AFCI Quarterly Input: UNLV October 1 through December 31, 2006

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AFCI Quarterly Input – UNLV
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1.0 University of Nevada, Las Vegas (UNLV)

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:

- Denis Beller gave a graduate colloquium in the Physics Department at ISU titled “The Need for Nuclear Power” on October 2.
- American Nuclear Society President Harold McFarlane gave a presentation in Las Vegas on the nuclear industry on October 4.
- Rhonda Hopkins, NSTec, Remote Sensing Laboratory presented a seminar at UNLV entitled “Scientific Work Conducted by the Remote Sensing Laboratory” on October 5.
- UNLV faculty participated in a DOE-Academia meeting in Chicago on DOE Nuclear Energy University Programs, October 24-25.
- Anthony Hechanova presented a seminar at the University of Toledo on Used Nuclear Fuel Recycling on October 26.
- UNLV faculty participated in a number of committee meetings, in particular on education, and chaired sessions at the winter meeting of the American Nuclear Society, November 12-16 in Albuquerque, NM.
- Two M.S. M&NE students presented an exhibit on the HP RACE Target for UNLV Engineering freshman recruitment on November 18 for about 50 students and parents. The exhibit resulted in at least two new students for the UNLV nuclear programs.
- Denis Beller gave a graduate colloquium at the Idaho State University Department of Physics titled “Atomic Time Machines: Back to the Future of Nuclear Power,” on November 27.
- Bob Summers, NSTec, gave a seminar on missions at the Nevada Test Site.
- Denis Beller completed work on the ANS President’s Special Committee on Federal Investment in Nuclear Education.

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

- **Academic Programs** – Meetings were held on November 8 and 30 to discuss developing a Ph.D. program in nuclear engineering to support education and research needs of organizations at the Nevada Test Site, the Yucca Mountain Project, the UNLV Institute for Security Studies, and other DOE-related activities.

- **New Radiochemistry Laboratories** – The UNLV Planning and Construction Office has hired a planning engineer to evaluate the penetrations into the roof and laboratory set-up for three new Radiochemistry Laboratories. All of the laboratory furniture was purchased. The UNLV Maintenance and Facilities Office will add two voltage circuits and make the required roof cuts.

- **Molten Metal Laboratories** – The TC-1 LBE loop has two graduate-student research projects associated with improving the control algorithm (Task 31) and studying the EM pump (Task 32).

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

- Prof. Leonid Ponomarev (MUCATEX) participated in the meeting of the Expert Group on ISTC Transmutation in Madrid, Spain December 18-19 to establish collaboration with Europe for the implementation of the program developed in the UNLV-sponsored program.

- Two faculty members, Yury Korovin and Vladimir Artisyuk, from the Institute for Nuclear Power Engineering, Obninsk, Russia visited UNLV December 21-24 to investigate potential collaboration on a textbook and research.

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.

- The Cs evaporator was completely assembled and installed in the system.
- An in-depth literature study was performed for chemical preparation of SiC surfaces to extend the previous approach of ion sputtering and annealing.
- An HF-based approach for SiC surface preparation was selected and a suitable fume hood was identified and cleaned. Furthermore, the necessary chemicals and instrumentation were ordered and set up in the HF-etching fume hood.
- A sample heating stage was developed, installed, and commissioned. The heating stage enhances the previous heating capabilities to higher temperatures and was used to desorb surface adsorbates after the HF etching step.
- Characterization by X-ray photoelectron spectroscopy after each preparation step revealed strong (complete) oxidation of the SiC single crystals. The vendor (MaTeck) was contacted about this issue and less oxidized replacement samples are expected.

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

- The project was presented at the Inert Matrix Fuels Workshop 11 in Park City, Utah.
- Synthesis of uranium containing ceramics was initiated and completed.
- The Soxhlet experiment has been started with uranium containing ceramics.
- Dimensions, volume, mass, and surface area were measured for all pellets.
- Elemental mapping was performed on all samples to determine homogeneity.
- Material imaged by optical microscopy to determine phase mixing.
- Phase constitution was determined qualitatively by XRD with LaB6 standard.
- Thermodynamic behavior determined by TGA/DSC.


- Hot Cell robot control: Work on the visual servoing of robots inside the hot cell continued. Focus was on the development of algorithms for the determination of object size, orientation, and location from camera images.

• Thermal analysis (TG/DSC) of a UN₂ sample showed that denitrification of uranium dinitride involves at least three transitions. These transitions were observed at around 500, 700, and 1100 C temperature values, and UO₂ was identified to be the primary phase in the final product after these transitions.

• After heat treating a UN₂ sample for 30 minute each at 500, 700, and 1100 C temperatures under research grade argon the sample contained UN₂, U₂N₃, and UN (6.5 % UO₂ as the secondary phase) phases respectively. Thus, the UN₂ denitrification to UN was identified to occur through an intermediate product U₂N₃.

• Synthesis of UN from UN₂ using ultra-pure grade argon at 1100 C as a function of heating time was also studied. This experiment showed that after 1 minute and 10 minutes the UN₂ sample is completely converted into U₂N₃ and UN. However, the UN phase quantity of these two samples was lower than 50 %. After 20 minutes of UN₂ denitrification, the sample contained 90.1 % of UN, 3.6 % UO₂, and 6.3 % U₂N₃.

• Two other possible methods to synthesize UN from UN₂ were also studied. Heating a UN₂ sample at 1000 C under high vacuum converted the UN₂ phase completely to the oxides UO₂ and U₃O₈. Use of N₂/H₂ (8 %) as the reducing gas only reduced the UN₂ to U₂N₃/U₂N₃+X (X = 0.1 through 0.5).

• Further investigation of UN₂ denitrification was performed using TG/DSC analysis under argon at 500, 600, 800, and 1200 C.

• At 500 and 600 C final temperatures, most of the UN₂ was converted into uranium oxides (UO₂ and UO₃). About 45 wt % of U₂N₃ phase was identified after 800 C. At 1200 C, the UN₂ sample was converted to UO₂ with a UN secondary phase. These results suggest that the oxidation predominates the denitrification of UN₂ under oxygen rich conditions found in the TGA.

• One hour heating using a set of temperatures from 500 to 950 C showed that the lowest temperature of U₂N₃ formation from UN₂ is 700 C. Complete transformation of UN₂ to U₂N₃ was identified from 700 through 950 C temperatures. The lowest temperature at which UN could be formed from UN₂ was identified to be 1000 C.

• ZrO₂ and Er₂O₃ reactions with NH₄HF₂ led to (NH₄)₃ZrF₇ and (NH₄)₃Er₂F₉ final products respectively. NH₄HF₂ reaction with Er₂O₃ is very fast. The ZrO₂ tends to react with NH₄HF₂ very slowly. After 36 days, only about 67 % of ZrO₂ is converted into its final product (NH₄)₃ZrF₇.

• Reaction of ZrF₄, (NH₄)₃Er₂F₉, and ThF₄ with NH₃ was also studied. The ZrF₄ tends to form mostly oxides where as (NH₄)₃Er₂F₉ formed ErN and ErF₃ at 800 C. ThF₄ reacts with NH₃ to form about 73 wt % of ThN₀.₇₉F₁.₆₃ at 800 C in 1 hour.

• The UN₂ denitrification at 1100 C using 5.0 grade Ar for 20 minutes led to form some UO₂, the same experimental conditions was used with 6.0 grade Ar with two Pt foils covering the UN₂ sample. This led to a sample containing only UN and some unreacted U₂N₃.

• UN synthesis from UN₂ at 1100 C occurs in 23 minutes.
• Use of Zirconium metal as an oxygen trap worked to synthesize UN with 97 wt% phase purity. Further investigation of the use of Zr-metal also revealed that the Zr-metal prevents oxygen from contacting with UN. Therefore, it is important to cover the sample (UN₂) in all directions, if possible, to reduce the formation of UO₂.

• The product of NH₄HF₂ with TcO₂ after one day is NH₄TcO₂. Oxides of Ce, Nd, Sm, and Y were also mixed/ball milled with NH₄HF₂. At this stage CeO₂ seems produce a final product (NH₄)₄CeF₈, and the reactions of the other compounds are to be investigated in future.

Solution-based Synthesis of Nitride Fuels (Task 34) Highlights.

• An inventory of existing synthesis equipment and supplies was conducted, and new equipment and supplies were ordered.

• Researchers received specific training for this project which covered radiation safety and handling of liquid ammonia.

• An extensive literature review on amide synthesis and formation of UI₃ in liquid ammonia was performed.

• Based on other ongoing research, characterization methods for UN were initiated for final product evaluation.

SEPARATIONS TECHNOLOGY

Immobilization of Fission Iodine (Task 15) Highlights.

• Additional synthetic approaches to producing MnO₂ were explored that would be suitable for the oxidation of iodide.

• The reaction of iodide with various MnO₂ preparations at pH 4, 5 and 6 were explored.

• The effect of iodide and MnO₂ concentrations, temperature and ultrasonic treatment on iodide oxidation rates were examined.

• Some test reactions in the presence of lignin or p-hydroxybenzoic acid were conducted to observe concurrent iodination on organic matter.


• An ASPEN-Plus test case for was initiated for validating the input/output communication from the ISOPRO (previously known as TRPSEMPRO) based on reviewer suggestions.

• The input and output parser module was improved from the ISOPRO software correlated to the data set schema from the ASPEN-Plus output.

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

• The synthesis of room temperature ion liquids (RTIL) were initiated.

• Reference electrodes for RTIL solution studies were prepared.

• Preliminary background studies on RTIL solutions were performed to determine the working electrochemical window.
Preliminary background studies on RTIL solutions with Ce were performed.

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

- TBP/dodecane was pre-equilibrated at 1M HNO₃.
- Extraction samples were prepared with 1M HNO₃, 0.01 M UO₂(NO₃)₂ and LiNO₃ concentration from 0-10 M.
- Organic and aqueous layers were separated.
- [U] was measured in aqueous phase using ICP-AES.
- [U] was measured in aqueous and organic phases using LSC.
- [NO₃⁻] was measured in aqueous and organic phases using IC.
- [H⁺] was measured in aqueous and organic phases by titration.
- NMR studies were performed on Uranium-AHA.
- U-AHA complexation constants were evaluated: β₁ = 6.78, RSD 0.099 β₂ =11.98.
- The above data was analyzed. Titration showed that the amount of acid extracted into organic phase increased with increasing nitrate concentration. ICP-AES data showed that the amount of uranium extracted increased with increasing nitrate concentration until 6M.
- Solubility of U-AHA: uranium concentration was measured in saturated solutions in acetonitrile, acetone, benzene, THF, dichloromethane, chloroform, diethyl ether, methanol, ethanol, water, toluene, and DMSO.
- Uranyl-AHA Crystals were sent to Thomas Albrecht-Schmidt (Auburn University) and an interesting uranyl tetramer structure was received.
- The Un-Scan-It software for digitization of uranium containing NMR spectra was received.
- Fe(III)-AHA was prepared in three different ways to demonstrate that the UAHA synthesis method works for analogues as well. IR, NMR, UV-vis of FeAHA, D₂O exchanged FeAHA.
- Reagents for NMR studies of effect of pH, ionic strength on UAHA (D₂O exchange, freeze dried) were prepared. NMR coupled with UV-vis showed that the UAHA has at least two, possibly three, binding moieties that are present in a pH-dependent distribution. This information will be important for modeling.
- The titrator was calibrated. A method for titration under inert atmosphere was developed.
- New Ion Chromatography unit was installed. A method for nitrate detection on new IC was developed.
- Further research was conducted on LSC data from November. The LSC counts as function of concentration measured on ICP were investigated. A pretty good correlation with aqueous samples was observed. A poor correlation with organic samples was also observed.

- The laser timing system was repaired and verified to be working correctly.
- Quenching of uranium fluorescence by nitrate was confirmed.


- Plans were developed to conduct experiments at ISU with the carbon-based neutron slowing down spectrometer to develop technology for assaying fuel rods and/or assemblies.
- Testing began on the Neutron Multiplicity Detector System (NMDS) for future use with the carbon slowing down spectrometer at ISU.

Synthesis and Properties of Metallic Tc and Tc-Zr Alloys as a Radioactive Storage Waste Form to Stabilize the Tc Waste Stream of the UREX+1 Process (Task 33) Highlights.

- Tc metal was prepared from NaTcO\(_7\) by steam reforming.
- Tc-Zr alloys were prepared with arc melting. 25 %, 50 %, and 75 % Tc alloy samples were prepared.
- Characterization of Tc-Zr alloys from arc melting.
- A manuscript on the formation of Tc-Zr alloys was prepared.
- Materials to reduce alloy oxidation during scintering were procured.

TRANSMUTATION SCIENCES

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

- Srinivas Chanda successfully defended his M.S. thesis on November 3, 2006.
- Experimental work and analyses of data related to this task are complete.

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

- The Scanning Electron Microscope was used to examine stainless steel samples that had been exposed to a gas-phase corrosion environment that models LBE corrosion.
- The XPS X-ray generation gun was received, mounted, and tested. XPS operation is expected to commence in January.
- Gas-phase experiments were conducted and results analyzed using the SEM.
- The spot size of the laser beam in the micro-Raman spectrometer was reduced to 3 microns. This is small enough to allow study of the chemical composition of some of the oxide layers, which range up to 20-30 microns in thickness.

• The determination of the work-hardening index using the conventional log true stress vs. log true strain plot revealed its gradual enhancement with increasing temperature up to 400ºC, indicating increased tendency to work-harden within the susceptible temperature regime, where the tendency for dynamic strain aging occurrence is sufficiently high. However, beyond 400ºC, the magnitude of the dislocation density was significantly reduced, suggesting a higher ductility in terms of failure strain.

• The characterization of microstructure by TEM revealed finer precipitates at 400ºC, compared to those at 550ºC, once again demonstrating enhanced dislocation movement at a temperature above 400ºC.

• The characterization of the metallurgical phases by X-ray diffraction verified the presence of chromium carbide of M23C6 type, irrespective of the Si content in the modified T91 grade steel.

• The results of SCC testing using the slow-strain-rate method indicate that increasing the Si content from 0.5 to 2 wt% increased the cracking susceptibility of modified T91 grade steel in an acidic environment at an elevated temperature (90ºC). However, no significant effect of Si content on the cracking tendency was noted at ambient temperature when tested in a similar environment.

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

• A cellular automata model of oxide layer growth with different scale removal rates under liquid metal environment was developed and studied.

• A parametric study by numerical modeling of oxide layer growth coupled with a scale removal effect using coordinate transform was performed.

• Study on corrosion behaviors induced by local flow is in progress.

• The numerical modeling of oxidation/corrosion behaviors under the microscopic scale with using molecular dynamics technique is in progress.

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

• A technique was developed to reliably deposit dense alumina on the central portion of the nanopillar areas to avoid bridging to the bulk alumina.

• A number of samples were fabricated using a technique for testing the integrity of the corrosion barrier coatings under thermal cycling.

• Chromium nanowires re-deposited showed improved uniformity; however, more investigation is needed to optimize for coating applications.

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

• UNLV researchers traveled to Idaho State University to conduct the final phase of ADS experiments. Results are being analyzed.

• Results from ISU experiments conducted in collaboration with CEA (France) during the RACE-ECATS phase of the project continue to be evaluated.
• Evaluation of experimental thermal and neutron generation continued for the UNLV High-power RACE target (experiments were conducted at ISU). Subsequently, the RACE Project at ISU concluded.

**Decoupling and Disturbance Rejection Control for Target Circulation (Task 31) Highlights.**

• The cooling control algorithm was improved.
• A new advanced algorithm was developed with disturbance rejection.

**Magnetohydrodynamic Simulation of Electromagnetic Pump in TC-1 (Task 32) Highlights.**

• An online database of articles and papers related to EM pumps was developed. It is located online and currently contains over 120 entries.

**Criticality Studies for UREX Processes (Task 35) Highlights.**

• Discussions continued to define the project scope and to determine the appropriate focus on cross-section sensitivity studies versus design of required criticality experiments. This included discussions with DOE-NE and others at the ANS Winter Meeting.

**Deep Burn Separations and Repository Behavior Highlights.**

• Studies were continued on the interaction of SiC with NH₄FHF to parameterize the influence of the fluorinating compound.
• Work was initiated on SiC interactions with U and cloud point extraction experiments for Eu-Cm separations.
• The phase of the SiC was studies and surface analysis performed.
• Initial studies on the separation of Eu from Cm by cloud point extraction were performed.
• Syntheses of a mono- and tri-functionalized DTPA per-6-ethyldiamino-β-cyclodextrin have been accomplished (m/z 1785.6 and 2142.2, respectively).
• The 1:1 complex of Tb³⁺ and per-6-thiopropionate-β-cyclodextrin complex has been detected by mass spectroscopy (m/z: 1957.4).
• Synthesis of a mono-6-tosyl-β-cyclodextrin (m/z of 1310.5 for the Na⁺ adduct) has been accomplished using literature methodology. Complete purification and optimization is underway.

**FUELS TECHNOLOGY**

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

The main focus in the past quarter was to identify and set up suitable procedures to prepare a clean single crystalline SiC surface. For this purpose an in-depth literature study was conducted. Based on this study, an HF-based approach was chosen. A suitable fume hood for etching was identified and cleaned, necessary chemicals and instrumentation were ordered and set up in the HF-etching fume hood.

A sample heating stage was developed and installed in the ultrahigh vacuum system. This heating stage enhances the previous heating capabilities to higher temperatures needed for the
second step in the sample preparation of the HF-etched SiC surfaces. The heating stage also enables heating to higher temperatures during metal deposition (up to approx. 1400°C) to simulate the conditions in a nuclear reactor.

SiC single crystals have been etched and heat treated according to the identified procedure to prepare a clean single crystalline surface. The samples have been characterized after each preparation step. Figure 1 shows the survey spectra of a SiC single crystal after several preparations steps. In addition to the Si and C lines, O and a small amount of N contaminations can be found on the as-introduced sample. O is reduced after the first HF-etching step but still visible after the subsequent heating step, which should not be the case. A second etching-heating cycle does not lead to an improvement of the situation. In fact, after the second etch the O intensity is increased due to adsorbed water which is removed after the next heating step.

The fact the oxidation cannot be removed by the applied cleaning procedure suggests that the most recent batch of crystals is strongly (completely) oxidized. This is confirmed by the fact that even a prolonged ion bombardment cannot remove the oxide layer. The vendor (MaTeck) was contacted about this issue and less oxidized replacement samples are expected.

![XPS survey spectra of a SiC single crystal after various surface treatment steps.](image)

**Figure 1.** XPS survey spectra of a SiC single crystal after various surface treatment steps.
Dissolution, Reactor, and Environmental Behavior of ZrO₂-MgO Inert Fuel Matrix (Task 19).

Ceramics were synthesized using MgO-ZrO₂ as the inert matrix and Er₂O₃ as a burnable poison as in previous studies; however, UO₂ is now being used as a more accurate PuO₂ analog than the previous CeO₂ containing ceramics. Table 1 summarizes the concentrations under investigation.

Table 1. Metal Concentrations for Uranium Containing Ceramics

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Zr %</th>
<th>Mg %</th>
<th>U %</th>
<th>Er %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>92.5</td>
<td>0</td>
<td>5</td>
<td>2.5</td>
</tr>
<tr>
<td>2</td>
<td>87.5</td>
<td>5</td>
<td>5</td>
<td>2.5</td>
</tr>
<tr>
<td>3</td>
<td>82.5</td>
<td>10</td>
<td>5</td>
<td>2.5</td>
</tr>
<tr>
<td>4</td>
<td>77.5</td>
<td>15</td>
<td>5</td>
<td>2.5</td>
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<td>5</td>
<td>72.5</td>
<td>20</td>
<td>5</td>
<td>2.5</td>
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<td>62.5</td>
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<td>5</td>
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<tr>
<td>7</td>
<td>47.5</td>
<td>45</td>
<td>5</td>
<td>2.5</td>
</tr>
<tr>
<td>8</td>
<td>32.5</td>
<td>60</td>
<td>5</td>
<td>2.5</td>
</tr>
<tr>
<td>9</td>
<td>17.5</td>
<td>75</td>
<td>5</td>
<td>2.5</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>92.5</td>
<td>5</td>
<td>2.5</td>
</tr>
</tbody>
</table>

A soxhlet experiment was initiated to determine the corrosion resistance of the ceramics. The setup was similar to the previous experiment except that smaller pellets (5mm diameter) were used. This enables the determination of the pellet surface area.

A TGA/DSC scan (Figure 2) was taken of the precipitated material to examine calcining and sintering behaviors. The material appears to change from the oxy-hydroxide precipitate to the oxide at the same temperature as the Ce containing ceramics (260ºC). The phase change also starts at the same temperature (510ºC), but it does not proceed as quickly and therefore shows a broader peak.

![Figure 1. TGA/DSC Scan of Zr0.775Mg0.15U0.05Er0.025O1.84](image)
XRD patterns were taken of all samples under investigation to qualitatively determine the phases present within the sintered sample. With no MgO present the UO₂ and Er₂O₃ only partially stabilizes the ZrO₂ resulting in a mixture of monoclinic and tetragonal zirconium oxide phases. With as little as 5% wt/wt MgO, the material fully stabilizes to form a pure cubic zirconium phase. Over 10% MgO results in an MgO phase, in addition to the cubic zirconia. This pure MgO phase increases with total MgO content. When there is no longer ZrO₂ in the sample an MgO phase dominates, while there is a minor cubic uranium erbium oxide phase. Quantitative analysis will be performed once TOPAZ software is obtained. Below is a typical XRD pattern.

![XRD Pattern](image)

**Figure 2. XRD Pattern of Zr₀.₈₂₅Mg₀.₁U₀.₀₅Er₀.₀₂₅O₁.₈₉**

SEM and optical microscopy were used to image the material and identify the nature of the phase mixing within the sample. The MgO phase appears darker than the ZrO₂ phase due to lower mass number. The color images show large areas of various colors, but higher magnification in grayscale shows a high degree of mixing the two phases.

Microprobe was also used to sweep large areas of the sample to determine where each element is concentrated. This shows that Zr, Er, and U are all within the same area (phase), while Mg is contained within its own phase. This compliments the XRD findings well. In the U and Er map, the brightness and contrast were enhanced because of the low concentrations of those elements.
Sample 6 (1x magnification) in color
Sample 6 (500x magnification) grey scale backscattering image

Figure 3. Optical Microscopy of Uranium Containing Ceramics
Figure 4. Elemental Scanning by Microprobe

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

**Geometric Measurements**

Figure 2 shows the camera spatial position relative to the target scene. A 3D point (X,Y,Z) is mapped to a 2D point (x,y) in the image plane. The coordinates of the point (x,y) in the camera image are

\[
\begin{align*}
k_x \ x_{\text{cam}} &= x - x_0 \\
k_y \ y_{\text{cam}} &= y - y_0
\end{align*}
\]
where the units of $k_x$, $k_y$ are [pixels/length].

$$\lambda \begin{pmatrix} x \\ y \\ f \end{pmatrix} = \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}$$

where $\lambda = Z/f$.

This can be written as a linear mapping between homogeneous coordinates (the equation is only up to a scale factor):

$$\begin{pmatrix} x \\ y \\ f \end{pmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix} \begin{pmatrix} X \\ Y \\ Z \\ 1 \end{pmatrix}$$

where a $3 \times 4$ projection matrix represents a map from 3D to 2D.

Figure 2. Perspective Projection

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

Using Matlab image processing routines a program was developed and tested that successively processes the CCD camera images, using algorithms for edge detection and for the recognition of geometrical patterns found inside the image. Progress to date is presented below.

Figure 3 shows the original scene, converted to a black and white bitmap image. A black cylindrical object is placed onto a white rectangular paper. In this example, the camera image plane is placed at a distance of 23” from the front edge of the sheet of paper, and at an elevation of 6” above the table plane. The origin of the image plane is referring to Figure 2, the camera’s X-and Z-axes are aligned parallel to the x-and z-axes of the rectangular sheet of paper. The camera’s vertical Y-axis is inclined relative to the vertical axis of the image plane by 5 degrees. A series of edge detection and filtering routines is applied to the image.

Figure 4 shows the detected edges after applying the edge detection algorithm.
Figure 3. Black and white bitmap image of the original scene

Test Photo

Figure 4. Detected Edges after Thinning
Figure 5 shows the part of the scene which is of actual interest, after removal of all irrelevant patterns. The image of Figure 5 contains 640 x 480 pixels. A point (x_{cam}, y_{cam}) in the image plane is related to coordinates (x, y) as seen in Figure 6.

\[
k_x x_{cam} = x - x_0 \\
k_y y_{cam} = y - y_0
\]

where the units of \(k_x, k_y\) are [pixels/length].

\[
x = \begin{pmatrix} x \\ y \\ 1 \end{pmatrix} = \frac{1}{f} \begin{bmatrix} \alpha_x & x_0 \\ \alpha_y & y_0 \\ 1 \end{bmatrix} \begin{pmatrix} x_{cam} \\ y_{cam} \\ f \end{pmatrix} = K \begin{pmatrix} x_{cam} \\ y_{cam} \\ f \end{pmatrix}
\]

where \(\alpha_x = f k_x, \ \alpha_y = f k_y\).

Figure 6. Image representation in the Camera

In general, a plane image point \((x \ y \ 1)^T\) is related to scene Point \((X \ Y \ Z \ 1)^T\) through a 3 x 4 transformation matrix defined by the spatial relationship between image and camera reference frames.

Project Abstract

Nitride fuels have appropriate properties for advanced fuels including high thermal conductivity, thermal stability, solid-state solubility of actinides, fissile metal density, and suitable neutronic properties. A drawback of nitride fuels involves their synthesis. A key parameter for preparing oxide fuels is the precipitation step in the sol-gel process. For nitride fuels, the current synthetic route is carbothermic reduction from the oxide to the nitride. If the nitride could be synthesized directly by a solution route then the impurities and other synthetic problems in the carbothermic reduction route could be eliminated or at least minimized. A solution route to nitride would also have the added benefit of providing several adjustable parameters that would allow control of the properties of the final solid product.

The objective of the proposed project is to develop solution phase synthetic routes for actinide nitrides for use in nuclear fuels. Recent work by the LANL collaborators investigated amido reactions in non-aqueous solvents where the reaction is:

\[ \text{AnI}_3(\text{solv})_4 + 3 \text{NaNR}_2 \rightarrow \text{An(NR}_2)_3 + 3 \text{NaI} + \text{solv} \]

From this result, a plausible route for the synthesis of nitride fuels is:

\[ \text{AnI}_3 \xrightarrow{\text{NH}_3(0)} \text{AnI}_3(\text{NH}_3)_4 \xrightarrow{3\text{NaNH}_2} \text{An(NH}_2)_3 \xrightarrow{\Delta, 2\text{NH}_3} \text{AnN} \]

where An is uranium, neptunium, plutonium or americium.

To achieve the solution synthesis of actinide nitrides the fundamental chemical coordination and speciation involved in the above reaction will be examined. The reaction will be performed with all the actinides listed. The non-aqueous synthetic route based on amido chemistry potentially provides property control over the nitride product similar to the sol-gel methods for actinide oxides. The resulting nitride product should be free of the impurities inherent in the carbothermic reduction technique. The experiments will be performed by a joint research team from UNLV and LANL, with actinide experiments performed at both laboratories and special emphasis on student participation in the project research. In addition to developing novel routes for the direct synthesis of nitride fuels, the project will also help train the next generation of radiochemists and actinide scientists with expertise in research areas crucial to the DOE and the country.

Work performed in previous quarter (July 2006 to September 2006)

This project was initiated in September 2006. The work performed in this month involved preparation of laboratory equipment and procedures for initial synthesis of uranium compounds. Discussions on research direction and efforts with the LANL collaborators were initiated.

Work performed in current quarter (October 2006 to December 2006)

The efforts in this quarter focused on developing and acquiring the laboratory equipment necessary for the synthesis. An inventory of existing synthesis equipment and supplies was conducted. Based on this evaluation new equipment and supplies were ordered. Researchers received specific training for this project which covered radiation safety and handling of liquid ammonia. The research team is composed of senior researchers, post-doctoral researchers, and undergraduates. An extensive literature review on amide synthesis and formation of UI$_3$ in liquid ammonia was performed. Based on other ongoing research, characterization methods for UN were initiated for final product evaluation.
SEPARATIONS TECHNOLOGY

Immobilization of Fission Iodine (Task 15).

Manganese (IV) oxide can be produced by a several different synthetic routes indicated below. The conditions used to produce the solid influence particle size, surface area and crystal structure. Examination of the reactivity of several different preparations began this quarter.

δ - Black Birnessite (10.6 m²/g) produced by oxidation of HCl by KMnO₄.
α - Cryptomelane (150 m²/g) produced by oxidation of MnSO₄ by KMnO₄.
δ - Acid Birnessite (58.4 m²/g) produced by stirring KMnO₄ in a sulfuric acid solution.
δ - Acid Birnessite (27.7 m²/g) produced by static (no stirring) incubation of KMnO₄ in a sulfuric acid solution.

The acid birnessites are evidently produced by oxidation of water to oxygen. The balanced reaction for this process is:

\[ 2\text{H}_2\text{SO}_4 + 4\text{KMnO}_4 \rightarrow 3\text{O}_2 + 4\text{MnO}_2(s) + \text{K}_2\text{SO}_4 \]

Another synthetic route was recently explored that involves the reaction of KMnO₄ with NaCl and dilute acid. The balanced reaction is:

\[ 8\text{H}^+ + 6\text{Cl}^- + 2\text{MnO}_4^- \rightarrow 2\text{MnO}_2(s) + 3\text{Cl}_2 \]

The same reaction was operative with the synthesis of black birnessite. The difference between previous synthesis and the new approach is that with the presence of brine (3M NaCl) the reaction proceeds quickly (a few hours) at room temperature. This reaction was run under proton limiting conditions, and the products from the reaction are presently being characterized.

Suspensions of MnO₂ were prepared by suspending 20 mg of the oxide in 50 mL of buffer solution. The suspension was generally sonnicated for 30 minutes in a bath style ultrasonic cleaner. The suspensions are stored a room temperature while constantly rotating the mixture end over end.

The reaction of iodide with the MnO₂ was followed by spectroscopically monitoring the formation of I₃⁻ (350 nm). Reactions were conducted in a quartz cuvette using a fiber optic spectrophotometer described in previous reports. The cuvette holder was maintained at a controlled temperature using a recirculating water bath. The generally 10 to 100 μL of the MnO₂ suspension was mixed with 2.5 mL of pH buffer. The reaction was started by adding 10 to 150 μL of 1.0 KI solution to the buffer. The contents of the cuvette were continuously stirred while the concentration of I₃⁻ was recorded. The concentration of I₃⁻ was calculated from absorbance at 350 nm using a response factor that was determined by an external calibration.

The formation of triiodide presumable involves the adsorption of iodide onto the MnO₂ surface (perhaps displacing a surface hydroxyl group). The iodide should be subsequently oxidized and release back into solution as IOH or I₂, which rapidly forms I₃⁻. To model the kinetic data, it was presumed that this process is first order in both MnO₂ and iodide and be represented by equation (1). Because this reaction involves multiple phases this conceptualization is likely inadequate.

\[ \frac{d[\text{MnO}_2]}{dt} = -k[\text{MnO}_2][I^-] \]  (1)
In the presence of excess iodide the reaction becomes pseudo first order in MnO$_2$ and the loss of MnO$_2$ would be represented by a simple exponential decay (2).

$$[\text{MnO}_2] = [\text{MnO}_2]_0 \times \exp(-k't) \quad (2)$$

In equation (2) $k'$ is $k*\left[\Gamma\right]$. Thus the appearance of I$_3^-$ in solution is approximated by equation (3)

$$\frac{dI_3^-}{dt} = k'[\text{MnO}_2] \quad (3)$$

Utilizing equation (2), the closed form solution to equation (3) is equation (4):

$$[I_3^-] = [\text{MnO}_2]_0 (1 - \exp(-k' t)) \quad (4)$$

Despite an undoubted oversimplification, the formation of I$_3^-$ can be fit to this simple equation and the value of the rate constant $k'$ can be estimated by least squares. For this fitting process the value of MnO$_2$ was also used as a fitting parameter. The values thus determined are comparable (but generally less than) the actual concentrations of the suspended MnO$_2$.

An example of the kinetic data obtained is illustrated in Figure 7. This data was from the oxidation of iodide by black birnessite ($\delta$-MnO$_2$) at 21°C. The increase in iodide oxidation rates with MnO$_2$ concentration is evident in the data.

Figure 7. Formation of I$_3^-$ in the presence of black birnessite at pH 4 and 21°C. This set of experiments was performed with birnessite that was not sonicated.

The best fit values for [MnO$_2$]$_0$ and $k'$ are illustrated in Figure 8. The best fit “concentrations” of MnO$_2$ are well correlated to the actual concentrations, although the correlation is not 1:1. The
rate constant should theoretically remain constant for this system, however, the best fit values for k’ increased with MnO₂ concentration.

Figure 8. Best fit MnO₂ concentration and rate constant as a function of the actual MnO₂ concentration.

Also, the influence of iodide concentration on the rate of I₃⁻ formation was examined. Figure 9 shows the best fit data for the “stirred” acid birnessite at pH 5 and 40°C. The experiments were conducted under constant MnO₂ concentrations. As noted above, the best fit MnO₂ concentration is lower than the actual and appears to increase slightly with increasing iodide concentration. As expected the pseudo first order rate constant increases with iodide concentrations, however, the data indicate that the order with respect to iodide is ~1.4 rather than 1. Deviation from the simple kinetic relationship suggested above is not surprising given that the reaction is heterogeneous in nature and equation (1) is, at best, a rough representation of the oxidation process.
The effect of temperature on the reactions was studied over the range of 12 – 52°C. The results indicate that the oxidation of iodide increases with temperature and the apparent activation energy for the process is 16.2 kJ/mol.
Figure 10. Temperature dependence for the pseudo first order rate constant k’ for oxidation of iodide by acid birnessite at pH 5. The iodide concentration was 0.01M and the MnO2 concentration was 88μM.

**Development of Integrated Process Simulation System Model for Spent Fuel Treatment Facility Design (Task 24).**

*Interface to Interact with ASPEN Plus through the ISOPRO Package*

A project review meeting was held on October 19-20, 2006. It was decided to rename the program to “Integrated System for Optimization PROgram (ISOPRO).” A further revised framework design, shown in Figure 11, defines the data flow from ASPEN-plus to AMUSE with the data set “parser module” in the middle.

An updated UREX+1, a process simulation flow chart was created, shown in Figure 12, which outlines the detailed input and output parameters discussed during the ANL visit on November 9, 2006. Detailed components and attributes for both “Input Table DB (database)” and “Output Table DB” are tabulated in Table 1.

A report file, as shown in Figure 12, is defined as the output file from “Solvent Extraction.” The same set of information also stores within the previously defined ACCESS database.
Table 1. Input and output component list.

<table>
<thead>
<tr>
<th>Category</th>
<th>Component</th>
<th>Attribute</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input Table DB</td>
<td>ID</td>
<td>Auto incremental; Unique for each process; Cannot be changed</td>
</tr>
<tr>
<td>Stream Name</td>
<td>TSADJ, SULF, UREX-IN, USOLV-IN etc.</td>
<td></td>
</tr>
<tr>
<td>Element #</td>
<td>Value of each element</td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>-----------------------</td>
<td></td>
</tr>
<tr>
<td>ID</td>
<td>Auto incremental; Unique for each process; cannot be changed</td>
<td></td>
</tr>
<tr>
<td>Stream Name</td>
<td>TSADJ, SULF, UREX-IN, USOLV-IN etc.</td>
<td></td>
</tr>
<tr>
<td>Element #</td>
<td>Value of each element</td>
<td></td>
</tr>
<tr>
<td>Success</td>
<td>Boolean Value - TRUE correct run and FALSE faulty run</td>
<td></td>
</tr>
<tr>
<td>Error Message</td>
<td>Message generated from faulty runs</td>
<td></td>
</tr>
</tbody>
</table>

### ISOPRO Modification

An ASPEN-Plus demonstration and discussion meeting was held on November 9, 2006 at ANL. ANL provided a stripped-down version of the ASPEN-plus *.bkp file that contains all input and output parameters needed for Solvent Extraction (a newer version of AMUSE). During the discussion, ANL determined the optimization processes will be carried out while performing the CCD-PEG and TRUEX simulations within the “Solvent Extraction” package.

As indicated in Figure 11, the process will be initialized from ASPEN-Plus and passed through the “Parser Module” in the middle and them to the AMUSE simulator. The completion of the entire simulation is controlled by the convergence of the ASPEN-Plus simulation.

The UNLV team will continue improving the ISOPRO program while waiting for the new version of the AMUSE-lite code and optimization module from ANL for code validation and verification.

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

During the last quarter, this task expanded its studies to include room temperature ionic liquid systems. Exploiting electrochemical difference in the actinide elements is a promising route to achieving selective, reversible, and tunable separations. However, the capacity to exploit, let alone systematically quantify and characterize redox properties of actinides is limited. A significant hindrance to the electrochemical analysis of lanthanide and actinide species in aqueous environments remains the potential window afforded in aqueous environments at Pt, Au, and glassy carbon (GC) electrodes. The potential window ranges from as little as 1.3 V to 2.5 V depending on the electrode used and the boundary provided by side reactions at positive (oxygen reduction) and negative potentials (hydrogen evolution). Under non-standard state conditions the potential window can be larger based on changes in kinetics associated with the electrode material and solution conditions.

Room temperature ionic liquids (RTILs) show significant promise due to the elimination of aqueous side-reactions and a corresponding expansion of the electrochemical window. These systems consists of organic cations such as imidazoles, pyridinium, ammonium, phosphonium, and sulfonium ions paired with a variety of anions including BF4-, C(Tf)3-, CF3CF2CF2CO2-, N(CN)2-, to name a few. The electrochemical windows for a variety of RTILs range from 4.5 to 6 V. A significant advantage to eliminating aqueous side reactions is that the potential is sufficiently large that previously inaccessibile electrochemical redox reactions can be resolved. For example the potential controlled deposition of Ti was achieved in RTIL. Electrodeposition of Ti from aqueous environments was achieved through intermediate Titanate/Benzoquinone hybrid films that can then be heated to 450°C to form TiO2 thin films. However, direct
deposition has not been achieved due to the low stability of Ti$^{2+}$ and Ti$^{4+}$ species in aqueous environments. In contrast, the direct deposition of TiCl$_2$ and TiCl$_4$ was achieved at Au and graphite electrodes in RTIL. The stability of Ti$^{2+}$ and Ti$^{4+}$ in the RTIL is enhanced relative to the ion in aqueous environments. The capability to directly reduce Ti in RTILs offers a similar route for performing the same reduction with actinide elements. The focus for the next quarter will be to utilize the RTIL system to expand the potential capabilities of separating Americium and curium.

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

*Project Abstract*

The speciation of hexavalent U and tetravalent Pu will be examined in the 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 (July 2006 to September 2006)*

During the previous quarter work focused mainly on IR spectroscopy. The new Varian 3100 FT-IR was installed as well as a diamond ATR attachment. Training on the instrument was completed including use of the ATR as well as AmTir plated liquid cells. IR spectra were obtained for TBP, dodecane and lithium nitrate. The Varian NMR was repaired and training on this instrument was obtained. A poster of this project was displayed at the AFCI technical review meeting in Santa Fe, New Mexico during the first week of September. On September 14th, a presentation on this research project was given at the 232nd ACS (American Chemical Society) National Meeting in San Francisco.

*Work performed in current quarter (October 2006 to December 2006)*

Work during this quarter focused on extraction of uranium in a system where acid concentration is constant and only total nitrate is changing. The amount of acid, nitrate, and uranium were measured in each phase. The evaluation of uranium concentration by scintillation counting was investigated in detail to assess any role played by uranium daughters. Studies examined the interaction of uranium with acetohydroxamic acid and the resulting complexes. Also training and method development for new instrumentation were performed.

*Sample Generation*

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 concentration of nitric acid was 1 M, and the total nitrate concentration varied by addition of LiNO$_3$. The amount of LiNO$_3$ ranged from 0 to 10 M. The uranium concentration investigated was 0.01 M UO$_2$(NO$_3$)$_2$. The organic phase of each sample consisted of a pre-equilibrated solution of 30% TBP (tributylphosphate) in dodecane. Volumes of 0.75mL of each phase were contacted by mixing for 2 minutes with a vortexor. 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 performed on both the organic and aqueous phases.

Concentration Determination by Scintillation Counting

The amount of nitric acid in each phase was measured by titration on a Metrohm Titrino instrument. Figure 1 demonstrates the relationship between the acid concentration in the organic phase increases and total nitrate concentration. These titrations were performed in air, but a new method was developed for titration under inert atmosphere and will be used in future experiments. A new Dionex ion chromatograph was installed and will be used to evaluate nitrate concentration.

![Figure 5. Organic acid concentration as a function of total nitrate](image)

In order to determine uranium concentration both liquid scintillation counting (LSC) and ICP-AES were compared. The LSC was used to measure the aqueous and organic phases; the ICP-AES was used only on the aqueous samples. These two methods gave differences in the measured uranium concentration. When LSC counts were examined as a function of concentration measured on ICP, there seemed to be a linear relationship for the aqueous samples, but not the organic (Figures 2 and 3).
The spectra of samples containing 0.01 M UO$_2$(NO$_3$)$_2$ in both aqueous and organic phases were compared (Figure 8). The spectra clearly show a peak shift that is sample dependent. This may be due to the fact that the organic UO$_2$(NO$_3$)$_2$ has been extracted and so there should not be any uranium daughter products. Further studies are necessary to verify the utility of scintillation counting for determining uranium concentration.
Uranium Acetohydroxamic acid (AHA) synthesis method

It was determined previously that manual grinding of Uranyl acetate with Acetohydroxamic acid solid in a molar ratio of 1:2 was the best method of synthesis. To further validate this method, it was employed to synthesize FeAHA. FeCl₃ was ground with 3 molar equivalents of AHA. A dark purple liquid formed very easily. This was removed to a glass vial with a plastic transfer pipet and heated at 105 °C for three days to remove the water and HCl byproduct. Part of the dark brown product was redissolved in acetone and filtered. This was not easy, as the acetone evaporated very easily. Methanol was used for the remaining product for greater success. These solutions were dried at 60 °C to yield a brick-red powder in about 90% yield. Most of the loss was probably due to the difficulty of controlling the acetone solution, and some acid hydrolysis during the drying.

To eliminate this problem, the FeCl₃ and AHA solids were finely ground and mixed by vortexing in a plastic centrifuge vial. About 500 μL of acetone was added to aid mixing, and a dark purple solution was formed. Three equivalents of sodium bicarbonate were added and the mixture was vortexed well for over ten minutes, vented frequently to remove the carbon dioxide. The solution was removed to a glass vial and dried at 105 °C for a day. The dark red solid was dissolved in methanol and filtered as above for a yield of 95%. The IR signature matched literature (Figure 9) [1] and did not seem to indicate ferric carbonate formation, but to rule it out, FeAHA was synthesized according to literature [2], using methanol instead of ethanol. The IR signatures of
the three purified products were almost identical; the differences seem to be due to increased water content of the solid-synthesis.

Figure 9. IR Spectra of Fe and U AHA

Complex Stoichiometry

UAHA solid was dissolved in three different solutions (Solutions 1-3 in Table 1), which were each diluted 1/10, 1/20, 1/50, and 1/100 in volumetric flasks using 0.1 N HNO₃ in millipore water. Each of these solutions was measured in duplicate samples with the Arsenazo master mix, which was calibrated from 0 to 500 μM uranyl from ICP standards, also diluted in 0.1 N HNO₃. The samples were in Corningware UV-vis microplates and the peak at 650 nm was monitored using the Cary50 microplate reader software, 5 reads averaged per measurement, two measurements, for an equivalent of 20 measurements per dilution. Dilutions with concentration values outside of the calibration curve were not used, and the concentration of uranyl was calculated from these dilutions.

Table 1. Composition of U AHA solutions

<table>
<thead>
<tr>
<th>Soln.</th>
<th>Mass (mg)</th>
<th>Vol. (mL)</th>
<th>[U] (mM)</th>
<th>[AHA] (mM)</th>
<th>[AHA]/[U]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.4</td>
<td>10</td>
<td>1.43</td>
<td>2.66</td>
<td>1.86</td>
</tr>
<tr>
<td>2</td>
<td>21.0</td>
<td>100</td>
<td>0.47</td>
<td>0.84</td>
<td>2.00</td>
</tr>
<tr>
<td>3</td>
<td>29.1</td>
<td>10</td>
<td>5.31</td>
<td>9.67</td>
<td>1.81</td>
</tr>
<tr>
<td>4</td>
<td>Sat.³</td>
<td>2</td>
<td>14.41</td>
<td>27.92</td>
<td>1.94</td>
</tr>
<tr>
<td>5⁴</td>
<td>5.5</td>
<td>10</td>
<td>1.24</td>
<td>2.10</td>
<td>1.72</td>
</tr>
<tr>
<td>6⁴</td>
<td>5.9</td>
<td>25</td>
<td>0.38</td>
<td>0.73</td>
<td>1.91</td>
</tr>
</tbody>
</table>

The FeAHA complex is much stronger than the UAHA complex, and so a 1 mM solution of FeCl₃ could be used to determine the concentration of AHA. The FeAHA peak at 500 nm was
monitored and calibration standards from 1 – 25 mM from an aqueous AHA solution were used. The concentration in the master solution was verified using potentiometric endpoint titration.

To test that these methods work in the presence of competing complexors (AHA for U in the Arsenazo assay; U for AHA in the FeAHA assay), standard solutions were also measured in a 2:1 AHA:U combination. The calibration curves were also linear and did not deviate significantly from the previous calibration curves. Solutions of 10 mM uranyl perchlorate, uranyl nitrate, and uranyl acetate were combined with the FeCl₃ and no change in the 500 nm absorbance was noted. AHA solutions up to 100 mM were added to the arsenazo assay and no affect was noted on the 650 nm absorbance.

![Arsenazo calibrations](image)

Figure 10. Arsenazo Calibration curve

Another solid sample was thoroughly dried at 105 °C for 5 days to remove residual water and acetone. This solution was evaluated as above, and by mass balance the stoichiometric amount of water was determined to be 4.5 +/- 0.5 waters. The stoichiometry was confirmed as the dihydroxamato complex.
**IR Spectroscopy**

The fingerprint IR is similar to the FeAHA complex, which has been shown to be bidentate [3], as shown below.

This indicates that the UAHA solid complex is also bidentate, with a ring IR structure. In addition, the 2:1 stoichiometry would indicate a bidentate binding to fill the uranyl coordination shell. It is unlikely that the UAHA complex includes a hydroxide, because the AHA, if bidentate, has an N-H stretch; if monodentate, also an N-H; if the AHA were bidentate via the hydroxamic O- and N-moieties, then any O-H stretch H should resemble that of uranyl hydroxide. The AcO-H peak is listed as 1392 cm$^{-1}$ [4], which is not seen in the UAHA. D$_2$O exchange shifts the stretches according to Hooke’s law, and a difference between N-H and O-H should be apparent. Finally, the UV-vis of the solid complex should show uranyl hydroxide, which has a very large molar absorptivity, and NMR of the compound in an aprotic solvent should show any uranyl hydroxide.

D$_2$O exchange of the UAHA complex was incomplete even after three dissolutions/evaporations. However, it was clear that there is only one hydrogen stretch, which is shifted from 3209 to 2411
cm^{-1} \). Hooke’s law calculations show that for N-H, the peak should shift to 1833 cm^{-1}, and for O-H, the peak should shift to 1805 cm^{-1}. The reduced masses of the two systems are altered by resonance and the uranyl binding, and so the peak should be confirmed using independent methods.

Figure 12. IR of UAHA complex

The advantage of the UAHA solid is that it can be studied using techniques that are difficult in the solution phase. In addition, it can be redissolved and studied in the absence of counterions,
except for those from water. Thus the UV-vis of the solid complex in an aprotic solvent, such as DMSO, and of the solid, can be compared to the aqueous spectra to confirm the absence of uranyl hydroxide.

Figure 13. UV-Visible spectra of U AHA in aqueous phases and DMSO

The UV-vis spectrum in the polar aprotic solvent DMSO is very similar to the UAHA complex under acidic conditions, which indicates that there is no hydroxide in the solid; it may form in aqueous solution under basic conditions, however.

U AHA NMR

The pH-dependent shift in the UV-vis of the UAHA system, reported in the previous quarterly report, indicates a change in speciation. The data below show the correlation of the change in UV-vis to a change in speciation, as tracked by the AHA methyl peak in D2O. The dissociation of UAHA is also seen in the free AHA peaks. At low pH, there is one type of UAHA methyl peak; at neutral pH, there are two types of UAHA methyl groups, as well as free AHA and broad peaks at 2.8 and 3.4, which may indicate uranyl hydroxide formation. The UV-vis spectrum looks like that of uranyl hydroxide. At high pD, the NMR shows free AHA, a new peak at 2.7, and some broadened peaks between 2.1 and 2.6, which are likely hydroxides. The 2.7 peak may indicate a different binding, indicated by the UV-vis spectrum, which has not been seen before in uranyl-AHA pH titrations. The high pD may indicate deprotonation of both the N and O of the hydroxamate, leading to an N,O bidentate binding. The chemical shift is downfield of even the E isomer of the free AHA, indicating deshielding consistent with a free carbonyl.

The NMR spectra of AHA at high pH demonstrate only the two methyl singlets at 2.0 and 1.8 ppm, indicating that the peaks between 2 and 2.6 are not due to any free AHA base-catalyzed decomposition or hemiacetal formation. Addition of AHA to this mixture gives an NMR spectrum with free AHA and the two UAHA peaks, with the distribution between the two shifted further towards the upfield Z-isomer. The small peak at 2.72 ppm remains, which indicates that it might be N,O-bidentate binding to the uranyl, or that it might be a residual breakdown product that remains in the solution.
Figure 14. NMR spectrum: from top to bottom: added DNO$_3$, neutral, added NaOD. Added AHA to NaOD solution.
Based on the chemical shift, and the difference in UV-vis absorption between the solid, which is a ring binding, and the low pH spectrum, we propose at least two aqueous binding moieties.

At the low pH, monodentate binding:

\[
\begin{array}{cc}
\text{HN} & \text{O} \\
\text{H}_2\text{O} & \text{O} \\
\text{U} & \text{O} \\
\text{NH} & \text{OH}_2
\end{array}
\]

Which can be stabilized by the presence of protons and intramolecular H-bond formation:
At circumneutral pH and higher, especially in the presence of excess AHA, the bidentate binding:

At very high pH, in the absence of excess AHA, possible formation of the N,N-bidentate product:

**Solubility**

The UAHA compound was dissolved to saturation in a variety of solvents. The suspensions were centrifuged and the supernatants filtered, where possible, before the concentration of U(VI) was measured using Arsenazo III. The solubility in water is likely limited by UAHA dissociation and the formation of insoluble uranyl hydroxide, as seen in the UV-vis spectrum.

**Thermal decomposition**

The product was placed in a 0.5mm ID borosilicate glass melting point tube and the decomposition was monitored visually (Figure 16). For comparison, the UAc and AHA starting materials were also studied, and to calibrate the thermometer, standards were used:

- Benzophenone, 46-47 °C (lit 47-49)
- Anthroquinone, 281-282 °C (lit 283-285)
- Acetohydroxamic acid, 56-58 °C (89-91). The sample became a clear liquid with solid at the bottom; likely wet, and dissolved at 56 °C
- Uranyl acetate, decomposed 280-300 °C (lit 300-400)
- UAHA, decomposed 260-270 °C

**Solid phase formation**
Crystallization microplates were obtained from Axygen. The solution to be crystallized is placed in a 4 uL drop hollow, and a crystallization buffer is placed in the adjacent 250 uL well. The cell is sealed and the two solutions equilibrate via water vapor. The well contains the more concentrated, hygroscopic solution with a greater volume and surface area.

Various methods were tried, including combining AHA and uranyl salt solutions in the well, and UAHA aqueous solutions of various concentrations, including uranyl salts alone, AHA alone, and sodium salts with AHA as controls. The drop size was varied from 1 to 3 uL. The volume of the salt and buffer solutions in the well was varied from 100-200 uL. Solutions of 1.1 M sodium acetate (NaOAc), pH 4.0; 3.0 M NaCl; 5 M NaClO4; 2 M NaClO4; and 2 M NaNO3 were used. An amorphous UAHA compound was the most common result.
Combinations of uranyl nitrate and uranyl perchlorate with AHA yielded crystals which corresponded to those in the uranyl salt controls. AHA polymerizes from solution in the controls and in combination with the uranyl salts, but it forms crystals in the presence of sodium perchlorate and sodium nitrate. The best results were obtained with UAHA solutions made from the solvent, and crystals were consistently obtained when the well was filled with 1.1 M NaOAc, pH 4.0, with volumes of 150-200 µL, allowed to crystallize for at least two days. A typical crystal system with 2 µL drop size and NaOAc well fill is shown below. This was allowed to crystallize for four days. These crystals were deemed too small to send for XRD analysis.
When the concentration of UAHA was increased threefold, crystallization was more immediate, but the crystals were not single and so were not sent for XRD analysis.

**Crystals from a solution with excess AHA.**

A solution of uranyl with 40x excess AHA was allowed to evaporate slowly in a flat-bottomed glass vial over three weeks. Large aggregates of UAHA crystals were obtained; some formed a chain. These crystals were deemed unfit for XRD because of their twinned nature.

**Crystallization from a saturated solution.**

Crystals were found in a solution that had been prepared four weeks previously. It was made to test the saturation concentration of UAHA in water. UAHA was dissolved in water with excess UAHA suspended in the solution. The sample was centrifuged and the supernatant was filtered through a 0.2 μm filter into a plastic 2 mL screw-cap vial. The solution was used for several experiments and untouched for 3 weeks. Later a red precipitate was seen at the bottom and pictures were taken with the confocal microscope. The crystals were determined to be suitable for XRD analysis and the structure was solved by collaborator Thomas Albrecht-Schmit at Auburn University.
The structure is shown below and has a large amount of DMSO.

The formula is \((\text{UO}_2)_4(\text{AHA})_2(\text{CO}_3)_2(\text{DMSO})_9\). Since DMSO was not introduced into the laboratory until after this solution was initially prepared, it must have contaminated it later. The crystallization conditions need to be reverse engineered.

The structure has a number of striking properties and its conditions are worth pursuing. It is a uranyl tetramer, which is unusual; the symmetry more precisely shows two types of uranium
atoms, so it is a dimer of dimmers. Each carbonate molecule bridges three uranium atoms together. Two types of binding are shown for AHA: the O,O bidentate ring structure, and the O,N-bidentate structure, and the AHA bridges the two uranium atoms in each dimer. The presence of DMSO cannot be explained. Acetone was used, but XRD can clearly discriminate between S and C. The carbonate is likely from the laboratory water equilibration with the atmosphere carbon dioxide.

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

Experiments were performed to determine the effect increasing nitrate concentration on the fluorescence spectrum of the uranium ion. In the course of this study, it became apparent that the system was undergoing static quenching due to the presence of the nitrate. This fact both helps and hinders the project as quenching rapidly decreases the quantum yield of the system while at the same time allowing the observation of a second order effect.

At this time, experimental methods to deal with the quenched system are being researched in order to appropriately deal with this situation. Since the quenching is dependant on the amount of quencher added, it may be possible to interrogate the system based upon the observed lifetime of the uranium.

The system was returned to the vendor during the last quarter for evaluation and repair. The problem with the timing generator was determined to be a physical problem within the hardware of the system. The system has been performing normally since it was returned. Time resolved functionality was restored and can be considered reliable.

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

Students continued to develop concepts and models for use of the $^3$He Neutron Multiplicity Detector System (NMDS, which was developed as part of Task 6) for Materials Protection, Accounting, and Control (MPAC). Plans are being developed to conduct experiments at ISU with the carbon-based neutron slowing down spectrometer. This work will be used to investigate technology for assaying fuel rods and/or complete assemblies.

Testing on the NMDS began for future use with the carbon slowing down spectrometer at ISU. In addition, the use of a multi-detector system is being investigated consisting of five large sodium-iodide crystals in conjunction with neutron multiplicity analysis. The system was manufactured by Exploranium for a homeland security project. Literature searches and computer code evaluation continued during this quarter.

**Synthesis and Properties of Metallic Tc and Tc-Zr Alloys as a Radioactive Storage Waste Form to Stabilize the Tc Waste Stream of the UREX+1 Process (Task 33).**

**TRANSMUTATION SCIENCES**

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

In addition to ongoing collaborative work with scientists at LANL and other locations, gas phase oxidation experiments began on the steels to determine details of the chemistry and mass transport issues surrounding the formation of protective and non-protective oxides in LBE.
Initial work showed that gas phase experiments are much more sensitive to minor contamination, due to the lack of a removal mechanism for surface species such as exists in LBE (dissolution, etc). Some interesting features were observed in the oxide layers produced by the gas phase experiments, discussed below.

In experiments the steel is exposed to an oxidizing environment controlled by a Cu/CuO mixed pellet (Figure 13). The oxygen concentration is controlled by the dissociation of the CuO at a temperature set independently from the oxidizing environment of the steels (Figure 14). Oxide layers formed after 100 hours at 550°C which were analogous to the oxide layers found on steel exposed to LBE (Figure 15).

In initial work (Gas Phase I) efforts were not focused to minimize water adsorbed to the evacuated quartz tube in which the experiment was performed. Water was evident in the oxide layers (Figure 16), and metals were found on the quartz envelope around the steels.

This result is supported by reports in the literature of water both being active in the formation of (as it turns out, non-protective) oxides in steel and that water can facilitate the migration of metals out of steels (i.e. loss of chromium as volatile oxides/acids).

In subsequent work (Gas Phase II, etc.) efforts were made to minimize water in the vacuum, which reduced the evidence of water in the oxide layers (Figure 17).

A Raman spectromicroscope was obtained from surplus and upgraded to operational condition. Raman spectroscopy examines energy losses in light scattering due to the excitation of molecular vibrations in the scatterer. Raman spectroscopy has several advantages over standard infrared spectroscopy. First, Raman spectroscopy can detect small shifts in frequency corresponding to low energy vibrational excitations, which are common in compounds of heavy atoms common in steel formulations. Second, the small wavelength of the light being shifted means that the possible probe beam size can be quite small: in this case the measured beam widths were below 3 microns. Third, the vibrational frequencies of a material are more chemically specific. While SEM can determine location of elements to micron scales, SEM can not distinguish a mixture of iron and oxygen from an iron oxide. XPS can determine species on the basis of oxidation state, but can not distinguish a mixed valence oxide like Fe$_3$O$_4$ from a mixture of FeO and Fe$_2$O$_3$.

Raman spectroscopy was used to determine in situ and unambiguously the presence of Fe$_3$O$_4$ as the surface species on some of the steel specimens.

Efforts are moving forward to utilize the high resolution of the Raman spectromicroscope to look at the multilayer oxides observed, and to characterize each layer (e.g. mixed Fe and Cr oxide or spinel) in situ in cross section.
Figure 13. Evacuated quartz tube with sample string and Cu/CuO oxygen source

Figure 14. Tube furnace arrangement to allow independent control of oxidation temperature and oxygen concentration.
Figure 15. SEM image of the oxide layer on D9 after 100 hr at 550 C. Note duplex oxide formation (metal at top, mounting epoxy at bottom, oxide just above scale marker).

Figure 16. XPS of the oxygen found in the oxide layer(s) in the wet, gas phase 1, experiments. Note the peaks at ~530eV (characteristic of metal oxides) and 538eV (characteristic of water).
Figure 17. Oxygen XPS spectra in the Gas Phase II experiment. Note single peak due to metal oxides and lack of water.

**Impact of Silicon on Corrosion Resistance of Stainless Steels in LBE Systems (Task 20).**

The previous quarterly report presented the results of tensile testing at temperatures ranging from ambient to 550°C. The superimposition of the engineering stress vs. engineering strain (s-e) diagrams at different temperatures exhibited reduced failure strain at temperatures up to 400°C, which was attributed to the occurrence of dynamic strain ageing (DSA) of T91 grade steel within a temperature regime of ambient to 400°C. Subsequently, significant efforts have been made to develop a basic understanding of DSA as a function of temperature. Since the occurrence of DSA is significantly influenced by the diffusion of solute elements into the metal matrix, the characterization of dislocation was necessary. Therefore, the dislocation density ($\rho$) within the susceptible temperature regime was determined using transmission electron microscopy (TEM). Simultaneously, the susceptibility of T91 grade steels to stress corrosion cracking (SCC) was evaluated as a function of temperature and silicon (Si) content, with and without the presence of an aqueous environment. In parallel, the evaluation of the localized corrosion behavior of these alloys is in progress. The key results generated in this quarter are summarized below.

The determination of the work-hardening index ($n$) using the conventional log true stress ($\sigma$) vs. log true strain ($\varepsilon$) plot revealed its gradual enhancement with increasing temperature up to 400°C, indicating increased tendency to work-harden within the susceptible temperature regime, where the tendency for DSA occurrence is sufficiently high. However, beyond 400°C, the magnitude of $\rho$ was significantly reduced, suggesting a higher ductility in terms of failure strain. The variation of $n$ with temperature is shown in Table 2.

It is well known that the reduced failure strain within the susceptible temperature regime is related to the locking of dislocations by the precipitation of solute particles, thereby impeding their movement from one grain to another. At relatively higher temperatures, the dislocation mobility is enhanced, thus resulting in greater failure strain. Such a phenomenon was observed
(Figure 18) by virtue of the calculated $\rho$ values at different temperatures, exhibiting the highest value of $\rho$ at 400ºC, where the failure strain was minimum.

The characterization of microstructure by TEM revealed finer precipitates at 400ºC, compared to those at 550ºC, once again demonstrating enhanced dislocation movement at a temperature above 400ºC. The TEM micrographs involving specimens tested at 400 and 550ºC are illustrated in Figure 19.

The characterization of the metallurgical phases by X-ray diffraction (XRD) verified the presence of chromium carbide of $M_{23}C_6$ type, irrespective of the Si content in the modified T91 grade steel.

The results of SCC testing using the slow-strain-rate (SSR) method indicate that increasing the Si content from 0.5 to 2 wt% increased the cracking susceptibility of modified T91 grade steel in an acidic environment at an elevated temperature (90ºC). However, no significant effect of Si content on the cracking tendency was noted at ambient temperature when tested in a similar environment. The effects of temperature and Si content on the true failure stress, time to failure and percent elongation obtained in SSR testing are illustrated in Figures 20, 21 and 22.

<table>
<thead>
<tr>
<th>Table 2. Variation of n with Temperature</th>
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<tbody>
<tr>
<td>Heat no. / Temp. (ºC)</td>
</tr>
<tr>
<td>-----------------------</td>
</tr>
<tr>
<td>2403 (0.5%Si)</td>
</tr>
<tr>
<td>2404 (1.0%Si)</td>
</tr>
<tr>
<td>2405 (1.5%Si)</td>
</tr>
<tr>
<td>2406 (2.0%Si)</td>
</tr>
</tbody>
</table>

![Figure 18. Dislocation Density vs. Temperature (ºC)](image-url)
Figure 19(a): TEM Micrograph showing Fine Precipitates within the Martensitic Laths (400°C, 2% Si steel)

Figure 19(b): TEM Micrograph showing Coarse Precipitates (550°C, 2% Si Steel)

Figure 20: True Failure Stress vs. Temperature

Figure 21: Time to Failure vs. Temperature
Oxide Film Growth Modeling in LBE Systems (Task 21).

Stochastic Analysis using a Cellular Automata model on the Oxide Structure under Liquid Metal Environment

Compared to the case in a static liquid metal environment, modeling the oxide layer structure in flowing liquid metal environment becomes very different due to scale removal effects and several possible oxide structures of stainless steels in liquid lead alloys with oxygen control which is shown in Figure 23. The previous cellular automata model of oxide layer growth was augmented with a different scale removal effects. Figure 24 shows the average front position and oxide layer thickness as a function of time. When there is no scale removal rate, the oxide layer growth follows a parabolic rate. Once there exists scale removal, the behavior of oxide layer growth clearly changes. From the figures, it is noted that there is an increase followed by a linear decrease at the outer oxide layer position that was enhanced by the scale removal rate. As seen in Figure 24 (c), the thickness of the oxide layer initially increases as time increases and then stays at a constant thickness. All of these phenomena can be explained once it is realized that, at the beginning, the removable iron is easy to diffuse to the outer layer due to the thin oxide layer, and the oxidation rate is faster compared with the scale removal rate, so the thickness of the oxide layer keeps increasing. Once the thickness of the oxide layer increases to a critical value, when the rate that removable iron diffuses to the outer layer is the same as the scale removal rate, then, the thickness of oxide layer will keep constant and only corrosion behavior can be found.

Figure 23. Possible oxide structures of stainless steels in liquid lead alloys with oxygen control
Numerical Modeling on the Diffusion-Controlled Oxidation Model with Scale Removal in Oxygen-Containing Liquid Metal Flow

A numerical diffusion-controlled oxidation model with scale removal in oxygen-containing liquid metal flow was developed. The scale removal effect was considered and the formation mechanism of a duplex oxide layer structure was analyzed and employed in the model. The volume expansion effect caused by the density difference during the oxidation was coupled with the consideration of the increasing weight of reacted oxygen. To solve the diffusion equations with an advection term caused by the moving boundaries, a coordinate transform technique was employed. The governing equations are analogized with the Stefan problem in heat transfer with phase change in the enthalpy formulation, and then solved numerically by a finite difference method. The schematic of oxygen-controlled oxidation process is shown in Figure 25. The present model has also been benchmarked with the available experimental and numerical data. Good agreement was achieved, as shown in Figures 26 and 27.
Figure 25. Illustration of the oxygen controlling oxidation process.

Figure 26. The weight gain from oxidation along with time for pure zirconium without scale removal.

Figure 27. Distribution of oxygen concentration at time $t = 0.5h$ ($Kr = 2 \times 10^{-9}$ m/s for the scale removal model).

Corrosion Barrier Development for LBE Corrosion Resistance (Task 23).
Sample Preparation for Testing

The preliminary samples created showed a problem under closer inspection: the dense alumina layer was physically connected to the steel substrates. To address this, a technique was developed to reliably deposit dense alumina on the central portion of the nanopillar areas to avoid bridging to the bulk alumina. A special masking scheme had to be developed to create these samples. A number of such samples were fabricated for testing the integrity of the corrosion barrier coatings under thermal cycling. The specific tests to be carried out with thermal cycling were also identified.

To carry out the thermal cycling testing of the samples, a furnace with the capability of going up to 600 degrees Celsius was purchased and installed. The furnace installation was delayed due to multiple circuit problems; however, the problems were finally addressed. The furnace was moved to its destined location and programming was carried out for the testing. Due to the high temperature of the furnace, extensive high-temperature exhaust and air intake systems had to be installed, which have been completed. The furnace is currently waiting for three-phase power connection, and will be ready for use upon completion.

To evaluate the adhesion properties of the coatings on the steel substrates, multiple test procedures were investigated and scratch testing was identified as the optimum method. After investigation of the literature, a nano-scratch tester was identified to be the optimum tool for evaluating the samples. A nano-scratch tester has the ability to quantify parameters such as friction force, and adhesive strength using a variety of complementary methods. During the test a sharp metal tip is drawn across the coated surface with an increasing load resulting in various types of failure at specific critical loads. Critical loads are identified optically using a built-in video microscope. Once known, these critical loads are used to quantify the adhesive and cohesive properties of different film/substrate combinations. Additionally, failure points can be determined by using frictional force and depth measurement. These parameters constitute a unique signature of the coating system under testing. Quotations for nano-scratch testers were obtained from different vendors, and the purchase of this equipment is under way.

Investigation of chromium nanowires

As reported in the last quarterly report, coatings on steel samples were created by filling nanoporous alumina layers with Ni nanowires. Ni nanowires were selected due to non-uniformity problems encountered with the deposition of Cr inside the nanoporous alumina. Since the Ni nanowires will be covered by a layer of dense alumina, it was decided that the coatings will not be compromised due to this replacement. However, Cr is still the material of choice for the filler material. As a result, the investigation to improve the uniformity of the Cr nanowires by controlling the deposition parameters has continued. The uniformity in the Cr nanowire showed significant improvement for depositions carried out at very low temperatures (1 – 4 degrees Celsius range) and at very low deposition currents. A cross-sectional image of such wires deposited inside the alumina matrix created on a silicon substrate is shown in Figure 28. As can be seen from the figure, the Cr nanowires show excellent uniformity, however, the pillar heights are very small due to the slow deposition rates. Investigations are currently underway to improve the deposition rates while maintaining the uniformity of the nanowires.
Figure 28. Cr nanowires deposited inside nanoporous alumina showing good uniformity. The nanowire heights are small due to the low deposition rates, which need to be increased.

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

UNLV collaborated with Idaho State University and the French Atomic Energy Commission (CEA) in a series of accelerator-driven subcritical (ADS) experiments at the Idaho Accelerator Center. UNLV researchers traveled to ISU to work with Christian Jammes of CEA and Konstantin Sabourov and Kevin Folkman of ISU to continue and conclude accelerator-driven subcritical experiments in the ISU RACE Subcritical Assembly (SCA). This series of ADS experiments was conducted with a low-power, 20-MeV electron accelerator coupled to the SCA with a tungsten-copper neutron generating target. Results are being analyzed.

Results from the ISU RACE experiments conducted at ISU in October are being compared with Monte Carlo radiation transport modeling to analyze effective delayed neutron fraction ($\beta_{\text{eff}}$) in our far-subcritical, under-moderated systems. MCNP is being used for this work. The simplest approach based on 2 k-eigenvalue predictions with and without accounting for delayed neutrons gives unsatisfactory results due to the lack of convergence. Calculations have been completed with and without a plutonium-beryllium neutron source. Figure 29 illustrates the slow convergence of the results versus number of Monte Carlo histories. Two more-suitable techniques based on different weighting functions are currently under investigation.
Evaluation of experimental thermal and neutron generation with the UNLV High-power RACE target (experiments were conducted at ISU) continued. A complex model of the Target using Gambit was completed, and CFD modeling with FLUENT is ongoing for comparison with experiments. The MCNPX transport model was refined to reduce statistical uncertainty.

In his role as national RACE Project Director, the PI concluded the National RACE Project with several universities and several European organizations. EUROTRANS participants may continue to evaluate experimental data. The UNLV portion of the RACE Project will be concluded during summer 2007.

**Decoupling and Disturbance Rejection Control for Target Circulation (Task 31).**

The cooling processing was investigated and revised. The old cooling control algorithm did not function at all. Figure 30 shows the temperature variation during the cooling process using the old control algorithm. It indicated a natural cooling process without any control interference. The logical errors in the existing control algorithm were fixed. Finally, the improved cooling control algorithm resulted in good temperature response as desired. The temperature difference between each zone should be kept within 20 °C with a cooling rate of 50 °C/hr, as shown in Figure 31.

An observer-based disturbance control algorithm was developed to compensate modeling uncertainties as well as external disturbances (such as a heat source from another zone and the EM pump). The difference between the actual output and simulated output from the nominal model was considered as an equivalent disturbance applied to the nominal value. The disturbance observer estimates the equivalent disturbance and suppresses or eliminates the disturbance. Therefore, when the disturbance observer is applied to each thermal control loop of the TC-1, each control loop can be considered as a decoupled simple inertial system. The principle of the disturbance observer is shown in Figure 32.

Control computer was suddenly stopped/or shut down after twenty seven hours continuously running during the cooling process as shown in Figure 31. In this case, there was no alarm signal sent out. It would be a serious accident if the system was in heating process without an operator on site. The connection between a watchdog and a control system still has defects in handling such case. A resolution was carried out and more defects were found in the alarm control algorithm in the existing system while revising the existing alarm subroutine.
Figure 30. Temperature variation of each zone during cooling process using old control algorithm

Figure 31. Temperature variation of each zone during cooling process using modified control algorithm.

Figure 32. Temperature control block diagram using disturbance observer.

Magnetohydrodynamic Simulation of Electromagnetic Pump in TC-1 (Task 32).

The goal of this task is to develop a fundamental understanding of EM pump technology that is sufficient for researchers at UNLV to aid in the design, fabrication and safe operation of EM pumps in advanced nuclear reactors. The main effort for this year lies in the following subtasks:

- An on-line database of articles and papers related to EM pump technology is to be created from a comprehensive literature review.
- Computational models of the TC-1 loop at UNLV will be developed and the results calculated from these models will be compared with experimental data.
- A parametric study of the TC-1 loop’s sensitivity to variations in operating conditions, materials properties, and geometric parameters will be conducted.
The on-line literature database was set up and now contains over 120 entries. Further work will continue this next quarter with the expansion of the number of entries and the incorporation of keyword searches into the database.

The present model calculates only the EM phenomena (current density, magnetic field, and electromagnetic body forces) in the pump. The velocity of the liquid was specified, not calculated. The next generation of the model will include both the EM as well as the fluid flow phenomena and will thus be a fully coupled MHD/CFD solver. The commercial package Comsol will be used for this task and in-house Fortran software will be developed for the calculations.

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

**Criticality Studies for UREX Processes (Task 35).**

The project was initiated in September with discussions with LANL, ORNL, and ANL regarding project scope and direction. Discussions continued to define the project scope and to determine the appropriate focus on cross-section sensitivity studies versus design of required criticality experiments. This included discussions with DOE-NE and others at the ANS Winter Meeting in Albuquerque. One conceptual study could focus on the capability to measure thermal feedback coefficients in dilute mixtures of plutonium with varying isotopic constituents. Another could involve the modeling of a liquid- or solid-core critical assembly to assess the ability to measure integral critical parameters with small quantities of higher actinides, rather than a full core of fuel containing higher actinides. Students continued to collect information on code systems and references on criticality and sensitivity studies and to research cross section uncertainties for Am and Cm at room temperature in UREX+1 separations processes.

**Deep Burn Separations and Repository Behavior (UNLV)**

**Fluorination Studies**

Studies were continued on the interaction of SiC with NH₄FHF to parameterize the influence of the fluorinating compound. Again no evidence SiC fluorination was observed. However data from the XAFS performed in August showed fluorination of UO₂ and was included in a manuscript on UO₂ fluorination by NH₄FHF to form uranium nitrides.

Work was initiated on SiC interactions with U and cloud point extraction experiments for Eu-Cm separations. The phase of the SiC was studied and surface analysis performed.

Initial studies on the separation of Eu from Cm by cloud point extraction were performed. The solution phase consisted of 1 % Triton-114 by mass and was 5 mL total volume. The ligand examined was 8-hydroxyquinoline, varied from 0 mM to 4.5 mM and the solution pH ranged from 3.5 to 5.5. The Eu and Cm were added and the solution, cooled to 4 °C, then mixed. The micelle phase was formed by heating to 80 °C for 5 minutes and the phases separated by centrifuge (Figure 33). The results show a final volume of heavy and light phase consistent over
Experimental range. In the extraction systems, the selectivity of Cm is found to be a function of pH and ligand concentration (Figure 34). Extraction selectivity for Cm was achieved at higher pH and higher ligand concentration.

![Figure 33 - Cloud point micelle formation upon heating (top) and separation (bottom)](image)

![Figure 34 - Cm selectivity for cloud point extraction with 8-hydroxyquinoline](image)

**Ligand synthesis**

The research goal 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:

- 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.

- 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.

Syntheses of a mono- and tri-functionalized DTPA per-6-ethyldiaminob-β-cyclodextrin have been accomplished (m/z 1785.6 and 2142.2, respectively). The purification of these derivatives from unreacted per-6-ethylenediamino-β-cyclodextrin and hydrolyzed DTPA dianhydride has been partially accomplished through Sephadex LH-20 column chromatography under basic conditions.
The 1:1 complex of Tb$^{3+}$ and per-6-thiopropionate-β-cyclodextrin complex has been detected by mass spectroscopy (m/z: 1957.4). This mass includes the complex, plus a water molecule that is most likely bound to the Tb and a methanol molecule that is thought to be included in the cavity. The 1:1 complex of Eu$^{3+}$ and per-6-thiopropionate-β-cyclodextrin complex has been detected by mass spectroscopy (m/z: 1833.1). This mass includes the complex and a methanol molecule that is thought to be included in the cavity. Synthesis of a mono-6-tosyl-β-cyclodextrin (m/z of 1310.5 for the Na$^+$ adduct) has been accomplished using literature methodology. Complete purification and optimization is underway.

Reactor Physics Analysis and Deployment of Deep Burn Reactor (General Atomics).

TRISO fuel for Deep Burn applications

The PISA code for TRISO particle fuel was modified to model deep burn. The modifications included additional failure mechanisms arising from kernel swelling, kernel migration, and attack of fission products on the SiC layer. The Monte Carlo treatment of the distributions of fuel dimensions and the uncertainties in the kernel and coating properties were used to predict structural failures for a number of cases.

For the fabrication Issues of TRISO fuel from LWR spent fuel tansuranics task, the conceptual design of a Remote Handled Automated (RHA) TRISO fuel fabrication facility was initiated. A mathematical model of the material balance was developed. A methodology was also developed.
to utilize the model to obtain the approximate sizing of equipment and modules needed for the RHA facility. Still to be implemented is a cost matrix to calculate operating costs and capital.

*Neutronics of Deep Burn systems*

For the advanced burnup and reactivity modeling task, the dependency of the fuel and graphite temperature were included on core geometry in the calculation of the 3-dimensional reactivity and depletion of transuranics using Montecarlo models. The integration of the General Atomics simple POKE model for gas cooled reactor thermohydraulics with the MCNP/Origen model was completed in order to obtain temperature-dependent transuranic mass flows.

For the core optimization task, the criteria were established for the optimization of Deep Burn gas cooled reactors using fully transuranic core loadings (1-pass deep burn). Sensitivity analysis was performed changing kernel size and packing fractions, as well as new fuel shuffling schemes, in order to maximize burnup or to improve the refueling cycle lengths. Also modifications of the fuel block geometry were considered in order to evaluate the impact of moderator to fuel ratio.

Furthermore, preliminary analysis was performed for Deep Burn gas cooled reactors using fully transuranic core loadings (2-zone, 1-pass deep burn) followed by a fast reactor recycle.

*Deep Burn fuel cycles for GNEP applications*

For the scenarios and mass flows task, the compilation of mass flows was initiated for Deep Burn scenarios (1-pass Deep Burn). A 2% yearly rate of increase was assumed for overall U.S. nuclear power production, and the Transuranics waste generation and Uranium consumption were evaluated using a scenario for the gradual introduction of gas cooled reactors, including both deep burn and LEU fueled reactors.

For the repository impact task, calculations of decay heat generation were initiated from the isotopes constituting the residual waste from deep burn gas cooled reactors. The decay heat generation was used from all the transuranic isotopes and also from the main fission products and compared the resulting integral heat production with that produced by the un-reprocessed LWR spent fuel. The calculations were performed for several deep burn scenarios.

Calculations of decay heat generation from the isotopes constituting the residual waste from deep burn gas cooled reactors were continued. In particular, the self-cleaning case (SC-MHR) was modeled.