases shown by XRD and to do elemental mapping over a relatively large area (512 x 512 microns).
- Images of all batches were taken by optical microscope up to 1000x.
SEM imaging was done on all batches.
Ten batches of $^{238}$U-containing ceramic were synthesized using the precipitation method.
XAFS and XANES were performed on the U-containing ceramics, scanning the uranium L$_3$-edge and the zirconium K-edge.
X-ray diffraction studies have begun on U-containing ceramics.
An adequate method for quantifying a glass phase by XRD has been identified.

**Design Concepts and Process Analysis for Transmuter Fuel Manufacturing (Task 22) Highlights.**

- A systematic study was completed seeking to arrive at an optimized plant configuration using value engineering techniques.
- A vision-based robot serving and automated plant safety monitoring is currently in progress.

**Impact of the Synthesis Process on Structure Properties for AFCI Fuel Candidates (Task 28) Highlights**

- The experimental set-up was optimized for precipitating spherical precursors for the production of TRISO-type kernels.
- The nitridization behavior of erbium-stabilized zirconia at 1700°C in N$_2$/8%H$_2$ atmosphere (8 h, and 14 h) and in N$_2$ atmosphere (3h, 8 h, 20 h) was investigated to quantify solubility limits of ErO$_{1.5}$ in zirconium-mononitride ZrN.
- XPS electron spectroscopy was performed at the DRI on samples of ZrN (LANL sample), ZrO$_2$ (Baddeleyite as purchased) and UO$_2$/U$_2$N$_3$/UN$_2$.
- Nitridization of UO$_2$ samples at 1700°C in N$_2$/8%H$_2$ atmosphere (8 h, and 12 h) was performed and resulted in the formation of U$_2$N$_3$ and UN$_2$ as minor phases, and the remaining UO$_2$ as the major phase.
- The first spherical precursors for the potential production of TRISO-type kernels could be produced and, after calcinations, kernel sizes between 400 µm and 320 µm were measured. For now the spheres show low isotropy and/or are hollow. The kernel quality has to be further improved.

**SEPARATIONS TECHNOLOGY**

**Immobilization of Fission Iodine (Task 15) Highlights.**

- It was established that iodide can be oxidized by MnO$_2$ to I$_2$ at pHs of 4-8 and moderate temperature.
- p-hydroxybenzoic acid was demonstrated to be iodinated by MnO$_2$ and KI at pHs of 2-8.
- Humic acids were shown to be iodinated by MnO$_2$ and iodide at room temperature in pH range of 4-8.

**Development of Integrated Process Simulation System Model for Spent Fuel Treatment Facility Design (Task 24) Highlights.**
• The UNLV-developed TRPSEMPro software package can access engineering modeling software ASPEN Plus through its own interface. The new interface eliminates the user interaction with the complex ASPEN Plus package and also provides input and output results for analysis purpose.
• Two separation processes, acid and plutonium separations, are near completion. The unit operations were finished while some sensitive chemical data for certain species are unknown.

Electrochemical Separation of Curium and Americium (Task 25) Highlights.

• The electrochemical characterization of Ce and Eu complexed with EDTA, NTA, and Citrate has been completed.
• Synthesis of the polymer substrate and the chelating ligand is underway. Approximately 50 grams of disulfide has been produced to produce the chelating thiol group required for the last set of studies.
• Gold substrates have been prepared to perform the 2-D surface chelation using the chelating disulfide and thiol. The goal is to determine the potentials required for chelation.
• Polymer gold composite systems have been prepared and characterized for use with the chelating ligands.

Fundamental Chemistry of U and Pu in the TBP-Dodecane-Nitric Acid System (Task 26) Highlights.

• More experiments on Ion Chromatography (IC) were performed to make sure it will be a reliable method for nitrate measurement.
• Extraction experiments were performed on 24 samples containing 0.1 M Uranyl, 0-12 M HNO₃, and 0-12 M LiNO₃ in the aqueous phase, and the pre-equilibrated samples previously prepared for the organic phase.
• A sample set of 24 samples was prepared with [HNO₃] from 0-12 M with varying [LiNO₃] and containing 0.05 M [U] and extracted with TBP/dodecane.
• 96 samples were prepared for analysis: (1) Samples consisted of two sets with 0.1 MU and 0.05 MU, (2) Nitrate concentrations varied from 0-12M as HNO₃ and LiNO₃, and (3) Both organic and aqueous phases.
• Samples were evaluated for nitrate concentration using Ion Chromatography.
• Samples were evaluated for uranium concentration using liquid scintillation counting.
• Evaluation of data: (1) Nitrate extracted into organic phase stays between 0.5 M and 1.5 M regardless of initial nitrate or uranium concentration; and, (2) Distribution coefficient for uranium shows a general increase with increasing nitrate and a general decrease with increasing acid.


• Laser system alignment was completed.
• Initial studies on $\text{UO}_2^{2+}/\text{NO}_3^-/\text{H}^+$ were completed.
• Preliminary work on uranyl/AHA and organic/aqueous interface systems were started.

Combined Radiation Detection Methods for Assay of Higher Actinides in Separation Processes (Task 30) Highlights

• The Neutron Multiplicity Detector System (NMDS) was re-configured for neutron multiplicity measurements and additional counting of a weak source as well as natural radiation was completed with both the old and new data acquisition systems for comparison.
• A new connector board was acquired to interface the remaining 32 detectors to the FPGA board for the full system to work.
• Students continued developing concepts for combined neutron-gamma and passive-active interrogation systems using the NMDS. One of these is to use multiple sets of NMDS along a length of pipe containing "stream 16" of the UREX-3 flowsheet. Another is to investigate a massive neutron-slowing-down spectrometer with active and passive neutron multiplicity measurements.

TRANSMUTATION SCIENCES

NeutronMultiplicity Measurements of Target/Blanket Materials (Task 6) Highlights.

• Task 6 was completed in December 2005 and remaining funds were used in January to cover the cost of an MCNPX course for several UNLV students. Work using the NMDS will henceforth be reported in Task 30.

Use of Positron Annihilation Spectroscopy for Stress-Strain Measurements (Task 14) Highlights.

• Microstructural evaluations by scanning electron microscopy and defects characterization of welded specimens by transmission electron microscopy are in progress to determine the dislocation density.
• Additional measurements of residual stress by positron annihilation spectroscopy are planned on welded specimens of similar and dissimilar materials at the ISU Idaho Accelerator Center during the spring/summer of 2006.
• Additional cylindrical specimens are being machined for tensile properties evaluation.

Corrosion Mechanisms and Kinetics of Steels in Lead-Bismuth Eutectic (Task 18) Highlights.

• Steel samples exposed to LBE at DELTA loop at LANL were received from LANL and SEM, XPS, and WDS examinations were completed.
• Raman studies of standards (Fe2O3, Fe3O4) and in situ tests (FeO(OH)) were completed.
• TEM samples of 316L stainless were prepared and analyzed.
• Raman spectrometer is now working with 10 micron spatial resolution, giving crystal phase compositional information.

- Tensile properties of T91 grade steels containing 0.5, 1.0, 1.5 and 2.0 weight percent (wt%) Si have been evaluated at temperatures ranging between ambient and 550°C. As anticipated, the magnitudes of the yield strength and the ultimate tensile strength were reduced with increasing temperature.
- The extent of failure strain (\(e_f\)) was not significantly affected by the variation in the testing temperature for steels containing 0.5 and 1 wt% Si. However, the magnitude of \(e_f\) was gradually reduced in steels containing 1.5 and 2 wt% Si in the temperature regime of ambient to 400 °C, followed by a significant increase at 550°C. The occurrence of reduced \(e_f\) in this temperature regime may possibly be attributed to dynamic strain ageing, which is currently under investigation by transmission electron microscopy (TEM).
- Stress corrosion cracking (SCC) evaluation by the slow strain rate technique is in progress involving steel containing 0.5 and 1.5 wt% Si.
- The localized corrosion study by the cyclic potentiodynamic polarization (CPP) technique revealed active-passive behavior with a positive hysteresis loop for steels containing 0.5 and 1.5 wt% Si. The magnitude of the corrosion potential became more active with increasing temperature. This behavior is consistent with the previous data on steels containing 1 and 2 wt% Si.

Oxide Film Growth Modeling in LBE Systems (Task 21) Highlights.

- A cellular automaton model using a method of global restructuring on the growth and corrosion during the formation of the passive layer has been developed.
- A stochastic model, which combines surface growth and internal oxidation, has been developed to explain the oxidation mechanism of steels in liquid lead alloys.

Corrosion Barrier Development for LBE Corrosion Resistance (Task 23) Highlights.

- It was investigated and confirmed that filling the nanoporous alumina pores with Ni nanoparticles will provide improved temperature cycling properties to the anticorrosion coatings.
- The Solgel technique was identified as the ideal method for the preparation of Ni nanoparticles for electrophoretic deposition, and the chemicals for such synthesis were identified.
- The process parameters for Ni deposition was developed experimentally.
- Ni nanowires were successfully deposited inside the nanoporous alumina on silicon substrates.
- Steel substrates with nanoporous alumina were prepared for Ni deposition.
- Experiments to synthesize Ni and Cr nanoparticles were initiated.
- The specialized substrate holder was fabricated for electrophoretic deposition of Ni nanoparticles inside alumina template pores.
- Trial experiments were carried out with CdSe nanoparticles.
• SEM images could not resolve the nanoparticles in cross-sectional imaging, and experiments with larger size nanoparticles have been initiated.

Reactor Physics Studies for the AFCI RACE Project (Reactor-Accelerator Coupling Experiments Project (Task 27) Highlights.

• Design-course students acquired and installed the FLUENT (R) CFD code then used it to continue analysis of cooling of the high-power target.
• The ERANOS reactor analysis code was received from the CEA. EUROTRANS/ECATS participants are developing accelerator-driven applications of ERANOS, and it has been used at the University of Michigan to evaluate TRADE and MUSE experiments.
• The student design group completed design and modeling of the High-Power RACE Target. Tungsten-copper disks were fabricated at ISU and the aluminum body was machined at UNLV. Additional components were purchased and the system was constructed and successfully leak-tested with high-pressure water.

Deep Burn Separations and Repository Behavior Highlights.

• Ligand synthesis was continued for actinide separations
• Thermal decomposition studies of ammonium uranium fluorides were continued.
• Ammonium uranium fluorides crystals were grown and delivered to ANL for single crystal x-ray diffraction studies.
• XAFS experiments were performed on samples.

1.3.3 Student Research Technical Summary

FUELS TECHNOLOGY

Interaction between Metal Fission Products and TRISO Coating Materials (Task 17).

This project is devoted to an in-depth study of the chemical and electronic impact of metal fission products on the coating layers in TRISO nuclear fuel. In particular, there is a focus on the investigation of Pd, Cs, and Ag and their interface formation with SiC and carbon-based substrates. A variety of surface and near-surface bulk sensitive probes that investigate the occupied and unoccupied electronic states of the substrate and the metal overlayer have been utilized. By a controlled and stepwise deposition of the metal overlayer, it is possible to gain substantial insight into the formation of interfaces and their intermixing behavior.

In the past quarter, there has been a focus 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 Dept. of Electrical Engineering. As an example from the thesis, Figure 1 shows 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. 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. Fig. 2 gives an example of a detailed UV photoelectron spectroscopy (UPS) study of the corresponding samples, 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 shown in Fig. 2, 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 in Figs. 1 and 2...
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 instrument to UNLV), can be well compared. In all cases, the presence of two additional carbon species at the interface are 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.
The Pd/SiC results are currently being prepared for publication in a peer-review journal. For this purpose, some additional data must be collected in order to allow a reliable quantitative analysis of the bonding and interdiffusion processes. This is necessary, because the old electron analyzer (ESCALab MkII) showed irreproducible background problems, as previously reported. At the

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**Fig. 2**: UPS spectra of the upper valence band as a function of Pd deposition. The as-introduced sample exhibits a large separation between valence band maximum (VBM) and Fermi energy, which is ascribed to surface contaminations. These contaminations can be effectively removed by the sputter cleaning, revealing the actual position of the SiC VBM. Upon deposition of Pd, a metallic Fermi edge is formed, which exhibits a shift towards lower binding energy due to the increased size of Pd islands on the surface.
time of writing of this report (mid-April), 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.

Finally, the new Inverse Photoemission set-up has been put to routine use. Figure 3 shows, as an
example, an IPES spectrum of a Ag reference foil, indicating both an excellent signal-to-noise
ratio as well as very good energy resolution. In all further experimental series, IPES can thus
now be included to give complementary information about the unoccupied electronic states, in
particular the conduction band minimum (CBM).

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.

**Dissolution, Reactor, and Environmental Behavior of ZrO$_2$-MgO Inert Fuel Matrix (Task 19)**

This project will examine inert matrix 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
will be 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 will be synthesized and characterized based on the reactor physics results. The
solubility of the fuel ceramics, in reactor conditions, reprocessing conditions, and repository
conditions, will be investigated in a manner to provide thermodynamic data necessary for
modeling.

The fuel matrix will be designed based on neutronic properties, repository behavior, and
reprocessing characteristics. The matrix should be as neutron transparent as possible. Burnable
poisons will be used to maintain constant reactivity. The matrix should also act as a suitable host
form for fission products and actinides in a repository environment. Finally, the matrix should
be compatible with reprocessing schemes under development in the advanced fuel cycle

**Work performed in previous Quarter (October 2005 to December 2005)**

The synthesis of the entire range of Zr to Mg, with Ce and Er concentrations being held at 5%
and 2.5% respectively, has been completed with enough material for characterization and
solubility studies. X-ray fluorescence has been performed on all ten batches to verify
concentrations. X-ray diffraction has shown the range of Mg required for a single phase solid
solution of cubic zirconia to be 10% to 28% Mg at current concentrations of Ce and Er. Pressure
vessel experiments have begun. Acid dissolution studies suggest that it could be possible to
leach uranium out of the ceramic without dissolving it. Therefore, these studies will be
performed with uranium samples once they are prepared. The soxhlet studies have yielded
quantitative data on water absorption, magnesium hydration, and corrosion of the ceramic.
Calculations were performed on 3 dimensional full core neutronic modeling of MgO-ZrO$_2$ fertile
free fuel with previously selected most promising burnable poison designs.
Work performed in current quarter (January 2006 to March 2006)

Optical Microscopy and SEM (scanning electron microscopy) were used to image the ceramic material. Elemental scanning by microprobe showed CeO$_2$ to be the least soluble in the ZrO$_2$. Microprobe analysis showed the periclase phase to be pure MgO and gave stoichiometric data on the ZrO$_2$ phase. The entire range of ZrO$_2$ to MgO was synthesized replacing CeO$_2$ with UO$_2$ as the plutonium analog. XAFS (X-ray absorption fine structure) and XANES (X-ray absorption near edge spectroscopy) were performed at Argonne National Lab. Pressure vessel dissolution studies showed that although the pellet could be physically destroyed, nothing was dissolved in the water. Sulfuric acid was successful in dissolving sintered material and may therefore be a possible head-in to a reprocessing scheme. The Soxhlet apparatus shows increasing corrosion rates with increasing MgO concentration.

Ceramic Fuel Synthesis and Characterization

Samples over the entire range of ZrO$_2$ to MgO with CeO$_2$ at 5% and ErO$_{1.5}$ at 2.5% were set in resin and polished so that they may be analyzed by SEM (scanning electron microscopy) and microprobe. Microprobe 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. This is further supported by CeO$_2$ not homogenously distributed in some samples as detected by elemental scanning by microprobe. This is believed to be due to insufficient sintering times and temperatures.
CeO$_2$ not homogenously distributed  

The periclase MgO phase appears black under SEM making it impossible to distinguish from pore space. Therefore, the ceramics were better imaged with optical microscopy.

![CeO$_2$ not homogenously distributed](image1)
![CeO$_2$ homogenously distributed](image2)

Zr$_{0.925}$Ce$_{0.05}$Er$_{0.025}$O$_{1.4875}$

200 times magnification

Zr$_{0.425}$Mg$_{0.50}$Ce$_{0.05}$Er$_{0.025}$O$_{1.4875}$

1000 times magnification

The entire range of Mg to Zr from 0 – 92.5% with U at 5% and Er at 2.5% has been synthesized using the precipitation method. No problems occurred in the incorporation of radioactive material into the ceramic and preliminary studies show that structurally the uranium ceramics have slightly different phase constitutions, specifically a higher solubility of UO$_2$ in cubic zirconia as compared with CeO$_2$. XAFS (X-ray absorption fine structure) and XANES (X-ray absorption near edge spectroscopy) were performed at Argonne National Lab and will be analyzed in the next quarter.

**XRD with Rietveld Analysis of Zr$_{0.125}$Mg$_{0.8}$U$_{0.05}$Er$_{0.025}$O$_{1.1875}$**
Dissolution Studies

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 UO₂ to soluble UO₂²⁺. Acid dissolution in boiling H₂SO₄ was successful in dissolving all species of the ceramic within 48 hrs. The dissolution follows first order kinetics as expected.
CeO\textsubscript{2} and ErO\textsubscript{1.5} Dissolution in H\textsubscript{2}SO\textsubscript{4}

\begin{align*}
  y &= 0.067404 + 0.26571 \log(x) \quad R = 0.99619 \\
  y &= 0.12425 + 0.2942 \log(x) \quad R = 0.99455
\end{align*}

ZrO\textsubscript{2} Dissolution in H\textsubscript{2}SO\textsubscript{4}

\begin{align*}
  y &= 1.8016 + 4.0508 \log(x) \quad R = 0.99764
\end{align*}

Continued experiments with the Soxhlet apparatus show increasing corrosion rates at 80\% MgO from that of 60\% MgO.
Design Concepts and Process Analysis for Transmuter Fuel Manufacturing (Task 22)

1. Concepts for Vision-Based Robot Control
A calibrated camera within its field of vision can guide the end effector accurately to its destination, and monitor the execution of the robot task at hand. Fig. 1 shows the example of pellet insertion into a cladding tube. While other sensors can be used to guide the robot, cameras are the most versatile. Cameras also can be positioned outside the hot cell, and thus reduce exposure and contamination risks.

Fig. 2 shows the robot motion control concept. The reference or controlled variable is generally a six-dimensional vector with 3 Cartesian location coordinates, and 3 angles defining the end effector orientation.
2. Work performed

The camera system and image recognition software were configured and tested. The image acquisition and processing is done with Matlab software tools. A remotely controllable Panasonic color camera is connected to the controller PC through a frame grabber.

The first step is image recognition. According to the requirements of the project, the greatest point of interest is cylindrical objects, i.e. fuel pellets. The pellet(s) present in the image are identified, and their spatial location and orientation is determined. Fig. 3 shows an example of pellet identification in Matlab. Undesired image elements are removed as seen in Fig. 4 and Fig. 5. The software for real time image acquisition and processing, and for camera control, is now operational.

Cylinder Recognition Procedure

For the recognition of the shape of a cylinder we examine first the contour of the shape, and then the shape with all its points inside.

A contour consistent with a cylinder is identified if
1. 2 lines are parallel and are the same length
2. Each end of the contour is a half-ellipse

A true cylinder must meet additional criteria:
1. One of the 2 ends is a complete ellipse
2. The other end is a half ellipse that has the same characteristics as the ellipse.

3. Work Plan for April to June 2006
• Calibrate Camera, and determine accuracy of location and orientation measurements of identified parts.
• Test camera system in noisy environments for the vision system’s ability to discern pellets from other objects present.
• Develop Matlab code and document results

*Fig. 3 Example of Pellet identification in Matlab*
Fig. 4 Example of Image Processing in Matlab, part 1
Impact of the Synthesis Process on Structure Properties for AFCI Fuel Candidates (Task 28)

Transmutation-related research work at the National Laboratories, e.g. Los Alamos National Laboratory, is focused on 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.

This project, task 28, supports the TRP program by delivering structural data on surrogate and radioactive fuels. Crystal structure and nanostructures of the individual fuel type, oxides and nitrides, as considered for GEN IV and HTR fuels are being determined. Therefore, three different approaches on fuel synthesis will be applied: (1) dry chemical route, (2) wet chemical route, and (3) sol-gel microsphere pelletization (SGMP) process.

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

Efforts to optimize the experimental set-up for precipitating spherical precursors for the production of TRISO-type kernels have been intensified. After the installment of a highly
accurate peristaltic pumping unit, uranyl-hydroxide-based microspheres with 0.5 mm – 1.0 mm diameters could be precipitated. Therefore a 1.49 \( M \) uranyl nitrate solution was injected into the sol-gel reaction column and uranyl-hydroxide-based microspheres could be precipitated (Figure 1). However, the kernels of the first batches did not survive the drying procedure, probably as a result of poorly chosen parameter, e.g. uranyl-hydroxide concentration, temperature, dropping speed, atmosphere. To further optimize the experimental set-up for the production of TRISO-type kernels, 3 \( M \) and 1.49 \( M \) uranyl nitrate concentrations were used to precipitate TRISO spheres. Uranyl-hydroxide-based microspheres could be precipitated but the result after drying was unsatisfactory and the spheres did not survive the drying procedure. In another batch experiment a 1 \( M \) uranyl nitrate concentration was used to precipitate precursor TRISO spheres (molar ratios of \( \text{UO}_2(\text{NO}_3)_2 \) to \( \text{NH}_4\text{NO}_3 \) to urea = 1 : 2.5 : 4). As a first success, some microspheres survived the drying procedure in wet atmosphere and changed their color to orange. The dried spheres were calcined at 400°C for 3 hours, but only few spheres survived calcination.

The first spherical precursors for the potential production of TRISO-type kernels could be produced and - after calcination - kernel sizes between 400 \( \mu \)m and 320 \( \mu \)m were measured (Figure 2). For now the spheres show poor isotropy. Some kernels are hollow and the overall kernel quality has to be improved much further.

Figure 1: \( \text{UO}_3 \times \text{H}_2\text{O} \) TRISO-type fuel kernel precipitated applying a Sol-Gel method with external gelation

Figure 2: \( \text{U}_3\text{O}_8 \) fuel kernels after calcination (400°C, 3 h)

**Electron Energy Loss Spectroscopy (EELS) on Fuel Samples**
Electron energy loss spectroscopy (EELS) was applied on radioactive fuel samples. Specimens were obtained after the carbothermic reduction/nitridization of precursor oxide solid solutions in the system ZrO$_2$-UO$_2$-ErO$_{1.5}$. The sample constitution is defined by the presence of a ZrN-based mononitride solid solution phase and a U(O,N)$_2$-based dioxide/dinitride solid solution phase. Electron-transparent specimen of the radioactive samples was able to be provided by dimpling and ion-milling (Figure 3a, 3b) and EELS spectra were obtained with nanometer spatial resolutions (Figure 4). However, at the current state EELS did not provide enough decisive information to distinguish oxides from nitrides. Since the EELS results are, for now, non-conclusive and published data are not available, in-house expertise as well as a data base of mono-phased zirconium and actinide standards must be developed in order to evaluate EELS spectra and to determine the presence of oxides, oxonitrides, and nitrides.

![Figure 3a: Nitride fuel sample at a magnification of 63,000 times](image1.png)

![Figure 3b: Nitride fuel sample at a magnification of 1,000,000 times](image2.png)

![Figure 4: EELS of Nitride fuel sample with the reference energy bands for nitrogen and oxygen](image3.png)
X-ray Photoelectron Spectroscopy (XPS) on Fuel Samples

The capability of the determination of oxygen and nitrogen contents in fuel samples as synthesized by the individual procedures is decisive for the evaluation and optimization of the process parameter in the synthesis of pure nitride ADS fuels. The oxygen content of ADS nitride fuels shall not exceed 3000 ppm = 0.3 wt.-%. In this context X-ray photoelectron spectroscopy (XPS) was applied on radioactive fuel samples (Figure 5). Specimens were obtained after the carbothermic reduction/nitridization of precursor oxide solid solutions in the system ZrO$_2$-UO$_2$-ErO$_{1.5}$. The sample constitution is defined by the presence of a ZrN-based mononitride solid solution phase and a U(O,N)$_2$-based dioxide/dinitride solid solution phase.

The XPS pattern of the nitride-based fuel sample is dominated by the intense bands of U 4f$^7/2$, Zr 3d, Er 4d, and the band of O 1s. After sputtering the surface with Ar, the N 1s band became visible, but the O 1s band never disappeared. The 1s band of nitrogen shows very low intensities and the N 1s band is overlayed by one of the intense 4f band of uranium (Figure 5, right image). Using XPS and the accurate determination of the energies for the U 4f bands it is - in principle - possible to distinguish UO$_2$ from UN. Literature data show that the binding energies of the U f4 bands in UN are lower than the corresponding bands on UO$_2$ by 1.2 eV or 2.7 eV. Unfortunately, the XPS equipment is located at the DRI and intensified studies on pure uranium system to begin with are associated with administrative hurdles. For now the XPS measurements on solid-solution systems cannot be understood without knowledge of the pure calibrated systems.

Carbothermic Reduction / Nitridization of Zr$_{1-x}$Er$_x$O$_{2-2x/2}$

In order to gain a better understanding of carbothermic reduction / nitridization to synthesize nuclear mononitride fuels the uranium-free system Zr-Er-O (-N) were studied. Fully stabilized zirconia Zr$_{0.7}$Er$_{0.3}$O$_{1.85}$ was synthesized and used as precursor. Zr$_{0.7}$Er$_{0.3}$O$_{1.85}$ was annealed for 20 h in a tantalum-lined high temperature furnace at 1700°C under oxygen-purified ultra-high pure argon.
Carbothermic reduction / nitridization of $\text{Zr}_{0.7}\text{Er}_{0.3}\text{O}_{1.85}$ leads to the formation of $\text{Zr}_{1-x}\text{Er}_x\text{N}$ (lattice parameter $a = 4.6085(3)$ Å) and $(\text{Zr}_{1-x}\text{Er}_x)_2(\text{N,O})_3$ (lattice parameter $a = 10.940(1)$ Å)(Figure 6). As a result we were able to synthesize Zr-Er-mononitride. The solubilities for erbium in the obtained Zr-based mononitrides define the solubility limit of Er in ZrN since the precipitation of a secondary Er-rich phase was determined. As an observation, the solubility limits of erbium in Zr-mononitrides are far lower than in zirconia. This finding on lower solubility limits in mononitrides compare to dioxides is important since it strongly influences the allowable chemical constitution in the oxide-precursor material to produce phase-pure zirconium-based mononitrides. To further determine the precise solubility limit of erbium (or other REE) in ZrN, electron microprobe analysis (EPMA) will be performed on a polished surface to determine the phase diagram.

Figure 6: Carbothermic Reduction / Nitridization of $\text{Zr}_{1-x}\text{Er}_x\text{O}_{2-x/2}$. After 20 h at 1700°C the nitridization was completed and the formation of $\text{Zr}_{1-x}\text{Er}_x\text{N}$ (lattice parameter $a = 4.6085(3)$ Å) and $(\text{Zr}_{1-x}\text{Er}_x)_2(\text{N,O})_3$ (lattice parameter $a = 10.940(1)$ Å) was observed.

**SEPARATIONS TECHNOLOGY**

**Immobilization of Fission Iodine (Task 15).**

Manganese oxide minerals (Mn(III) or Mn(IV)) were demonstrated as also being capable of oxidizing iodide under mild conditions (pH 4-8) at ~25°C. For example, treatment of a 0.02M solution of p-hydroxybenzoic acid (PHBA) with 0.1M KI (pH 8.5, 0.1 M NaHCO$_3$ buffer) resulted in the formation of 3-iodo-p-hydroxybenzoate and 3,5-diodo-p-hydroxybenzoate. Both products were identified by GC/MS of the silanated derivatives.
Figure 1: The chromatogram from an experiment where 0.1M KI (pH 8.5) was allowed to react with p-hydroxybenzoic acid in the presence of MnO₂ (Birnessite). The three peaks were identified (in order of retention time) p-hydroxybenzoic acid (1), 3-iodo-p-hydroxybenzoic acid (2) and 3,5-diiodo-p-hydroxybenzoic acid (3).

The formation of iodine (as I₃⁻) was also confirmed in several different buffered solutions of potassium iodide that have been exposed to manganese oxide minerals. From these preliminary results it is clear that oxidation of iodide can occur at moderate pH. An example of this is shown in Figure 2.

Formation of Iodine at pH 8.5

Figure 2: Formation of I₂ in 0.01M KI (pH 8.5) in the presence of MnO₂ (Birnessite) at room temperature.

Previously, it was demonstrated that phenolic compounds undergo aromatic substitution in the presence of iodine. With the availability of iodine acceptor such as p-hydroxybenzoic acid the loss of iodine can be followed with an iodide specific electrode. The results of one such study is
shown below (Figure 3a). A 0.001 M solution of KI buffered with tris (50 mL) was allowed to react with 0.100 grams of $\gamma$-MnO$_2$ and 0.02M PHBA. The reaction resulted in transfer of iodide to the PHBA ring (aromatic substitution). The reaction sequence is as follows:

$$4H^+ + 2\Gamma + MnO_2(s) \rightarrow I_2 + Mn^{+2}$$

$$I_2 + PHBA \rightarrow I-PHBA + HI$$

A plot of the natural logarithm of iodide concentration (Figure 3b) indicates that the reaction appears to slow with time. Since the PHBA and MnO$_2$ are both in excess, the slowing in reaction may reflect a deactivation of the surface of the manganese (II) oxide.
Figure 3a: Iodide concentration is plotted as a function of reaction time for an 0.001 M KI solution buffered with tris. PHBA is 0.02 M and with 0.1 g of MnO$_2$. 

Tris pH 7 PHBA (0.14g/50 mL) 
γMnO$_2$(0.1g/50 mL)
Figure 3b: The date is plotted as the natural logarithm of iodide concentration with time. Two “first order” regions are apparent.


1. Interface to interact with ASPEN Plus through the TRPSEMPro Package

1.1. To generate the interface between TRPSEMPro and ASPEN Plus, two major element types, “Streams” and “Blocks”, in ASPEN Plus are identified. Streams can be further divided into two parts, Input and Output that hold the values before and after simulations. Blocks are used to retrieve more system related information.

1.2. The interface shown in Figure 1 provides following functions:

1.2.1. The “Browse” button allows the interface to access ASPEN Plus BKP files.

1.2.2. The “Process” function interacts with the ASPEN Plus and return simulation results back to the interface.

1.2.3. The “Save As” function is the font-end of the database population and multiple run data collector. The function will be executed transparently on the background for compiling report for analysis.

1.3. Since the AMUSE code needs to be part of the optimization process, it will be integrated as a user defined function (UDF) associated with the ASPEN Plus. The optimization strategy between ASPEN Plus and AMUSE simulations need to be formulated soon.

1.4. Chemical flow conventions are different between ASPEN Plus and AMUSE, therefore, conversion process is required.

1.5. The simulation results can be generated iteratively. Database tool will be implemented for data management.
2. Construction of detailed ASPEN Plus separation processes

2.1. There are two processes, acid and plutonium separations, near completion. Unit operations associated with those processes are finished. Chemical data for certain species are still unknown. The third process, vitrification, is still under development.

2.2. Acid separation process
   2.2.1. Feeds include acetic acid, nitric acid, water, and nitrate salt.
   2.2.2. As shown in Figure 2, the top section includes nitric acid and water while the bottom section includes acetic and nitrate salts.

2.3. Plutonium separation process
   2.3.1. The plutonium separation system takes the strip product from the NPEX process as its feed as shown in Figure 3.
   2.3.2. Three blocks are used to perform the plutonium separation as shown in Figure 4.
   2.3.3. Plutonium nitrate in Block 1 is reacted with oxalic acid to produce plutonium oxalate. The output is entered in the Block 2. Plutonium oxalate in Block 2 is then reacted with air to produce plutonium oxide that enters into Block 3 and reacts with hydrogen fluoride to produce plutonium tetra fluoride.

2.4. Vitrification separation process
   2.4.1. Virtually no material on vitrification process in literature was found.
   2.4.2. Vitrification processes are very time specific (quick cooling of liquids). Certain user defined functions are needed to take into account the time-dependent issue.
Figure 2. The Acidic separation process.

Figure 3. The plutonium separation system that takes the strip product from the NPEX process as its input.

Figure 4. The plutonium separation process.

Electrochemical Separation of Curium and Americium (Task 25).

This research report outlines the current status and progress associated with the electrochemical separation of Curium and Americium. The following pages outline the progress on our project to date. For two and a half years, research has been actively performed on this project, and is currently on schedule for the proposed timelines.
Data collection and analysis of the Ce$^{3+}$/Ce$^{4+}$ redox couple complexes has been accomplished using EDTA, NTA and Citrate ions. All complex systems were investigated at Pt, Au, and Glassy Carbon working electrodes as a function of pH. Analysis of these data was accomplished by performing appropriate background subtractions to reveal net peaks due to Ce redox behavior. Successful identification of the Ce redox couple was achieved in many cases at pH values greater than two. This is well beyond the typically pH = 2 used to resolve the redox couple. Figure 1 shows the voltammetric response of Ce at pH = 2 and from pH = 2 to 12 with an equimolar concentration between EDTA. The redox couple for EDTA is centered at $E_{1/2} = 1.55$ V vs. Ag/AgCl. In contrast the redox couple shifts to $E_{1/2} = 0.85$ V vs. Ag/AgCl when complexed with EDTA. This represents a 0.70 V shift to lower energy. In addition the redox couple is clearly resolved at pH = 10. The Ce redox couple is not observed at pH = 12.

For comparison the redox couple for Eu is presented in Figure 2. The redox couple for Eu is observed at $E_{1/2} = -1.15$ V vs. Ag/AgCl. However, this redox couple is not observed at any pH for Pt electrodes in the absence of EDTA. The redox couple in complex form shifts the potential of the couple, which allows resolution to be achieved.

Figures 3 and 4 display the cyclic voltammetric response of graphite and Pt electrodes in solutions containing Ce and Citrate ion as a function of pH. The graphite electrode shows the best resolution for the uncomplexed and complexed couple at pH = 2. However, the voltammetry of the uncomplexed Ce is observed at $E_{1/2} = 1.45$ V. The complex with citrate is observed at $E_{1/2} = 0.75$ V. The complex shifts to 0.70 V lower potential. However, the process is kinetically limited above pH = 2 showing pseudo reversible behavior. For the Pt electrode the best resolution is observed at pH = 6. The data clearly demonstrates that complexation of the redox species can shift the potential significantly and produce stable voltammetry at pH values typically not accessible in acidic solutions. The complex keeps the Ce from precipitating at high pH values as a hydroxide.
Figure 1. Cyclic voltammetric response of a Pt electrode for Ce uncomplexed and complexed with EDTA as a function of pH.

Figure 2. Cyclic voltammetric response of a graphite electrode for Eu complexed with EDTA as a function of pH.
Figure 3. Cyclic voltammetric response of a graphite electrode for Ce uncomplexed and complexed with Citrate as a function of pH.

Figure 4. Cyclic voltammetric response of a Pt electrode for Ce uncomplexed and complexed with Citrate as a function of pH.

In the next six months the separation of Ce, Sm, and Eu will be attempted individually and from mixtures to determine if the potential mediated chelation using the chelating ligand dispersed in PANI/Au composite materials is possible.

**Fundamental Chemistry of U and Pu in the TBP-Dodecane-Nitric Acid System (Task 26).**

The speciation of hexavalent U and tetravalent Pu will be examined in the Tributylphosphate (TBP)-dodecane-nitric acid systems. This topic is chosen based on data needs for separation modeling identified by the AFCI. Emphasis will be placed on studying the influence of nitrate
and acetohydroxamic acid on U and Pu speciation as well as conditions where a third phase forms in the organic phase. The organic phase will be 30% TBP in dodecane. Equal volumes of aqueous and organic phase will be used. The speciation of the actinides in the aqueous and organic phase will be determined by a number of different spectroscopic and radiochemical techniques. Additionally the actinide distribution between the phases as a function of conditions will be determined. The project data will be incorporated into models to evaluate separations under a variety of conditions.

Work performed in previous quarter (October 2005 to December 2005)

Efforts in the past quarter focused on methods for the determination of nitrate concentration in the experimental system. The HPLC primarily used and was found to be precise but not vary reliable. Ion Chromatography (IC) was examined as a method for nitrate determination and was found to be suitable. The IC to be used is a Dionex ICS 2000 for measuring cations, and a Dionex ICS 2500 for the anions. It has an autosampler and dual injection system in order to run both at the same time. The 2000 is able to measure Li⁺, Na⁺, Ca²⁺, K⁺, and Mg²⁺. The 2500 can measure F⁻, Cl⁻, NO₂⁻, SO₄²⁻, Br⁻, NO₃⁻, PO₄³⁻. Both have conductivity suppressors which the samples go through before reaching the detectors.

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

- formation of the compound HUO₂(NO₃)₃.xTBP [¹]
- formation of U(VI) polymer [²]
- modification of nitrate binding and formation of hydrogen bond with water or acid nitric present in the third phase [³]

According to EXAFS result obtained in this study the following was found for the different theories. The hypothesis i is rejected since the formation of an eventual HUO₂(NO₃)₃.xTBP will lead 6 O(N) atom at 2.50 Å and this was not found. Hypothesis ii can not be completely rejected, and it might be possible that [UO₂(NO₃)₂.2TBP]₂ and UO₂(NO₃)₂.2TBP are simultaneously extracted in the heavy third phase. Hypothesis iii corroborates the observation from 15 M HNO₃ media but is not verified in 8M and 12 M HNO₃ media. In 8 M and 12 M nitric acid media, in the light and heavy phase, EXAFS measurement show that the environment around UO₂²⁺ is the same and constituted by 2 NO₃ and 2 TBP group.

Work performed in current quarter (January 2006 to March 2006)

This quarter involved work on extraction samples containing two different uranium concentrations. The samples were analyzed for nitrate and uranium concentrations by IC (ion chromatography) and LSC (liquid scintillation counting), respectively. This data will be helpful in understanding how nitrate and uranium are distributing between the two phases and the dependence of this effect on total nitrate concentration.

Sample Generation

The samples were made of an aqueous phase and an organic phase. The aqueous phase consisted of nitric acid, lithium nitrate, uranyl nitrate and water. The concentrations of nitric acid varied from 0 M to 12 M. The total nitrate concentration varied by addition of LiNO₃ and ranged from the acid concentration to 12 M. There were two sets of uranium concentrations investigated; they were 0.1 M and 0.05 M UO₂(NO₃)₂. The organic phase of each sample consisted of a pre-equilibrated solution of 30% TBP (tributylphosphate) in dodecane. Volumes of 0.75 mL of each phase were contacted by mixing for 2 minutes with a vortexor. Then the samples were centrifuged for 3 minutes to ensure complete separation of the two phases. Each phase was extracted and stored separately. The analyses were run on both the organic and aqueous phases.

Nitrate Determination

The concentration of nitrate in the samples was determined by IC. The IC was run with an elugon of 30mM KOH on a dionex anion exchange column. This was done on both the aqueous and the organic phases. The only difference is that the conductivity detector was used on the aqueous samples while the UV detector was used on the organics. The data collected is summarized below. Figures 1 and 2 show how the amount of nitrate in the organic phase varies with initial acid concentration. Figures 3 and 4 show how the amount of nitrate in the organic phase varies with initial nitrate concentration. The nitrate concentration for 0 M NO₃ listed in the figures excludes the nitrate contribution from the uranyl nitrate. The data demonstrates a slightly increasing trend, but generally the amount of nitrate extracted into organic phase stays between 0.5 M and 1.5 M regardless of the varying initial nitrate, acid or uranium concentrations.

Figure 1. Nitrate Distribution in the organic phase with 0.1 M Uranium
Figure 2

Nitrate Distribution (0.05 M U)
Uranium Determination

The uranium concentration of the samples was measured using LSC. The count time was one hour, and the amount of sample was 0.1mL in 10mL of scintillation fluid. Both the aqueous and
organic phases were analyzed for uranium concentration. The distribution ratio, $K_d$, was found by the following:

$$K_d = \frac{[U]_{\text{organic}}}{[U]_{\text{aqueous}}}$$

The data is summarized in the following graphs. Figures 5 and 6 show how $K_d$ varies with initial acid concentration.

**Uranium Distribution (0.1 M U)**

![Graph showing uranium distribution for 0.1 M U](image1)

**Figure 5.**

**Uranium Distribution (0.05 M U)**

![Graph showing uranium distribution for 0.05 M U](image2)

**Figure 6.**

Figures 7 and 8 show how $K_d$ varies with initial nitrate concentration.
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 off around a $K_d$ value of 10 which occurs around 10 M acid and nitrate.

**Other Accomplishments**

The titrator that will be used to measure acid concentration has been repaired and now has autosampling capabilities. The new NMR is operational, and methods for using this on
radioactive samples must now be determined. A new FT-IR has been ordered and should be arriving soon.

In March, a presentation on this research project was given at the 231st ACS (American Chemical Society) National Meeting in Atlanta, Georgia.

**Investigation of Optical Spectroscopy Techniques for On-Line Materials Accountability in the Solvent Extraction Process (Task 29).**

**Aqueous Uranyl System**

Initial studies on the uranyl/nitrate/acid system have been completed. Full spectra were taken of each sample in order to determine ligand effects on the entire uranyl spectra. Effects relating not to the nitric acid concentration, but the total nitrate ion present were observed (Fig. 1). The effect was generally a linear increase with total nitrate added. However there was a slight variation associated with the total acid concentration which can be seen in (fig 2). A peak shift, indicative of a speciation change was also observed.

Preliminary analysis has shown that the general peak shape and height can be qualitatively predicted from the total nitrate in the system. Conversely, a change in nitric acid concentration could be qualitatively detected by spectral analysis.

The presence of the peak shifting and the peak broadening in figure 1 suggests that there is a change in speciation occurring. Based solely on the peak shift, it appears that the nitratoo (mono- or di-) species becomes the dominant spectroscopic contributor around $[\text{NO}_3^-]_{\text{total}} \approx 6.00$ M. There has also been some speculation that the uranyl ion is dimerizing under these conditions. However, these, at this time, are still only hypotheses.

In order to resolve the speciation, and the spectra, of this system, potentiometric titrations and/or EXAFS experiments are being considered.
In order to more accurately determine the presence of a speciation driven peak shift in process, derivative spectra analysis is being looked into (fig. 3). With a first derivative spectrometer setup, the peak shift associated with an increase in nitrate concentration could be carefully monitored. This method has the potential to allow near real time analysis of process parameters without the need for a full spectrum. A region of interest on the order of 20-30 nm could be monitored.

Further work on the aqueous system will involve the addition of other ligands that are present in the UREX+ system, specifically, AHA. Also, the direct addition of chromophores to the process streams is being considered.

Due to the large fluorescence and absorption properties of the uranyl ion, efforts are being directed to adapting UV-Vis and TRLFS procedures into denial methods that could certify a stream as being uranium free, thus eliminating the need to monitor downstream for uranium. This methodology has the potential to be expanded to the other actinides of interest as well.

**Laser Fluorescence Laboratory**

The TRLFS system is in final stages of setup. Time resolution problems are in the process of being resolved. Problems due to a mismatch between the laser output aperture and the spectrometer entrance have been corrected with the addition of an optical periscope. Spectrometer has been effectively calibrated with Hg:Ar calibration source and is ready. Final installation of barrier curtains is ready pending final configuration by Princeton Instruments.

**Combined Radiation Detection Methods for Assay of Higher Actinides in Separation Processes (Task 30).**

**Purpose and Problem Statement**

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 U.S. Advanced Fuel Cycle Initiative (AFCI). Recycling of used fuel by chemically separating it into uranium, fission products, and HA would be the first step in this new fuel cycle. The Material Protection, Accounting, and Control (MPAC) are necessary for materials accounting, criticality monitoring, and assurance of proliferation resistance. The objective of the 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 the 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 linacs for producing photoneutrons in situ, for photon activation of HA, or for stimulating emissions processes (e.g. x-ray fluorescence).

Personnel

Principle Investigator: Dr. Denis Beller (UNLV Mechanical Engineering)
Co-PI: Dr. Warnick Kernan (UNLV Physics and Remote Sensing Lab, Bechtel-Nevada)

Students: A new graduate student, Quinten Newell, joined the project in January. Quinten will focus on the design and analysis of a large neutron slowing down spectrometer for assay of entire fuel assemblies and/or fuel rods. Pavan Kumar Attur, Electrical and Computer Engineering Department, continues to test and upgrade the NMDS. Lawrence Lakeotes, a graduate student in Mechanical Engineering, is employed part time to conduct literature searches, concept development, and radiation transport studies. Mr. Brice Howard, an undergraduate student in Mechanical Engineering, used MCNPX to model detector performance for measuring neutron emission rates and neutron multiplicity with actinide containing processes. However, he has taken a full-time position and has left the MPAC project.

National Laboratory Collaborators: Dr. Mark Schanfein (Safeguards and Security Group, Los Alamos National Laboratory) and Dr. James Laidler (National Technical Director Separations and Waste, Argonne National Laboratory).

DOE Collaborator: Dr. Thomas Ward (UNLV Russian Collaboration Science Adviser, TechSource, Inc.)

Summary Report for October-December 2005

The $^3\text{He}$ Neutron Multiplicity Detector System (NMDS) that was developed as part of Task 6, including a new data acquisition system (DAQS), has been transferred to the MPAC Project for use in radiation detection systems. The NMDS was re-configured for neutron multiplicity measurements and additional counting of a weak source as well as natural radiation was completed with both the old and new data acquisition systems for comparison. A new connector board was acquired to interface the remaining 32 detectors to the FPGA board, such that the entire NMDS can now be operated with either the Russian DAQ or the new high-rate DAQ. Comparison testing is ongoing.
Students continued developing concepts for combined neutron-gamma and passive-active interrogation systems using the NMDS. One of these is to use multiple sets of NMDS along a length of pipe containing "stream 16" of the UREX-3 flow sheet. Another is to develop a massive neutron-slowing-down spectrometer with active and passive neutron multiplicity measurements.

Technical staff from N-1 Safeguards Science & Technology Group, N-2 Advanced Nuclear Technology Group, and N-4 Safeguards Systems Group at Los Alamos National Laboratory visited UNLV to discuss ongoing and potential MPAC projects, to tour labs, and to meet with students.

Three students attended a MCNPX class at UNLV offered by Los Alamos National Lab.

Publications/presentations:


TRANS_MUTATION SCIENCES

Neutron Multiplicity Measurements of Target/Blanket Materials (Task 6).

Purpose and Problem Statement

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 a nuclear chain reaction in subcritical systems. Fission neutrons then transmute fissile waste isotopes as well as other problematic isotopes such as technetium-99 and iodine-129. 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. This project was developed to test a Russian-built Neutron Multiplicity Detector System (NMDS) for measuring neutrons generated in a central target by a variety of accelerators. To assist in experiment design and evaluation, we use the most advanced high-energy radiation transport code, MCNPX, to model experiments. Experimental results are compared to computational predictions and discrepancies are investigated. Initial plans were to conduct experiments using a 70-MeV proton cyclotron at the
Crocker Nuclear Laboratory at the University of California at Davis and/or a 20 to 40 MeV electron linac (linear accelerator) at the Idaho Accelerator Center (IAC) at Idaho State University (ISU). Finally, we planned to use the 800-MeV proton linac at the Los Alamos Neutron Science Center at Los Alamos National Laboratory and to compare the performance of the NMDS.

**Personnel**

**Principal Investigator:** Dr. Denis Beller (UNLV Mechanical Engineering)

**Students:** Ms. Shruti Patil, a graduate student, worked on her M.S. thesis to upgrade the NMDS for future use as a non-proliferation detection system. Ms. Patil is majoring in computer engineering at UNLV. She upgraded the capabilities of the NMDS to increase data acquisition speed, to record more information for each detected neutron, and to improve data analysis software. Mr. Brice Howard, an undergraduate student (Mechanical Engineering), was using MCNPX to model detector performance. Mr. Timothy Beller, an undergraduate student (M.E.) working on another TRP task with considerable experience with the NMDS, also consulted with Mr. Howard and with Ms. Patil on the project. Pavan Kumar Attur, a graduate student in the Electrical and Computer Engineering Department, was hired in December to assume the responsibilities of managing the NMDS.

**UNLV Graduate Student Thesis Advisor:** Prof. Venkatesan Muthukmar, Electrical and Computer Engineering, UNLV, is Ms. Patil’s and Mr. Attur’s thesis advisor.

**National Laboratory Collaborators:** Dr. Eric Pitcher (AFCI Experiments, LANSCE-12, Los Alamos National Laboratory); Dr. Stephen Wender (LANSCE-3 Group Leader, Los Alamos National Laboratory); and Dr. Michael Todosow (Brookhaven National Laboratory).

**DOE Collaborator:** Dr. Thomas Ward (UNLV Russian Collaboration Science Adviser, TechSource, Inc.)

**Issues:**

**Budget:** The budget was expended.

**Management:** The project was terminated without completing accelerator testing as the system could not perform at the counting rates required for existing high-energy accelerators operating at any reasonable current. The NMDS will now be used in a new project to assay separations processing streams for Materials Protection, Accounting, and Control (TRP Task 30).

**Summary Report for January-March 2006**

Task 6 was terminated in December and remaining funds were used in January to cover the cost of an MCNPX course for several UNLV students. Work using the NMDS will henceforth be reported in Task 30.

**Corrosion Mechanisms and Kinetics of Steels in Lead-Bismuth Eutectic (Task 18).**
Personnel

Four graduate students in our group are pursuing degrees under this task. The students and the working titles of their thesis or dissertation are listed in the following table.

<table>
<thead>
<tr>
<th>Student</th>
<th>Thesis/dissertation</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brian Hosterman</td>
<td>masters thesis</td>
<td>Studies of corrosion of steel by lead-bismuth eutectic studied by micro Raman spectroscopy and x-ray diffraction</td>
</tr>
<tr>
<td>Dan Koury</td>
<td>doctoral dissertation</td>
<td>Study of pitting corrosion of steel by lead-bismuth eutectic</td>
</tr>
<tr>
<td>Thao Ho</td>
<td>doctoral dissertation</td>
<td>Study of corrosion of iron-silicon alloy steel by lead-bismuth eutectic</td>
</tr>
<tr>
<td>Umar Younas</td>
<td>masters thesis</td>
<td>Fundamental processes in lead-bismuth corrosion of steel studied by a small test facility</td>
</tr>
</tbody>
</table>

In addition, two undergraduate students, Jenny Welch and Karen Levy, are members of the research group.

Karen Levy, undergraduate biology major, joined the group during the quarter. There is now a total of 6 students, including 4 graduate students and 2 undergraduate students.

Collaboration with LANL has been continued: task leader Ning Li, postdoc Jinsuo Zhang, graduate student Peter Hosemann, other people associated with DELTA loop at LANL.

Facilities

Room CHE 112C has been renovated into a High Temperature Materials Experimental Facility (HTMEF). The final renovation of the power and air conditioning was finished in March 2006.

Graduate student Brian Hosterman has assembled and debugged a laser Raman microscope for examination of corroded metal samples. The beam from an ion laser (Argon or Krypton) is focused on the sample, and the resulting fluorescence is analyzed by a spectrometer with an optical multichannel detector. Raman spectroscopy reveals the vibrational frequencies of samples, and has the advantages of smaller spot size (down to ~1 micron) and convenient access to the lower frequency vibrations expected in inorganic materials. The laser Raman microscope will be used for Brian Hosterman’s master’s thesis. Recent results obtained by Hosterman are discussed below.

Publication and presentations

*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, Allen L. Johnson, Dan Koury, Jenny Welch, Thao Ho, Stacey Sidle, Chris Harland, Brian Hosterman, Umar Younas, Longzhou Ma and John W. Farley, presentation by Allen Johnson at the AFCI materials working group, March 2006, Santa Fe, NM.

Publication

Spectroscopic and microscopic study of the corrosion of iron-silicon steel by lead-bismuth eutectic (LBE) at elevated temperatures, Allen L. Johnson, Eric P. Loewen, Thao T. Ho, Dan Koury, Brian Hosterman, Umar Younas, Jenny Welch, and John W. Farley, accepted at Journal of Nuclear Materials (in press Dec 29, 2005). Page proofs were received during the first quarter of 2006.

Publications in preparation

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. Allen L. Johnsona, Dan Koury, Jenny Welch, Thao Ho, Stacey Sidle, Chris Harland, Brian Hosterman, Umar Younas, Longzhou Ma and John W. Farley (in preparation).


Representative Experimental Results

A large number of studies of corroded samples were conducted using SEM, XPS, probe, and the TEM. Samples from the DELTA loop at LANL and from other sources were examined. Also, the investigation of 316 class stainless steel in LBE is continuing. Fig. 1 shows the Fe-Cr ratios of the protective thin oxide of a sample of cold-rolled 316 L stainless steel that has been exposed to LBE for 1000 hr at 550 C. The sample shows a Cr-rich oxide layer as revealed by XPS with sputter depth profiling. The top 100 nm shows an increasing Fe content, perhaps as a result of reaction of dissolved Fe with the oxide.

Corroded samples of D-9 steel have been in the process of being studies, which is a variant of 316 stainless steel that is optimized for resistance to swelling. The D-9 samples are notable for the process in which a localized failure of the protective oxide layer becomes widespread corrosion. The research group is examining the D-9 samples using a variety of surface microscopic techniques. A Wavelength Dispersion Spectroscopy (WDS) map of an etched, corroded D-9 sample is shown in Fig. 2 below. It shows a rich morphology, with oxygen transport channels, anisotropic etching of the metal, and a strongly textured metal-oxide interface. A summary of the D-9 results was presented by Allen Johnson in March to the annual meeting of the AFCI research, and a detailed manuscript is in preparation for submission to the Journal of Nuclear Materials.

Raman spectroscopy reveals the vibrational frequencies of samples, and has the advantages of smaller spot size (down to ~1 micron) and convenient access to the lower frequency vibrations.
expected in inorganic materials. For example, wustite (FeO), hematite (Fe₂O₃) and magnetite (Fe₃O₄) are all iron oxides with Fe/O ratios near 1:1, but they have different vibrational frequencies. Typical data is shown in Figs. 3-5. The presence of the 670 cm⁻¹ Raman peak in the corrosion layer of the 316 (annealed) sample (fig. 5) demonstrates that magnetite (Fe₃O₄, Fig. 4) and not hematite (Fe₂O₃, Fig. 3) was being formed on this sample, consistent with our previous results.

![Graph](image)

Figure 1. Iron/chromium ratio of the surface layer in cold rolled 316L stainless exposed to LBE for 1000 hrs at 550°C as determined by XPS sputter depth profiles. Note the increase in iron concentration in the top 100 nm of the oxide layer, perhaps due to reaction of dissolved iron with the surface oxide.
Figure 2. WDS image of D9 stainless as above. Note oxygen channels, etch anisotropy, and highly irregular metal oxide interface.

Figure 3. Raman spectrum of Fe$_2$O$_3$ standard.
Figure 4. Note the new peak at 670 cm$^{-1}$. The other peaks are Fe$_2$O$_3$ peaks from impurities in the Fe$_3$O$_4$ standard.
Figure 4. Annealed 316L exposed to LBE – 10 minute Raman spectra. Notice the peak at 670 cm\(^{-1}\), characteristic of Fe\(_3\)O\(_4\).


The purpose of this collaborative research project involving the University of Nevada Las Vegas (UNLV), Los Alamos National Laboratory (LANL) and Idaho State University (ISU) is to evaluate the effect of silicon (Si) content on the corrosion behavior and radiation-induced embrittlement of martensitic stainless steels having chemical compositions similar to that of the modified 9Cr-1Mo steel. Recent studies at LANL involving Alloy EP-823 of different Si content have demonstrated that increased Si content in this alloy may enhance the corrosion resistance in molten lead-bismuth-eutectic (LBE). Since very little data exists in the open literature on the beneficial effect of Si content on the corrosion properties, it seemed appropriate to initiate a research project to address this technical issue. This task is intended to study the effect of Si content not only on the corrosion resistance but also on the radiation-induced embrittlement of martensitic stainless steels. The susceptibility of these alloys with different Si content to stress corrosion cracking, general corrosion and localized corrosion will be evaluated in the molten LBE and aqueous environments of different pH values using state-of-the-art testing techniques. Testing in the aqueous media is intended to develop baseline data for comparison purpose. Radiation-induced embrittlement of these alloys will initially be studied by irradiating the test specimens with bremsstrahlung gamma radiation from 20-40 MeV electron beams at ISU. These gammas induce (\(\gamma\), n) reactions in the giant dipole energy region. The principal radiation damage from these irradiations, in turn, stems from the recoiling residual nucleus (with average kinetic energy of approximately 20,000 eV) after the neutrons are emitted. The high penetrability of gammas, whose range is of order one meter in steel, ensures that the resulting
damage will be uniform over the volume of the sample. The induced activity of these specimens will have very short half-lives (typically minutes) due the systematics of (slightly) proton-rich nuclei. The resulting radiation-induced hardening can subsequently be evaluated by proper experimental techniques. Later, similar studies can be performed using specimens radiated by neutrons at LANL.

**Plans for the Next Quarter**

- Perform SCC testing using T91 grade steels containing 0.5 and 1.5 wt% Si by SSR technique with and without controlled potentials.
- Perform Charpy impact testing using V-notch specimens.
- Perform crack-growth experiments using compact-tension and double-cantilever-beam specimens.
- Continue DSA study by TEM.

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![Figure 1. s-e Diagram versus Temperature](image-url)

Figure 1. s-e Diagram versus Temperature
Figure 2. s-e Diagram versus Temperature

Figure 3. s-e Diagram versus Temperature
Figure 4. s-e Diagram versus Temperature

Figure 5. CPP Diagram of T91 Grade Steel Containing 0.5 wt% Si at 60°C

Oxide Film Growth Modeling in LBE Systems (Task 21).
Global restructuring cellular automaton model on growth and corrosion behavior during the formation of passive layer

The corrosion induces a restructuring in the layer, which will induce porosity in the part of the oxidation layer. Figure 1 shows the snapshots of the simulated layer with the presence of corrosion. For different control parameters, the layer exhibits for different porosity. Figure 2 shows the height of the growth front and the global porosity in the case with corrosion as a function of time steps. As shown in the figure, the slope of the corresponding straight line is about 0.5, which approximates the growth front as the square root of time. Hence, this model can be interpreted by the Wagner theory, and the parabolic law is suitable for this case.

Figure 1. Snapshots of the simulated layer in the presence of corrosion. They correspond to $10^5$ time step. The black dots are either metal or oxide sites. The white spaces are occupied by either solvent or corrosion sites. The initial interface between metal and solvent locates at $j = 400$. $n$ represents the number of entity of metal particles which locates on single metal site.
Figure 2. Global porosity and dimensionless growth height for the case with corrosion as a function of time steps. The growth height is normalized by spatial difference.

(2) Stochastic modeling on the surface growth and internal oxidation
In this model, 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 simulated. The diffusion process is modeled by the Kawasaki random walk model. This model also includes the effect of volume expansion on the oxide layer growth during oxidation. Figure 3 shows the snapshots of simulated duplex layer with presence of corrosion and precipitation. As seen in Figure 3, the duplex oxide layer can be found in this model. The structure of oxide layer coincides with Robertson theory, and the oxide growth mainly is controlled by the outward diffusion of iron. Figure 4 shows the variation of growth/corrosion front as a function of time step. Since the mechanism of the process of formation of oxide layer is controlled by diffusion of A and B, parabolic growth rate is suitable for both growth fronts and corrosive front.
Figure 3. Snapshots of the simulated layer in the presence of corrosion and surface growth. They correspond to $10^4$ time step. The red dot is $\text{Fe}_3\text{O}_4$ site; the blue dot is $\text{Cr}$ site; the green dot is $\text{Fe}$ site; the cyan dot is $\text{Cr}_2\text{O}_3$ site. Upper side of layer is filled with liquid LBE with low oxygen concentration. Lower side of the oxide layer is steel. The corrosion probabilities of $\text{Fe}$ and $\text{Cr}$ are taken as 0.5.

![Figure 3](image)

Figure 4. Variation of growth/corrosion front as a function of time step. The curve with symbol circle is the growth front and the curve with symbol triangle is the corrosion front.

![Figure 4](image)

(3) Two conference papers have been accepted and will be presented in 2006 International Congress on the Advances in Nuclear Power Plants (ICAPP '06)

1. Huajun Chen, Yitung Chen, Jinsuo Zhang, Modeling on Oxygen Transfer in the Forced Convection Lead-bismuth Eutectic Flow, ICAPP'06.

**Corrosion Barrier Development for LBE Corrosion Resistance (Task 23).**

During the past quarter, one full time graduate student and one half-time undergraduate student researcher worked on this project. The major accomplishments during the past quarter are summarized below:

**Deposition of Ni nanowire inside alumina template pores**

As reported in the last quarterly report, synthesis of Cr nanowires was found to be problematic in terms of uniform coverage. Hence Ni was identified as the alternative metal 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. While Ni can provide very good structural integrity to the porous alumina, one potential problem is its higher dissolution rate in LBE. However, since the Ni layer will be protected by a thick layer of dense alumina on top, this is not expected to pose a major problem. After a detailed consideration, it was decided that Ni filling of the porous alumina structure can provide very valuable information about performance of the coating layers under thermal cycling. In parallel, process development for uniform deposition of Cr nanowires will also continue, which if successful, will be included in the final coating structure.

Deposition of Ni nanowires was achieved by using the following procedure. The electrochemical deposition of the Ni nanowire was carried out in a two-electrode arrangement with a Pt-mesh as anode, and a thin layer of Pt underneath the template acting as a cathode. A Watts solution was used (a mixture of NiSO₄·6H₂O, NiCl₂·6H₂O and H₃BO₃) for the Ni source. The wires were grown at a potential difference of 1 V between the anode and the cathode. The deposition was done at ambient temperature. Two different deposition times (60 sec and 80 sec) were used for the wire growth. The deposition current as a function of time was used to monitor the growth rate of the wires. Time variations of deposition current are furnished below, which show uniform time dependence with occasional fluctuations common for electrochemical depositions.

The Ni nanowire samples were characterized by Field Emission SEM. The figures below show cross-sectional images of Ni nanowires deposited for different time lengths. The figures show excellent position uniformity and coverage. Thus the problem encountered previously with Cr nanowires is solved by the selection of Ni as the nanowire material. The next step will be to deposit a thick layer of dense alumina on top by sputter deposition, after which the samples will be ready for testing.
Investigation of Cr nanowire deposition uniformity

As mentioned previously, a significant problem was encountered with uniformity of Cr nanowires synthesized inside the alumina pores. This was somewhat puzzling since a well-established recipe for the deposition of Cr was used. One explanation for the observed non-uniformity is the restricted space inside the nanopores that may not be conducive to the Cr synthesis chemistry. During the last quarter, further investigation of this phenomenon has been initiated in order to develop the process for more uniform deposition of Cr nanowires. Towards this objective, alumina structures with large pore diameters (100 nm) were synthesized by carrying out anodization in oxalic acid. Next, Cr will be deposited electrochemically inside the alumina pores and imaged to investigate the position uniformity.

Reactor Physics Studies for the AFCI RACE Project (Reactor-Accelerator Coupling Experiments Project (Task 27).

Purpose and Problem Statement

In the RACE Project of the U.S. Advanced Fuel Cycle Initiative (AFCI), a series of accelerator-driven subcritical systems (ADSS) experiments is being conducted at the Idaho State University’s Idaho Accelerator Center (ISU-IAC) and at the University of Texas (UT) at Austin, and will be conducted at the Texas A&M University. In these experiments electron accelerators are used to induce bremsstrahlung photon-neutron reactions in heavy-metal targets; this source of $10^{10}$ to $10^{13}$ n/s initiates fission reactions in the subcritical systems. These systems include a compact, transportable assembly at ISU and TRIGA reactors at UT-Austin and Texas A&M. These experiments will provide a variety of cores, fuel types and enrichments, and target/reactor configurations for many separate accelerator coupling studies. The UNLV portion of this project will be a three-year, three-phase project employing a principal investigator (as well as the UNLV TRP RACE Project Director), a graduate student, and undergraduate students to support computational and experimental research at the ISU and the Texas universities, to integrate the UNLV Transmutation Research Project with this accelerator-driven transmutation research, and to further develop UNLV’s computational infrastructure for reactor physics research.
Figure 1. 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.

Personnel

Principle Investigator: Research Prof. Denis Beller, Department of Mechanical Engineering, UNLV.

Students: Mr. Evgeny Stankovskiy, graduate student, Department of Mechanical Engineering, came to UNLV from the Institute of Nuclear Power Engineering in Obninsk, Russia, to pursue a doctorate. He will design, conduct, and analyze an accelerator-driven subcritical experiment at Idaho State University. Mr. Timothy Beller, Mr. Brice Howard, and Mr. Ryan LeCounte, undergraduate students in the Department of Mechanical Engineering, conducted an undergraduate design study in support of future high-power experiments in a TRIGA reactor.

UNLV Graduate Student Thesis Advisor: Prof. Robert Boehm, Department of Mechanical Engineering, UNLV.

National Laboratory Collaborator: Dr. George Imel, Argonne National Laboratory (former director of experiments in the MUSE and TRADE programs in Europe).

DOE Collaborator: Dr. Thomas Ward, TechSource, Inc. (UNLV Russian Collaboration Science Adviser)

Summary Report October-December 2005:

M.E. undergraduate students Ryan LeCounte, Brice Howard, and Timothy Beller continued a two-semester senior design project to design, construct, and test a new high-power, uranium-containing water-cooled target for Texas RACE. They have dubbed the target the Cooled Electron Target--Optimized for Neutron Production, or CETON. During the second semester, after analyzing and constructing a prototype of a compact version of CETON, they determined that a design change was needed. The new design includes a tungsten electron-photon converter, an aluminum cooling shroud, and a cavity for inserting an aluminum-clad natural uranium photon-neutron converter. They sized the cavity for natural uranium rods being transferred from Rensselaer Polytechnic Institute to Idaho State University. They also acquired and installed the FLUENT® CFD code, then used it to begin analysis of cooling of the
high-power target. The students then completed the final design of the high-power target and initiated purchasing and fabrication of components. The aluminum body and spacers were fabricated in the UNLV College of Engineering machine shop, and tungsten-copper (80% tungsten) disks were machined at the Idaho Accelerator Center. The CETON was assembled and successfully leak tested with high-pressure water. Additional testing to measure neutron generation and heat transfer while coupled to a 25-MeV electron linac will be conducted at ISU’s IAC in April.

Ph.D. student Evgeny Stankovskiy is evaluating a variety of code systems for modeling neutron generation and transport and thermal feedback effects in accelerator-driven TRIGA as well as other reactors. The group considered ERANOS, RELAP, PARCS, and APOLLO. The group has the INL’s RELAP5 code system for thermal-hydraulic reactor analysis, and the ERANOS reactor analysis code was recently received from the CEA (France). EUROTRANS/ECATS participants are developing accelerator-driven applications of ERANOS, and RACE collaborators at University of Michigan have used it to evaluate TRADE and MUSE experiments. Because of evolution of DOE priorities, the UNLV RACE research has been refocused to concentrate on the testing of the high-power target and on conducting and analyzing ADS Experiments at ISU. Unless substantial funding is found for UT and/or Texas A&M, UNLV will not participate in Texas RACE except in the design of the target for high-power RACE in 2007.

Three students attended a MCNPX class at UNLV offered by Los Alamos National Lab. In his role as national RACE Project Director, the PI continued to coordinate activities of several universities and several European organizations to contribute to target and experiment designs for High-Power RACE. Currently an international meeting of this group in April is being planned.

Publications:


Deep Burn Separations and Repository Behavior

Deep burn separation and repository studies will be performed by a collaborative comprising UNLV, SRNL, and the University of Iowa. The UNLV team will evaluate treatment of TRISO fuel in a fluidized bed as a reprocessing step. Repository behavior of fuels will also be performed. The SRNL will assist in the development of X-ray absorption fine-structure (XAFS)
spectroscopic studies to provide information on the average coordination environment of specific elements of interest. This technique which reveals information on local structure can be conducted with amorphous as well as crystalline materials. Working with radioactive samples at synchrotron facilities and the acquisition of XAFS spectroscopic data from radioactive samples poses challenges for researchers. The purpose of this work is to mentor students in the area of XAFS data acquisition with radioactive samples in an X-ray user facility at a national laboratory. SRNL researchers arrange the user time, meet the safety guidelines required for the work at the user facility, determine detector needs, assist with the handling/manipulation of the samples at the user facility and X-ray beam line set-up, help the UNLV students with the acquisition of quality XAFS spectra and answer questions regarding XAFS analyses. The University of Iowa partner will synthesize ligands for the separation of lanthanides from actinides and actinides from other actinides. The University of Iowa partner will synthesize ligands, perform initial studies with lanthanides, and provide ligands for actinide studies at UNLV.

Work Performed in Previous Quarter (October 2005 to December 2005)

Further studies have been performed on the reaction between uranium dioxide and ammonium bifluoride. This effort is part of a reprocessing scheme using fluorination to treat TRISO fuels prior to chemical leaching. X-ray diffraction studies were performed to identify the reaction products between UO$_2$ and the ammonium bifluoride. The long term stability of the product was also investigated. SRNL supported XAFS data analysis with UNLV. SNRL also developed a joint XAFS proposal with UNLV. The University of Iowa partner continued synthesis of ligands for actinide-lanthanide extraction.

Work Performed in Current Quarter (January 2006 to March 2006)

Studies on the fluorination of uranium by ammonium bifluoride for treatment of TRISO fuels continued in this quarter.

1.1. Fuel treatment by fluorination

Ammonium bifluoride is being investigated as a chemical deconstruction agent for TRISO-coated fuels. Solid-solid reactions have been observed between ammonium bifluoride and oxides of vanadium, zirconium, thorium, uranium, and plutonium. Past work has focused on fundamental physical parameters in the reaction between ammonium bifluoride and uranium dioxide. Current work focuses on the reaction products obtained. Samples of the following compounds were prepared and analyzed:

1. (NH$_4$)$_4$UF$_8$
2. $\gamma$-(NH$_4$)$_2$UF$_6$
3. (NH$_4$)$_7$U$_6$F$_{31}$
4. $\beta$-NH$_4$UF$_5$
5. (NH$_4$)$_3$UO$_2$F$_5$

Samples were analyzed using a variety of crystallographic techniques. Power X-ray Diffraction (XRD) was used on all samples. Extended X-ray Absorption Fine Structure (EXAFS)
Spectroscopy was used on some compounds that showed differences between the powder XRD patterns and those calculated from published structures.

1.1.1. Structure of (NH$_4$)$_3$UO$_2$F$_5$

The observed powder pattern of (NH$_4$)$_3$UO$_2$F$_5$ (Figure 1) differs from that calculated from the published structure. The current literature shows the structure to be tetragonal, with cell dimensions of a=9.70 Å and c=18.91 Å [4]. The UO$_2$F$_5^{3-}$ group is described as a pentagonal bipyramid with all five fluorine atoms at the same distance. A best fit (Table 1) of the EXAFS data (Figure 2) is obtained with a more complicated structure. The structure is still essentially a pentagonal bipyramid, but the symmetry is lower than indicated by the previous structure description. Single-crystal x-ray and neutron diffraction will be performed to confirm a new structure.

<table>
<thead>
<tr>
<th>Sphere</th>
<th>Coordination number</th>
<th>Distance (Å)</th>
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<tbody>
<tr>
<td>oxygen</td>
<td>2 (fixed)</td>
<td>1.78(2)</td>
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<tr>
<td>fluorine</td>
<td>0.92</td>
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<tr>
<td>fluorine</td>
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</tr>
<tr>
<td>fluorine</td>
<td>1.97</td>
<td>2.47</td>
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</table>

Table 1 – EXAFS Fit for (NH$_4$)$_3$UO$_2$F$_5$

---

1.1.2. $\gamma$-(NH$_4$)$_2$UF$_6$ analysis

$\gamma$-(NH$_4$)$_2$UF$_6$ has four polymorphs identified. The $\alpha$, $\beta$, and $\delta$ phases are not present in the thermally-decomposing system. Analysis was attempted by assuming analogous behavior with the ammonium platinum fluoride system. EXAFS analysis (Figure 3) revealed that the structure crystallizes in the calcium fluorite structure type with NH$_4^+$ and UF$_6^{2-}$ ions occupying
the F- and Ca$^{2+}$ sites, respectively. Fluorine atoms occupy a single sphere around the uranium sites at a distance of 2.27 Å.

**Figure 3 – Fit of $\gamma$-(NH$_4$)$_2$UF$_6$ EXAFS data**

1.2. XAFS studies

SRNL provided assistance to Post Doctoral Staff (Dr. Frederic Poineau) on uranium and zirconium EXAFS data analyses, theory, interpretation and software as needed. Guidance on uranium X-ray absorption near-edge structure spectroscopy (XANES) data interpretation was also provided. Future XAFS experiments with UNLV were developed. This was presented in the user proposal that was prepared and submitted as a user proposal for more XAFS beam time to be taken in the late spring/early summer at the APS. We are awaiting the results of the review.

SNRL completed safety paperwork that was required for actinide XAFS experiments at the synchrotron (the APS). For these studies, UNLV prepared and shipped samples for the March XAFS experiments at the APS. The samples were placed in holders that SNRL designed and procured for XAFS studies with radioactive sample holders. Approximately 40 of these sample holders were sent to UNLV in mid February.

Actinide XAFS experiments at the APS synchrotron were performed. During these studies, the SRNL collaborators negotiated with the APS so that the appropriate training could be given to UNLV students and staff to conduct experiments. Support for the access of the students and post docs of UNLV to obtain hands on experience with the X-ray beamline was provided.

Discussions were initiated on the need for future UNLV sample (containment) boxes for use at the APS with UNLV. Our goal is to avoid using another laboratory at Argonne National
Laboratory prior to the APS. If one can avoid this additional step, which requires placing our samples in another researcher’s “box” instead of in a box of our own that we could design, we would save time and effort during these studies. We will pursue the design of a new box with UNLV for future use. This box will need to be tested for suitability and the approval of its use will be required by the APS safety staff.

1.3. **Ligand Synthesis**

The goal of our research is to develop a rational, scalable method to separate Americium (Am) from Curium (Cm) using ligands that take advantage of coordination preferences and size selectivity within Am and Cm coordination spheres. Specifically the following aims will be addressed:

1. Development of new ligands for the separation of Am$^{3+}$ from Cm$^{3+}$. The proposed ligand groups exploit the principle inner-sphere coordination preferences of the actinides. These ligands are attached to rigid architectural groups that also enforce size discrimination.
2. Determination of the ligand affinities for the lanthanide and members of the actinide series. The affinity will be thermodynamically and kinetically quantified. The data will be incorporated into models to evaluate trivalent actinide separations under varying conditions.

Per-6-thiosalicylate-$\beta$-cyclodextrin has been synthesized and characterized by mass spectroscopy.

![Chemical Reaction](attachment:image.png)

The pKa’s for the acid groups of per-6-thioglycolate-$\beta$-cyclodextrin have been determined by acid-base titrations.

<table>
<thead>
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<th>Proton</th>
<th>pKa</th>
<th>Std. Dev.</th>
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<td>6</td>
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</table>
Determination of binding constants of per-6-thioglycolate-β-cyclodextrin with various lanthanides has been performed. These values were determined by acid-base titrations. Each titration was carried out in triplicate.

<table>
<thead>
<tr>
<th>Lanthanide</th>
<th>logK_{110}</th>
<th>Std. Dev.</th>
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<tbody>
<tr>
<td>Lanthanum</td>
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</tbody>
</table>

The pKa’s of per-6-thioglycolate-β-cyclodextrin and its binding constants with various lanthanides were determined by acid-base titration. All experiments were done in 20 mL of 0.1 M KCl electrolyte and at 20°C. A measured quantity of per-6-thioglycolate-β-cyclodextrin was dissolved in the electrolyte and then an acidic solution containing the desired lanthanide was added. Titrations were carried out with a 2:1 ligand:metal ratio to eliminate the formation of the solid metal hydroxide. The solution was titrated with 0.1 M KOH (carbonate free) using a Brinkmann Metrohm Titrino auto-titrator. Analysis of the data was performed using the Hyperquad software package (*Talanta*, 1996, 43, 1739-1753). The log K_{110} for the majority of the lanthanides tested is around 100. The rigidity of the ligand and close proximity of the carboxylic acids may be the primary factors for the large binding constant. The cause of the lower binding constants of lanthanum and cerium is not readily apparent.

Per-6-thiosalicylate-β-cyclodextrin was synthesized using a modified procedure of Adam et al. (*J. Med. Chem.* 2002, 45, 1806-1816). The synthesis was accomplished by dissolving 0.208 g of per-6-iodo-β-cyclodextrin in 8 mL of dry DMF. Thiosalicylic acid (0.5 g) was then dissolved in the reaction mixture. To this, 0.150 g of potassium carbonate (K₂CO₃) and 0.115 g sodium dithionite (Na₂S₂O₄) were added. The reaction mixture stirring was heated at 70°C for 3 days. Initial analysis of the crude product mixture by mass spectrometry indicated that the desired product had formed, however non-per-functionalized derivatives were also present. The desired product was obtained by dissolving the crude product in alkaline water (pH ~14) and passing down an LH-20 chromatography column. Separation was achieved as indicated by the mass spectrum. Each isolated fraction had different relative intensities of the M⁺:M³⁺:M⁵⁺ charge states. The most pure fractions were identified by the M³⁺ charge state (~694 m/z) as seen in the mass spectrum in the Appendix. Lyophilization of the columned fractions was not completed at the time of writing; therefore a final yield is not available. Analysis of the crude material by mass spectrometry indicated that a yield of 80-85% was obtained. In depth characterization via $^{13}$C NMR, COSY, and HMBC will be completed in the near future.

1.3.1. Appendix
Mass spectrum of per-6-thiosalicylate-\(\beta\)-cyclodextrin fraction: