9-30-2006

AFCI Quarterly Input: UNLV July 1 through September 30, 2006

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

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

- UNLV graduated Robert O'Brien with the Master of Science in Materials and Nuclear Engineering. He is the second graduate of UNLV’s nuclear engineering M.S. degree program.
- Prof. Micha Polak, Ben-Gurion University of the Negev, gave a seminar on Aug. 30 entitled “Alloy nanocluster compositional structure and heat-capacity based on TB coordination-dependent bond energetics and the statistical-mechanical FCEM approach.”
- Prof. Denis Beller participated in a week-long seminar for federal judges titled “The Environmental Consequences of Energy Use: Policies for Progress” held September 11-15 in Bozeman, MT.
- Alan Dobson and Chris Phillips from Energy Solutions (formerly British Nuclear Group, America) gave a seminar on the British recycling program to the UNLV Radiochemistry Group on September 27.
- Eleven graduate students and seven faculty members staffed an informational booth at the Town of Pahrump Fall Festival September 29 to October 1. This is the program’s major community outreach to discuss nuclear issues with the citizens of Nye County, Nevada.

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

- The hazard control plan for the TC-1 Loop modification that will install a test section was approved by the UNLV’s Department of Risk Management and Safety.
- The TC-1 control algorithm improvement project accomplished a set of nine experiments to obtain the dynamic response of each heating zone. The transfer functions of each zone were identified. The safety and alarming control loop was modified.
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.”

1.2.2 **International Collaboration Highlights**


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 21 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.

- Planning of the Cs evaporator was completed; all necessary parts were received. Assembly of the evaporator is currently under way.
- Two additional undergraduate students joined the group in the framework of senior independent studies in Chemistry. They will jointly perform the Pd/SiC experiments and, if successful, also begin the Ag/SiC studies.
- Preparation of Pd/SiC samples for the transmission electron microscope is ongoing. A sample was thinned to 2 µm, which needs to be dimpled, reducing its thickness to about 100-200 nm.
Dissolution, Reactor, and Environmental Behavior of ZrO₂-MgO Inert Fuel Matrix (Task 19) Highlights.

- A reliable method for XRF was developed involving ashing the individual oxides, then preparing standards through the dry synthesis route.
- A second XAFS experiment was performed at Argonne National Lab on uranium containing samples. The data however was not reliable due to inconsistencies in beam current.
- The work using cerium as a plutonium analog has concluded. The completed section was presented at Inert Matrix Fuels Workshop 11, in Park City, Utah in September 2006. Similar studies using uranium as a plutonium analog are underway.


- Hot Cell robot control: Work on the visual servoing of robots inside the hot cell continued. Camera servoing functions were implemented and tested in Visual Basic. The pan, tilt, and zoom functions of a remotely controllable CCD camera (Sony EVD30) are controlled from the PC.


- The solubility limit for erbium in zirconium nitride was determined. Zirconium-erbium oxide precursor material was converted to mononitrides using carbothermic reduction/nitridization.
- The solubility limit for erbium in zirconium nitride was determined to be 9 at-% based on electron-beam microprobe analysis. Exceeding the solubility limit in the precursor oxides produced the formation of an additional (Er₂Zr)₂O₃ sesquioxide phase with bixbyite-type structure.
- Phase-pure mononitrides with the composition Zr₀.₉₇Er₀.₀₃N and Zr₀.₉₄Er₀.₀₆N were synthesized for the first time.
- Microstructure and nanostructure of oxides and nitrides were evaluated by optical microscopy and TEM. The low sample densities and the poor mechanical strength could be increased after applying an additional sintering step under inert or slightly reducing conditions.
- Samples in the ternary system Zr-Er-N were sintered at 1650°C in a ceramic tube furnace under Ar/H₂ atmosphere. Since no inner tantalum metal was used, re-oxidation of the samples became evident. A TEM sample was prepared to perform EELS studies and to verify phase constitution.
- High resolution electron microscopy and electron-energy-loss spectroscopy (EELS) were performed on ternary samples in the systems Zr-Er-O and Zr-Er-N.
Solution-based Synthesis of Nitride Fuels (Task 34) Highlights.

- 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.

SEPARATIONS TECHNOLOGY

Immobilization of Fission Iodine (Task 15) Highlights.

- Research on the reaction of iodide with lignin in the presence of MnO₂ continued.
- Additional MnO₂ experiments were performed at pH 4.
- A colorimetric procedure for iodine was developed.
- The potential for nitrite and nitrate to react with iodide under mild conditions (pH 4, 7 and 25°C) was examined.
- The examination of iodine and iodate distribution is a recent soil/sediment continued.


- The TRPSEMPro system architecture was modified based on recommendations from ANL collaborators from the last review meeting.
- The beta version of TRPSEMPro was delivered to the ANL collaborators for review.

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

- The EDTA/thiol studies with PANI/Au electrodes were initiated.
- The coverage of EDTA/thiol on Au electrodes was measured to determine the mol/cm² coverage of the chelator.
- Polymer growth on a quartz crystal electro-balance was attempted, but found that the current cell configuration is not suitable for measuring the polymer/Au production and must be modified to be a flow through cell.

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

- NMR and IR spectroscopy were performed to evaluate the uranium-nitrate-TBP system. IR spectra were evaluated for several of the compounds used in the extractions.
- Error analyses were performed on some of the data that had been previously obtained.
- Further studies were performed on uranium acetohydroxamic acid interactions.


- Initial investigations were conducted into Fluorescence of Uranyl ion in the presence of perchlorate and nitrate.

- General maintenance was conducted on the Neutron Multiplicity Detector System.

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.

- This project was initiated in September 2006. Prior research was performed from July 2006 in collaboration with Dr. Gordon Jarvinen of LANL that was used as the basis of this project.
- Experiments examined the sorption of TcO₄⁻ to cation exchange resins and the preparation of Tc metal from the sorbed TcO₄⁻. The resins Dowex Marathon and Reillex resins are examined.
- Three separate studies were performed: (1) Thermal gravimetric analysis (TGA) of the resins, (2) Batch sorption of TcO₄⁻ to the resin, and (3) Pyrolysis and steam reforming of the pertechnetate sorbed to the resin.
- The steam reforming of the Tc-resin material resulted in the formation of Tc metal.

TRANSMUTATION SCIENCES

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

- The maximum residual stress in terms of the S-, W-, and T- parameters was observed near the fusion-line (FL) of the welded specimens consisting of austenitic Type 304L stainless steel and martensitic Alloy EP-823.
- The residual stress in terms of these three line-shape parameters was reduced at locations away from the FL.
- The residual stress due to welding was higher in Alloy EP-823 compared to that of the austenitic material.
- The dislocation density, determined from the TEM micrographs, was higher at the heat-affected-zone (HAZ) of the welded specimens compared to that of the base material.
- The size of the HAZ was higher on the Alloy EP-823 side of the weld, irrespective of the weld configuration.

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

- Gas phase experiments started.
- The liquid metal transport mechanism was verified for the liquid lead test facility.
- The Raman facility became operational.
- Concerns about oxidation kinetics in the LBE led to anticipated experiments that probe the hypothesis about an oxygen source in LBE corrosion of steel.

- A gradual drop in failure strain ($e_f$) was noted for all four heats at temperatures ranging from ambient to 400 °C. Beyond 400 °C, the magnitude of $e_f$ was enhanced possibly due to temperature-induced plastic flow.
- The phenomenon of reduction in ductility in terms of $e_f$ has often been cited to be the result of reduced dislocation mobility through the grains, possibly due to diffusion of interstitial and substitutional solute elements and their subsequent accumulation near the grain boundaries. This dynamic strain aging concept is being investigated using both parameters.
- The characterization of dislocations is ongoing using transmission electron microscopy.
- The development of new phases resulting from transformation at elevated temperatures may influence the tensile properties. Thus, characterization of these phases, if any, is in progress using the XRD technique.
- Fractographic evaluations by SEM revealed brittle failure at room temperature and ductile failures (dimples) at elevated temperatures.

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

- The cellular automata modeling of oxide layer growth with scale removal was developed.
- Quantitative cellular automata modeling on inward oxidation mechanism was studied.
- Development of a numerical model using a finite difference method on oxide layer growth with scale removal is ongoing.

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

- SEM characterization was performed on the top of the samples.
- Deposition of dense alumina on the full area of the nanopillars caused problems by bridging.
- Deposition of dense alumina was carried out on the central portion of the nanopillar areas.
- 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 programmable furnace was acquired for thermal cycling experiments.
- Installation of the programmable furnace was continued, which was delayed due to a short circuit.
- The tests to be carried out with thermal cycling were identified.

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

- Researchers participated in accelerator-driven experiments at ISU with CEA and ISU engineers in August and prepared for follow-up experiments in October.
- Researchers conducted thermal and neutron generation experiments at ISU with the UNLV High-power RACE target.
Decoupling and Disturbance Rejection Control for Target Circulation (Task 31) Highlights.

- Discussions were held with the UNLV Office of Risk Management and Safety and faculty to discuss lead monitoring.
- The signal feedback from the heaters was installed to control the system.
- A 24-hour monitoring system was developed with connection to TC-1 control system.
- The dynamic response of TC-1 system was identified.
- The TC-1 Control Algorithm was successfully heated from room temperature to working temperature (200 °C) with the modified code. However, the cooling process did not work as expected.

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

- A literature survey database related to the EM pump was established.

Criticality Studies for UREX Processes (Task 35) Highlights.

- The project was initiated with discussions with technical staff members from LANL, ANL, and ORNL to define the project scope and to determine the appropriate focus on cross-section sensitivity studies versus design of criticality experiments.

Deep Burn Separations and Repository Behavior Highlights.

- Fluorination studies on SiC with NH₄FHF were performed by the UNLV team. No degradation of the SiC was observed.
- The SRNL team provided assistance to Dr. Frederic Poineau with the U- and Tc-EXAFS data collection and data analyses while at the APS during the August experiment.
- Actinide Sample Boxes were developed and produced for future XAFS experiments. The UNLV team performed further data analysis from the August 2006 XAFS experiments.
- Ligand Development – DTPA dianhydride was reacted with per-6-(2-amino(ethylamino))-β-cyclodextrin to yield a tri-functionalized cyclodextrin which is observable via mass spectrometry (m/z = 2497). However, the purification of this derivatized cyclodextrin has proven difficult. Acid-base titrations of the sodium salt of per-6-thiopropionate-β-cyclodextrin with the lanthanides have been completed.

FUELS TECHNOLOGY

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

The main focus of the quarter was the training of students to perform planned experiments on Cs/SiC and Pd/SiC systems. This training includes sample handling and transfer, principles of photoelectron spectroscopy, and experimental procedures with the instrument.

The technical preparation of the experiments continued, in particular the planning and construction of an alkali metal evaporator for the planned Cs/SiC experiments was prepared. A
A sketch of the evaporator is shown in Figure 1. All necessary parts were ordered and recently arrived at UNLV.

![Figure 1 - Sketch of the Cs-evaporator.](image)

The second experiment, which is currently being prepared by the two new undergraduate students, is to verify Pd/SiC data. This data was collected using the old ESCALab MkII electron analyzer. The new analyzer, installed in the spring of 2006, now allows the collection of spectra with significantly improved resolution (to discern the different C- and Si-species that were previously observed) and signal-to-noise ratio. Even more importantly, the new analyzer does not show the background instabilities of the old instrument, and thus gives more reliable data for a quantitative analysis.

The electron-beam evaporator for the Pd/SiC experiments was set up and two undergraduate students are currently training in the experimental techniques and will start with the experiments next quarter. Furthermore, transmission electron microscopy samples of the Pd/SiC interface are currently being prepared. Since the primary interest is in a cross-sectional analysis, the preparation of suitable thinned samples is quite difficult.

The new variable-temperature Scanning Probe Microscope (SPM) was repaired. This locally resolving approach will give further valuable insight into the lateral morphology of the in-situ grown samples. In particular, the SPM (primarily in the Atomic Force Microscopy mode) will be utilized to accompany each deposition step during the Pd/SiC and then the Cs/SiC interface formation. Note that the SPM operates in ultra-high vacuum and is directly connected to the existing surface science system, such that photoemission and SPM data can be obtained from the same sample surface without exposure to air.

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

A reliable method for XRF was developed involving ashing the individual oxides, then preparing standards through the dry synthesis route. It was believed that the samples that showed heterogeneous cerium distribution were due to insufficient sintering times. Therefore, one such sample was removed from resin, resintered, and elemental mapping was performed a second time. This second mapping shown in Figure 2 had a homogenous distribution of cerium proving the hypothesis.
A second XAFS experiment was performed at Argonne National Laboratory on uranium containing samples. The data however was not reliable due to inconsistencies in beam current. High resolution TEM, scanning TEM, EDX, and elemental mapping were performed using the Tecnai 300 kV Transmission Electron Microscope located in the Harry Reid Center. Results are shown in Figure 3.

This concludes the work using cerium as a plutonium analog. The completed section was presented at the Inert Matrix Fuels Workshop 11, in Park City, Utah in September 2006. Similar studies using uranium as a plutonium analog are underway.
Figure 3. (a) EDX, (b) high resolution TEM of cubic zirconia (Zr$_{0.865}$Mg$_{0.069}$Ce$_{0.041}$Er$_{0.025}$O$_{1.918}$), and (c) SAD of cubic zirconia (Zr$_{0.865}$Mg$_{0.069}$Ce$_{0.041}$Er$_{0.025}$O$_{1.918}$).

Camera Control

The camera graphical user interface (GUI) for the operator-based camera control was implemented in Visual Basic 6 and is illustrated in Figure 4.

![Camera GUI for operator-based camera control](image)

**Figure 4.** Camera GUI for operator-based camera control.

Expanded Recognition of Cylindrical Fuel Pellets by the CCD Camera

Continuing from previous efforts reported in July 2006, additional scenarios of increasing complexity regarding the presence of noise in the images were analyzed. The Matlab codes were continuously refined to enable the recognition software to discriminate image noise in multiple forms from useful information representing actual 3D-shapes. Figures 5 and 6 present examples of image noise.

*High Resolution Electron Microscopy on ZrN-based Zr$_{1-x}$Er$_x$N Inert Matrix Fuels*

In an effort to determine the solubility limit of erbium in zirconium-mononitride surrogate fuel, mono-phase precursor oxide-solid solution in the system Zr$_{1-x}$Er$_x$O$_{2-x/2}$ was synthesized. ZrN-based mononitrides in the system Zr$_{1-x}$Er$_x$N were produced by applying carbothermic reduction/nitridization of the precursor material. Further densification of the material was achieved by sintering the samples at 1650 °C for 12 hours in Ar-H$_2$ atmosphere. To complete earlier data on the crystallography of these mononitrides, extensive studies were performed on their nanostructure using high resolution electron microscopy. TEM sample preparation on ceramic fuel samples is a rather challenging task, since the final sample thickness is only about 1/50 to 1/100 of the average ceramic grain sizes, and less than one in four attempts were successful so far. In recent studies, the nanostructures were able to be compared before and after carbothermic reduction/nitridization.

An electron-transparent TEM sample of Zr$_{0.96}$Er$_{0.04}$O$_{1.98}$ (ZE 6) was prepared. At 120,000 times magnified, ZE 6 showed 10-30 nm-sized domains of lower electron transfer (darker regions), which could either indicate defect accumulation through sample preparation, or erbium-enriched domains within the erbium-depleted zirconium oxide-based matrix. However, selected area diffraction of the electron transparent sample section does reveal the crystal structure of a Zr$_{0.96}$Er$_{0.04}$O$_{1.98}$ single crystal in a zone axis close to (100) and no satellite peaks of a secondary phase were observed (Figure 7b). Based on a lack of software assistance the true nature of the zone axes was not identified. The nanostructure of ZE 6 is displayed at high, atomic resolution (Figure 8). The lattice fringes are resolved towards the grain edge, while within the grain bulk...
potential grain-grain overlay or defect accumulation provided a cloudy image due to the interference of several electron transfer sub-functions.

Figure 7. TEM image of a sample before carbothermic reduction/nitridization ($\text{Zr}_{0.96}\text{Er}_{0.04}\text{O}_{1.98}$, 120,000 magnified) (a) and selected area diffraction (SAD) (b) of the same sample (ZE 6 oxide).

Figure 8. High resolution TEM image of ZE 6 oxide ($\text{Zr}_{0.96}\text{Er}_{0.04}\text{O}_{1.98}$) 1,000,000 times magnified.

Through carbothermic reduction/nitridization oxide precursor material was completely converted into mononitrides in the system $\text{Zr}_{1-x}\text{Er}_x\text{N}$ for $0<x<0.1$, and phase constitution and crystallographic parameter were determined by X-ray diffraction and Rietveld analysis (Figure 9).
In accordance to the thermodynamic phase-stability field in the Zr-rich region of the system Zr-Er-N, phase-pure \textit{alpha}-solid solution phases were synthesized after optimizing thermal treatment and chemistry. The reaction products were basically free of zirconium oxides (baddeleyite, zirconia) and only minor impurities of 0.3-0.5 wt-%, involving tantalum, which serves as oxygen protection and oxygen getter, were observed.

After carbothermic reduction/nitridization the microstructure of the nitrides is characterized by a rather low theoretical density and grain-grain interfaces are poorly developed (Figure 10). TEM sample preparation required additional annealing at 1650 °C for 12 hours in Ar-H\textsubscript{2} atmosphere to provide sufficient mechanical strength and to increase the theoretical densities.

An electron-transparent TEM sample of Zr\textsubscript{0.94}Er\textsubscript{0.06}N (ZEN 7) was prepared, and for the first time pure Accelerator-Driven System-type nitride fuel samples were investigated by this task by high-resolution transmission electron microscopy. At 120,000 times magnified ZEN 7 showed 10-40 nm domains of higher electron densities and lower electron transfer (darker regions) which
indicates the formation of erbium-enriched domains within the zirconium-oxide-based matrix (Figure 11a). Even though the XRD/Rietveld analysis as well as electron-beam microprobe analysis (earlier results) stated the high purity of the ceramic solid solution, the imaged nanostructure (120,000 times magnified) reveals the formation of domains of different chemical character. In accordance to this statement the selected area diffraction pattern shows the formation of weak satellite peaks additional to the diffraction pattern of the host single crystal. The zone axes of the single crystal diffraction image could not be identified, and additional imaging software assistance might be required in the near future. The nanostructure of $\text{Zr}_{0.94}\text{Er}_{0.06}\text{N}$ (ZEN 7) was imaged at magnification of up to 1,000,000 times (Figure 12).

![Figure 11. TEM image of Zr$_{0.94}$Er$_{0.06}$N, ZEN 7, (a) 120,000 times magnified and (b) the selected area diffraction pattern (SAD) of ZEN 7.](image1)

![Figure 12. High resolution electron microscopy (HREM) on Zr$_{0.94}$Er$_{0.06}$N (ZEN 7) and the corresponding (a) Fast-Fourier Transformed (FFT) image and (b) enlarged region of ZEN 7.](image2)
The average lattice fringe distance in the high-resolution images of Zr$_{0.94}$Er$_{0.06}$N (ZEN 7) reflect the crystallographic unit cell, and in particular the unit cell parameter $a$. The lattice parameter $a$ increases as a function of erbium-substitution from 4.595(1) Å to 4.618(1) Å, and a lattice fringe distance of 4.4(2) Å was observed (Figure 12b).

Furthermore, an electron-transparent TEM sample of Zr$_{0.92}$Er$_{0.08}$N (ZEN 8) was prepared and the nanostructure could be imaged (Figure 13). At 120,000 times magnified, ZEN 8 showed view domains, similar to those of ZEN 7, and in addition stress-related fringes from up-left to down-right. At magnifications of 1,000,000 times, minor distortions of the lattice fringes become visible. The observed distortion of the crystal lattice is in compliance with the rather large peak profile parameter determined by Rietveld analysis in the high 2-theta region (see also Figure 9b) and could be explained by chemical nano-sized domains with 2 to 5 nm in size. This statement is in compliance with the observed bending of lattice fringes at the interface between regions of higher (darker) and lower (brighter) electron density and, respectively, lower and higher electron transparency (Figure 13a).

![TEM images of Zr$_{0.92}$Er$_{0.08}$N (ZEN 8) at magnifications of (a) 120,000 times and (b) 1,000,000 times.](image)

**Figure 13.** TEM images of Zr$_{0.92}$Er$_{0.08}$N (ZEN 8) at magnifications of (a) 120,000 times and (b) 1,000,000 times.

**SEPARATIONS TECHNOLOGY**

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

Experiments continued that focus on iodide sequestration using sphagnum peat. For these experiments the iodide solution was buffered to pH 4 with acetate buffer and the solution (1.0 L) was circulated through a column containing peat (0.5 g) and γMnO$_2$ (0.2 g) using a peristaltic pump. The flow rate was ~5 mL/min. The iodide content of the reservoir was continuously monitored with an iodide specific electrode that had been calibrated with iodide standards in the same buffer system. The data is presented in Figures 14 and 15 for two different initial
concentrations of iodide. The iodide concentration was digitally smoothed to clarify the trend in the data. The results indicate that iodide can be removed from the solution. Pyrolysis analysis of the sphagnum peat demonstrated that iodide was being incorporated into the peat.

Iodide Sequestration MnO2/Sphagnum Column
Smoothed Data pH 4, Co=1e-3

![Graph showing iodide sequestration](image)

**Figure 14.** Iodide sequestration in flow through system at pH 4, Co=10^{-3}M.

Iodide Sequestration Experiment
Spagnum/MnO2, pH4, Co=1e-4

![Graph showing iodide sequestration](image)

**Figure 15.** Iodide sequestration in flow through system at pH 4. Co=10^{-4}M.
Some development work was done to adapt a colorimetric analysis for iodide to the experimental system. The concentration range for this analysis was less than $10^{-5}$-$10^{-4}$ M. The procedure involved the oxidation of iodide to iodate with bromine saturated water (0.5 mL of bromine saturated water per 1.0 mL of sample). The excess bromine is then selectively destroyed (reduced) with formic acid. A portion of the sample (0.2-0.4 mL) is transferred to 2.5 mL of KI (0.01) solution acidified with concentrated HCl (10 uL). The excess iodide reacts with iodate in the sample forming triiodide, which can be quantified spectroscopically at 350 nm. Alternatively a small amount of starch solution can be added and the iodine can be measured at 600 nm. This method is still being evaluated. Preliminary results indicate that nitrate and nitrite are severe interferences and these anions must be eliminated (by reduction) if present. In addition, soluble organic matter may also interfere. An example calibration plot is shown in Figure 16. This method was used with the iodide uptake experiments with MnO$_2$ and sphagnum, and good agreement with the iodide electrode method was achieved.

![Iodide Colorimetric Analysis](image)

**Figure 16. Calibration plot for colorimetric iodide analysis.**

During this last quarter, the potential for nitrite and nitrate to oxidize iodide to molecular iodine (or triiodide) was examined. Nitrite oxidation is well known under acidic conditions, but has not been extensively explored in the neutral pH region. The reaction was suggested to be (Anschutz et al., GCA 64, 2000, 2751-2763):

$$4H^+ + 2NO_2^- + 2I^- \rightarrow 2NO + I_2 + 2H_2O$$

Experiments were performed at pH 7, 4.5 and 4. At pH 4 and below nitrite reacts with iodide and the reaction can be followed by UV-Vis spectroscopy (triiodide at 350nm).

The reaction was not observable at pH higher than 4. Some of the example experiments are reported in Figure 17. The production of iodine (triiodide) in a 0.02M KI and 0.002M KNO$_3$ solution was linear. Under these conditions neither iodide nor nitrite becomes limiting so that the production of triiodide is constant. In the presence of ~40μg/mL alkali lignin the production of iodine becomes concave indicating a slowing of triiodide production. This is a result of the reaction of iodine with the alkali lignin. Similar results were obtained with p-OH benzoic acid.
Figure 17. Nitrite oxidation of iodide at pH 4 produces iodine (as triiodide) that can then react with organic matter.

Some batch experiments were also performed with $10^{-4}$ M KI, $10^{-4}$ M NaNO₂ and 0.1 g of alkali lignin. After 72 hours, results indicated that 80% of the iodide was removed from solution. Pyrolysis of the alkali lignin demonstrated the presence of organically bound iodine in the lignin. Nitrate was also examined as a possible oxidant. While nitrate can oxidize iodide under very acidic solutions the reaction was not observable for pH 4-7.

Research on the distribution of iodine (iodate, iodide and organic iodide) in soil/sediment obtained from the Virgin River in the vicinity of Lake Mead (Black Butte Series) continued. The results are presented in Figure 18 and indicate that organic iodine is the dominant form of iodine in these sediments. The small difference in iodide measured before and after sample reduction indicates that iodate is a minor species.
Comparison
Soluble iodide and
Organic Iodide, Virgin River Sediment

Figure 18. Iodide, iodide + iodate, and organic iodide in a sediment/soil sample from the Virgin River.


Interface to interact with ASPEN Plus through the TRPSEMPro Packages

The TRPSEMPro was modified to open the ASPEN-Plus file through the interface and to temporally store the information in text file for a faster response. Once the user starts to execute ASPEN-Plus within the TRPSEMPro, the intermediate steps generated from ASPEN-Plus will
be handled by internal ASPEN-Plus procedures. The converged ASPEN-Plus results, therefore, will be stored within the TRPSEMPro database system and passed to the AMUSE interface for further chemical separation calculations.

The ASPEN-Plus interface version 0.26 was created and shipped to ANL for a review associated with a summarized user manual. There were issues generated from referencing local modules. By removing the referenced file and rebuilding the “FSSimulation” and associated references, the program worked with Aspen Tech Software. However, ANL still experienced problems connecting to the ASPEN-Plus software.

**TRPSEMPro Modification**

The middleware architecture associated with the TRPSEMPro package was modified, as shown in Figure 19. The labels “1” and “2” in Figure 19 shows the middleware interface between external software packages, such as ASPEN-Plus and AMUSE macros while the label “3” shows the communication and optimization module that interacts with above two interfaces. The detailed parameter parsing algorithm will be determined with ANL shortly.

Documents for the TRPSEMPro interface to AMUSE were updated. The major purpose for the documentation is to provide user manual guidelines for AMUSE programmers/users with easy tracking, easy coding, and fast referencing and modification features.

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**Figure 19. Modified TRPSEMPro system architecture.**
Electrochemical Separation of Curium and Americium (Task 25).

During the last quarter Au/EDTA thiol electrodes were produced and desorption studies of the monolayer were performed to determine the ultimate surface coverage. Studies were initiated with the EDTA-Thiol on planar Au electrodes to determine the potential window that can be used in electrochemical experiments. The goal is to determine the unique electrochemical potential for a given species to be chelated. These studies will be extended by looking at the potential dependent chelation at 2-D planar gold electrodes modified with the EDTA thiol group. The final step will use the polymer/Au/thiol electrodes to chelate species of interest using potential dependent methods. Figure 20 shows desorption of the EDTA thiol from planar gold electrodes. The final step involves incorporating the EDTA-Thiol into Polyaniline/Au materials based on the schematic in Figure 21.

![Figure 20. EDTA-Thiol Desorption from a planar Au electrode.](image)

The data indicates that the potential window for chelation is positive of -0.8 V, where desorption is first observed as a small sharp peak followed by a larger peak at -1.1 V. The charge associated with these two voltammetric waves indicates that the EDTA-Thiol forms a monolayer on Au with coverage of 0.32. Therefore, the thiol takes up approximately one third of the gold surface. This is consistent with thiol monolayers deposited on Au. The thiol deposition is based on the spontaneous adsorption of the thiol and is shown below for clarity.
Figure 21. (a) Schematic of a conductive polymer/Au composite electrode. (b) Chelating ligand to be bound to the gold dispersed in the conductive polymer. (c) Potential mediated separation of a metal species from solution using chelation.

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

Spectroscopy

A new Varian 3100 FT-IR was installed as well as a diamond ATR attachment. IR spectra were obtained for TBP, dodecane and lithium nitrate and are shown in the Figure 22. The LiNO₃ spectrum shows the N-O peaks around 1650 and 1340 cm⁻¹, and the TBP spectra show P-O peaks around 1300 and 1000 cm⁻¹. These peaks will likely be useful in analyzing the spectra of future extraction samples.

Uranium-Acetoxyhydroxamic acid interactions

It was discovered that a little mechanical energy input will cause uranyl acetate dihydrate and acetoxyhydroxamic acid (AHA) solids to react to form uranyl-AHA, solid. The likely mechanism is that water is liberated from one or both to catalyze the reaction. The aqueous behavior of the uranyl-AHA system was studied as a function of pH and of constituent concentration. The stock solutions were uranyl acetate or uranyl perchlorate and aqueous AHA solutions prepared fresh daily. To minimize uranyl polymerization and due to the extinction coefficient of the U-AHA complex, most studies were done at 0.1 to 1 mM U.
Prepared solids of uranium and AHA were evaluated and the molar ratio of materials compared. The solids were washed batch-style in acetone to remove the unreacted AHA, unreacted uranyl acetate, and excess water/acetic acid and under vacuum. The 1:1 product has the highest recovery because the AHA is almost fully reacted and does not wash away. The yield steadily decreases with increasing AHA:U. It remains to characterize the ratio of AHA:U in the final product to ensure that it is 2:1 and not a polymerization. This will be done in triplicate by dissolving a known amount and measuring the [U] using arsenazo and the [AHA] using potentiometric titration. U-AHA was precipitated from a 4:1 AHA:U water solution over the course of several days. Acetone solutions of uranyl acetate (UAc) and AHA will form dissolved U-AHA when there is a large excess of AHA. These solutions precipitate a mixture of AHA solids and UAc solids. Acetone stocks of AHA and UAc will precipitate U-AHA. This phenomenon has not been explored in detail. AHA will crystallize out of acetone as large needles as shown in Figure 23. It was attempted to extract aqueous solutions of uranyl perchlorate and AHA with several solvents: CHCl₃, CH₂Cl₂, TBP, 30% TBP/dodecane (v/v), and diethyl ether. The chlorinated solvents and ether failed to extract any uranyl. TBP extracted U-AHA and the 30% TBP/dodecane mixture extracted free uranyl. These phenomena were determined by measuring the UV-Vis spectra of the extractants and aqueous residue. The TBP/dodecane extraction was repeated three times with the same result.

A supersaturated solution of U-AHA will precipitate from the deep red-purple solution to an orange solid overnight, shown in Figure 24. This phenomenon was also seen in the presence of the chlorinated solvents and in TBP. IR characterization of these solids (Figure 25) showed some water, TBP, and AHA residue in the TBP precipitate, and water/AHA residue in the others. The solids were more crystalline in these precipitates than in the solid-state synthesis, which forms a powder, but still appeared amorphous under the microscope.
Figure 23. AHA crystallized from acetone. The crystal on the right has a length of about 0.5 mm.

Figure 24. U-AHA precipitated from slow-evaporation of acetone solution. (a) UAc crystal on top of AHA evaporate. (b) U-AHA crystallized out as plates.

The product formed from milling a 2:1 molar ratio of solid AHA:UAc, then washed immediately with acetone, is identical to the product formed from precipitation from water, followed by drying under vacuum. The precipitate from acetone looks a little different, most notably the disappearance of the peak at 1261 cm\(^{-1}\) and the appearance of a small peak at 1213 cm\(^{-1}\). The amount of product available from the water and acetone precipitations was not as high as the other product, which may account for some of the noise in those spectra. This peak is tentatively assigned to the N-O stretch (shifted to lower energy from the free AHA). The strength of the peak at 1614 cm\(^{-1}\) means that it is most likely the C=O, not the N-H bond. Once the identification of the peak at 1614 cm\(^{-1}\) is confirmed, it can be proved whether the binding is linear through the amine OH group or cyclic, incorporating the C=O group. The N-H peak at 3400 cm\(^{-1}\) will also be affected by the D\(_2\)O exchange.
The distance from U-C is not characteristic of a ring structure (based on uranyl acetate literature, including UAc’s crystal structure), but of a more linear structure as suggested in Figure 26, with two bound for each uranyl atom (2:1 AHA:U seems to be the equilibrium balance). Fits with nitrogen and oxygen as the neighboring atom were less successful.

The source changeover at 400 nm affected the quality of the spectra. The detector changeover at 350 nm had no discernable effect.

*Laser Fluorescence*

Laser fluorescence data were obtained for the solid uranyl acetate (Figure 27), but problems with the laser precluded spectra collection for the U-AHA solid. A technique for solids using capillaries was developed and a small support stage was made.
Fit considering shell of C and O atoms. FT k [3,12.5] Å⁻¹

Figure 26. EXAFS of the solid compound, manufactured as a 2:1 AHA:U molar ratio and dried (no acetone wash), seems to indicate a linear structure.

Figure 27. Laser fluorescence study of uranyl acetate.
The effect of ionic strength on the U-AHA aqueous complex was explored. Sodium nitrate and sodium perchlorate, both very weak complexing anions, were used to balance the ionic strength at 0.1 and 1.0 M (including the contribution of the uranyl starting material and the buffer, if used). There was no difference seen between the two salts, as expected, but a large difference between the two ionic strengths. This may explain the difference seen between the stability constants calculated from data at 1.0 M (this work), 2.0 M (Choppin), and 0.1 M (literature).

It is more apparent to see the difference if the ratio of the two peaks at 374 and 476 nm is plotted against the AHA/U ratio as shown in Figure 28. The ratio between the two, as a rough measure of equilibrium, reaches a steady state almost immediately at a low ionic strength (1:1 molar ratio), but takes much longer at a high ionic strength (10:1 AHA:U). In addition, the shape of the spectrum is changed; the peak ratio is higher, indicating that the peak at 374 nm is relatively higher than that at 476 nm at the higher ionic strength. This indicates that even weakly complexing anions such as perchlorate and nitrate can compete with and affect the speciation of the uranyl-AHA aqueous complex. Future work will quantify the effect on the pKa of AHA to determine if it is a competition or a pKa effect that changes the stability constant.


**TRLFS in the Uranyl nitric acid system**

Experiments were initiated to gauge the effects of ligand concentration, metal concentration, and total ionic strength on the fluorescence lifetime and fluorescence spectra. First, the goal was to determine the lifetime of the free uranyl ion in perchloric acid media, and then look for other lifetimes as a function of increasing ligand concentration. In addition, as with the UV-Vis work, the absolute shape of the spectra (peak position, peak ratios, etc.) were also examined as a qualitative measure of what is happening in the spectrum. As summarized in Figure 29, the characteristic fingerprint of the free uranyl species (Sample 1) is observed to be suppressed by the presence of nitrate ions in the system. As the nitrate concentration increases (Samples 2
through 5 in increasing order), the characteristic shape of the fluorescence is suppressed. The overall fluorescence of the system (non-time resolved) was also observed to change greatly with respect to the amount of nitrate added. This effect on the spectrum cannot be directly associated to nitrate complexation, and may be the result of ionic strength or quenching effects.

![Uranyl fluorescence as a function of increasing $[\text{NO}_3^-]$](image)

**Figure 29.** The characteristic fingerprint of the free uranyl species (Sample 1) is observed to be suppressed by the presence of nitrate ions in the system. As the nitrate concentration increases (Samples 2 through 5 in increasing order), the characteristic shape of the fluorescence is suppressed.


Students continued to develop concepts and models for use of the $^3$He Neutron Multiplicity Detector System (NMDS) for Materials Protection, Accounting, and Control, including testing with a carbon neutron slowing down spectrometer (CSDS) at the Idaho Accelerator Center (IAC) and for monitoring process streams (for one concept, see Figure 30). The NMDS was upgraded with a new digital data acquisition system (DAQS) and computer for acquiring and processing data at higher count rates such as those that would be expected from fissile materials in process. Planning is now underway to conduct experiments at the IAC with the CSDS in January.
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).

This project was initiated in September 2006. This report covers research performed from July 2006 that was used as the basis of this project and was performed in collaboration with Dr. Gordon Jarvinen of Los Alamos National Laboratory. The experiments in this quarter examined the sorption of TcO$_4^-$ to cation exchange resins and the preparation of Tc metal from the sorbed TcO$_4^-$. The resins Dowex Marathon and Reillex resins are examined. Three separate studies were performed:

- Thermal gravimetric analysis (TGA) of the resins
- Batch sorption of TcO$_4^-$ to the resin
- Pyrolysis and steam reforming of the pertechnetate sorbed to the resin

The steam reforming of the Tc-resin material resulted in the formation of Tc metal.

**TGA Analysis of Resins**

The Dowex Marathon and Reillex resins were evaluated by TGA to determine the appropriate temperature profile to achieve high resin mass loss during pyrolysis or steam reforming. Approximately 10 mg of each resin was placed in a Retsch TGA under Ar atmosphere. The temperature was ramped at 10 °C/min from 22 °C to 930 °C. The results are presented below (Figure 31). Both resins exhibited high mass loss beginning at 400 °C, reaching stable masses near 600 °C. The Dowex Marathon resin had only 40 % mass loss while the Reillex resin showed over 90 % mass loss. The TGA data was used to develop a method for the resins pyrolysis and steam reforming. Based on the TGA data, the initial step in the pyrolysis will be heating the sample under Ar to 450 °C for 1 hour to remove the bulk of the resin mass. The temperature will then be increased to 750 °C at held for 1 hour.
Batch sorption studies of $\text{TcO}_4^-$

The batch sorption of Tc to the resins was evaluated with two different Tc concentrations. The lower concentrations were used in initial pyrolysis studies to confirm no formation of volatile Tc aerosols. For each study 100 mg of resin was placed in a vial containing 10 mL of 0.01 M HNO$_3$. In the initial study the solution phase concentration was $8\times10^{-6}$ M $\text{TcO}_4^-$ and the second study use $0.02$ M $\text{TcO}_4^-$. The kinetics of $\text{TcO}_4^-$ removal from solution are examined for both Tc concentrations. In these experiments 200 µL samples are periodically removed from the solution phase and added to 10 mL of scintillation fluid to determine Tc solution concentration. The Reillex resin demonstrated superior extraction $\text{TcO}_4^-$ (Figure 32 and Figure 33). Furthermore, the resulting Tc sorption kinetics for Reillex resins are superior compared to the Dowex Marathon resin (Table 1). Based on the Tc sorption kinetics and TGA data, it appears the Reillex resin has superior properties for Tc waste form formation from pyrolysis.

Figure 31. TGA of Dowex Marathon and Reillex Resins under Ar.
Figure 32. Kinetics of TcO₄⁻ removal from solution with initial [TcO₄⁻]=8E-6 M by Dowex Marathon and Reillex resins.

Pyrolysis and Steam Reforming

The initial study examined the resin material with sorbed Tc with a total [Tc]=8E-6 M. A pyrolysis procedure was examined to evaluate if any aerosols containing Tc were produced. The resins were placed in a platinum envelope and set in a crucible which was then placed into a tube furnace under Ar atmosphere. The temperature was increased to 450 ºC and held at that temperature for 1 hour, then increased to 750 ºC and held at that temperature for a further hour. During this time the Ar atmosphere flowed through the furnace and upon exiting the tube entered two 500 mL traps of 0.25 M NaOH. The traps were periodically sampled and evaluated for Tc by scintillation counting. No Tc was found to enter the traps indicating the absence of volatile Tc compounds.
Figure 33. Kinetics of TcO$_4^-$ removal from solution with initial [TcO$_4^-$] = 0.02 M by Dowex Marathon and Reillex resins.

The next study examined the resins from the 0.02 M Tc batch solutions. The 100 mg resin samples were placed in Pt envelopes and separately subjected to pyrolysis under Ar for 1 hour at 450 °C and held at that temperature for 1 hour, then increased to 750 °C for another hour. The resulting product was black in color with the shape of the resin beads. X-ray diffraction analysis of both the Dowex Marathon and Reillex indicated both samples were amorphous with no indication of Tc metal.

The pyrolyzed Tc containing resin material was subjected to steam reforming by diverting the Ar into a water filled bubbler prior to its entrance into the furnace. The furnace temperature was increased to 900 °C and held at this temperature for 6 hours. The resulting product was grey in color and retained the shape of the resin bead. X-ray diffraction analysis showed the grey material to be Tc metal (Figure 34). Optical microscopy showed the metal to have the shape of the resin (Figure 35).
Figure 34. XRD Analysis for Dowex Marathon Resin with Sorbed Tc after Steam Reforming. The result shows the formation of Tc metal.

Figure 35. Optical microscopy of Tc metal from steam reforming of Tc sorbed to Reillex resin.
TRANSMUTATION SCIENCES

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

This project is focused on the evaluation of residual stress in candidate target structural materials by both destructive and nondestructive methods. The most recent studies were performed involving welded specimens of similar and dissimilar materials to characterize defects such as dislocations at different regions of the welded specimens by transmission electron microscopy (TEM). In addition, an activation technique, based on the positron-annihilation-spectroscopy (PAS) was used to characterize residual stresses in these specimens in terms of three line-shape parameters, S, W and T. While the S-parameter is directly proportional to the residual stress, W and T-parameters are inversely proportional to the internal stresses.

Figures 36 and 37 provide results for the T-parameter and TEM micrographs. Table 2 provides the dislocation density at various locations.

![Figure 36. T-parameter versus Distance from Fusion Line for welded specimens of similar materials.](image-url)
Table 2. Magnitude of $\rho$ at different locations.

<table>
<thead>
<tr>
<th>Weld Configuration</th>
<th>$\rho$ (No./m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Base Material</td>
</tr>
<tr>
<td>304L SS/304L SS</td>
<td>$5.1 \times 10^{13}$</td>
</tr>
<tr>
<td>EP-823/EP-823</td>
<td>$7.6 \times 10^{13}$</td>
</tr>
<tr>
<td>304L SS side of 304L SS/EP-823</td>
<td>$1.7 \times 10^{13}$</td>
</tr>
<tr>
<td>EP-823 side of 304L SS/EP-823</td>
<td>$6.5 \times 10^{13}$</td>
</tr>
</tbody>
</table>

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

Gas phase experiments were initiated, which are models of the corrosion of the steels in LBE. A CuO/Cu oxygen source in an evacuated quartz envelope is in use to set the oxygen levels in the gas phase to be similar to those in LBE. The initial stages of oxidation were examined, which is of critical importance to the behavior of steel in LBE, particularly after damage to the initial protective oxide layer. There are some austenitic 316 class steel samples as well as iron-silicon alloy samples to determine the role of silicon in corrosion protection in LBE.

**Gas phase Experiment 1**

Raman studies – Spectra taken on all gas phase samples (Figure 38) show that the major oxide on the surfaces is Fe$_3$O$_4$. 

![Figure 37. TEM micrographs of Type 304L SS/Alloy EP-823 welded specimen (Type 304L SS side).](image1)

![Figure 37. TEM micrographs of Type 304L SS/Alloy EP-823 welded specimen (Type 304L SS side).](image2)
Figure 38. Spectra of gas phase samples taken with Raman spectroscopy.

Scanning Electron Microscope – The oxide layers created on Fe-Si alloys (Figure 39) show that their thickness and porosity decreases with the increase of silicon content in the alloys.

![Figure 39. Scanning Electron Microscopy images of gas phase samples.](image)

The oxide layer formed on 316 annealed is discontinuous and is about 2.8μm thick while 316 cold rolled samples show localized oxidation (Figure 40).
Figure 40. Scanning Electron Microscopy images of gas phase samples.

X-ray Photoelectron Spectroscopy (XPS) – XPS studies have found that the surfaces of the steels were particularly prone to segregate and enhance the minor elements in the system. This behavior is well known: temper embrittlement is a result of segregation of (e.g.) tin to the surface of the steels. Gas phase experiments have shown these minor constituents whereas the LBE exposed steels have had their surfaces “cleaned” by dissolution of surface components. In any event, the presence of these minor elements will certainly be present in the LBE and thus potentially active in corrosion.

Sputter depth profiling of samples show enhancement of iron (for iron-silicon alloys) and enhancement of chromium (for stainless steels) near the surface. This confirms the identification of iron oxide (for iron-silicon alloys) and chromium oxide (for stainless steels). The sputter depth profile study of the Fe3Si sample (3.83 wt. % Si) in Figure 41 shows the effect of silicon in protecting the alloy from further oxidation. Silica (SiO2 in iron-silicon alloy) and chromium oxide (in stainless steel) are thought to play important roles in developing a protective oxide layer.

The possible concentration of free oxygen in LBE is limited by the formation of lead oxide. The dissociation equilibrium pressure of oxygen above lead oxide at (e.g.) 870 K is very low, on the order of $10^{-16}$ atm ($10^{-13}$ torr). UHV surface science practice shows that there is an upper bound that can be established for the formation rate of surface species. The surface layer can grow no faster than the incidence frequency of the reactant on the surface multiplied by the reaction probability. The relevant quantity, pressure • time, is the Langmuir, the pressure • time necessary to make on average one collision on every surface atom in a standard metal. One Langmuir is $10^{-6}$ torr seconds. One layer of oxide can form no faster than one atom layer per second at an oxygen partial pressure of $10^{-6}$ torr in the gas phase experiments. At $10^{-13}$ torr, $10^7$ seconds would be needed to form a single monolayer of oxide. Clearly this is not happening in LBE.
Figure 41. Sputter depth profile of Fe3Si.

Conceptually, a very thin vacuum layer is being placed between the LBE and the steel – this either may be underestimating the flux of oxygen to the steel, or another oxygen containing species is active in the formation of the oxides on steel in LBE. The most likely oxygen containing species seems to be water: At the operating temperatures any hydrogen (ubiquitous in steel) in the vicinity would allow the formation of water, and water is non-reactive to lead (hydrogen is more electropositive than lead) and not detected by the zirconium oxide sensors currently being used to track oxygen levels in LBE. Experiments using the KALLA Oxygen Control System are being planned to look at the oxide layer formation on steel with constant oxygen concentration but changing water concentration in the cover gas above an LBE corrosion experiment. Water in oxidation of steel tends to lead to porous oxides, similar to what is observed in LBE.


This task is primarily focused on the evaluation of the effect of silicon (Si) content on the susceptibility of modified 9Cr-1Mo-0.24V steel to stress corrosion cracking (SCC) and localized cracking in both molten lead-bismuth-eutectic (LBE) and an aqueous solution of acidic pH. Further, significant efforts are in progress to characterize the deformation mechanism of modified T91 grade steel as a function of temperature and strain rate. Simultaneously, surface analyses of the tested materials are ongoing using state-of-the-art techniques including scanning electron microscopy (SEM) and transmission electron microscopy (TEM). In addition, the characterization of phases due to the transformation at the testing temperatures is in progress using X-ray diffraction (XRD) technique.

Stress-strain diagrams for T91 grade steel with Si contents of Development of high temperature deformation mechanisms as a function of Si content of 0.5, 1.0, 1.5, and 2.0%, are shown in
Figures 42-45, respectively. SEM micrographs of T91 grade steel with 1.5 and 2.0% Si content at various temperatures are shown in Figure 46.

Figure 42. s-e diagram for T91 grade steel having 0.5% Si.

Figure 43. s-e diagram for T91 grade steel having 1.0% Si.
Figure 44. s-e diagram for T91 grade steel having 1.5% Si.

Figure 45. s-e diagram for T91 grade steel having 2.0% Si.
Oxide Film Growth Modeling in LBE Systems (Task 21).

Cellular automata modeling of oxide layer growth with scale removal.

To simulate the scale removal effect on oxide layer growth, the previous cellular automata model of oxide layer growth was improved by considering a scale removal effect. In the present model, the scale removal rate is taken as linear. It is assumed that the oxide layer sites which are close to the oxidant site have a possibility $P_r$ to move away. In this instance, it is 0.004. The global random walker model is still used to simulate the solid state diffusion of the ionic metal site in the oxide layer. Figure 47 shows the snapshots of simulated layer at different time steps. From the figure, it can be found the scale removal rate has an evident effect on the upper surface of the oxide layer. Due to the scale removal, the Wagner theory is not suitable to interpret the oxide layer growth. The phenomena of oxide growth can be explained under the frame of the Tedmon theory. As shown in Figure 48, an increase followed by linear decrease on the outer oxide layer position can be found.
Figure 47. Snapshots of the simulated layer in the presence of corrosion with scale removal. They correspond to a 2.5×10⁴ time step. The red dot is oxide site; the blue dot is walker site. Upper side of layer is filled with solvent. Lower side of the oxide layer is pure metal. The corrosion probability of metal is taken as 0.5. The possibility of scale removal of oxide site close to solvent is 0.004.

Figure 48. Averaged front position as a function of time.

Stochastic modeling with cellular automata method on the surface growth and internal oxidation

The quantitative cellular automata model of the inward oxidation mechanism was developed. The stochastic rule to the population of particles is based on the exclusion principle. Considering the exclusion principle which permits at most one particle per site, a particle moves to its targeted site if this site is free and simply does not move if the site it targeted has already occupied. To avoid the conflict between particles competing for a single free site, the following
rule was adopted. When more than one particle attempts to move to a single open site, only one of the competing particles, which will be chosen randomly from among them, is allowed to move to this open site and the others do not move. Figure 49 shows the benchmark of the developed numerical model with the theoretical solution. A good agreement between cellular automata modeling and theoretical solution was achieved.

![Graph showing the benchmark of the developed numerical model with the theoretical solution.](image)

**Figure 49. Distribution of oxygen concentration at 0.5 hour.**

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

**Multi-layer dense alumina**

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 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 this replacement. Ni nanowires inside nanoporous alumina created on steel substrates was carried out using the procedure developed earlier. In parallel, samples were also created on silicon samples to aid in cross-sectional imaging. The Ni nanowires and the nanoporous alumina layers were then coated with a thick layer of dense alumina deposited by pulsed DC sputtering. While the pulsed DC sputtering technique allowed the deposition of thick layers of dense alumina, the deposited layers showed some defects that traveling from the substrate to the top.

A detailed study was carried out to reduce the defect density by adjusting the process parameters; however, it could not be significantly reduced. It was clear that the defect density was arising due to room temperature deposition of the dense alumina, and a high temperature annealing step would eliminate them. However, such high temperature annealing or high temperature depositions were not carried out to avoid compromising the experimental testing. It may be
noted, that in real life application, thermal cycling would most probably anneal all the defects. To circumvent this problem, a technique was developed for a two-layer dense alumina deposition. The first layer was deposited using electron-beam evaporation, a technique that creates very uniform and defect free layers, albeit very thin layers. For this purpose, alumina charge was obtained and the electron beam evaporation system in the UNLV Nanodep system was used to carry out to deposit the first thin layer. Following this, a thick layer of dense alumina was deposited using the pulsed DC sputtering technique. The thin layer of dense alumina is expected to stop propagation of the defects from the sputter deposited film and the nanoporous layer.

Sample Preparation for Testing

The preliminary samples created by the technique described above were characterized under the microscope. One problem became evident under inspection. Since the dense alumina layer was physically connected to the steel substrates, it was believed that the thermal cycling results would be compromised. To address this, samples were created such that the top dense alumina layer was disconnected from the steel substrates. A schematic of the structure is shown in Figure 50. A special masking scheme had to be developed to create these samples.

![Figure 50. Schematic cross-section of specially masked samples to separate the dense alumina layer from the steel substrate.](image)

Furnace Installation

To carry out the thermal cycling testing of the samples, a furnace with the capability of going up to 600 C was purchased and installed. The furnace installation was delayed due to circuit problems, however, the problems were addressed and the furnace connected finally. The furnace installation required extensive installation of high temperature exhaust and air intake systems. The furnace is currently being programmed for testing of the samples.
Reactor Physics Studies for the AFCI RACE Project (Reactor-Accelerator Coupling Experiments Project (Task 27)).

The High-power RACE Target was transported to the ISU Idaho Accelerator Center in August for further tests to measure neutron generation and heat transfer while coupled to an electron linac. An accelerator-driven neutron production experiment was conducted and the temperatures were recorded at several points.

UNLV collaborated with ISU and CEA in a series of accelerator-driven subcritical (ADS) experiments at the Idaho Accelerator Center. Accelerator-driven subcritical experiments were conducted 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. Twenty experiments were conducted to measure breakpoint frequency of the coupled system at reduced criticality with just 142 of 150 enriched-uranium fuel plates loaded in the SCA. In addition, several flux stability measurements were made using the full core and a variety of frequencies, currents, and pulse widths. Other experiments included a long-duration reference pulsed-neutron-source experiment, a beam trip experiment, and a variable criticality experiment, which was conducted by observing the neutron response while water was drained from the SCA.

The RACE Project is being concluded with several universities and several European organizations. These organizations have contributed to several aspects of the RACE Project, including target design and analysis for High-Power RACE. Contracts supporting RACE Project work at the University of Michigan, Texas A&M University, and University of Texas at Austin ended during the summer, the Idaho participation will be terminated in December, and the UNLV portion of the RACE Project will end next summer.

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

The processes of heating-up, cooling-down, non-circulation and circulation with the electrical magnetic pump running for the Russian-built TC-1 loop were studied based on experiments conducted in IPPE (Obninsk, Russia) in 2001 and experiments conducted at UNLV in 2005. As shown in Figures 51 and 52, temperatures of different zones were not well controlled within the designed range. Temperatures for all zones were expected to be within the range of 190°C-200°C. Instead, the temperature difference (maximum and minimum) for all heating zones was about 80°C.

Experimental studies of different heating zones were carried out to obtain the system identification individually. The system identifications were achieved by heating up one zone from room temperature to 50°C, while keeping others off. 50°C was selected to avoid large temperature differences. The transfer functions, which are used to describe dynamic response of a system, were identified and showed strong agreement between the experimental data and the predicted data by the transfer function.

Some mistakes were found in the parts of the heating rate calculation, the heating control loop, and the alarm loop for the previous version. One 24-hour monitoring device was installed and
wired to the main program. It can automatically dial out when temperature is too high or if there is abnormal current passes through EM pump. The current transformers were assembled to detect actual heater ON/OFF statuses. Signals were regulated and recorded by a data acquisition system.

Based on the correction and modification of existing control program, the current control algorithm has shown a significant improvement. The heaters of all heating zones were well controlled to maintain temperatures of all zones within the desired range, as shown in Figure 53. The difference between maximum and minimum is only about 5 °C.

Figure 51. Temperature profiles of all zones (desired range is 190°C-200°C) from experiments conducted in Obninsk, Russia, in 2001.

Figure 52. Temperature profiles of all zones (desired range is 190°C-200°C) for experiments conducted at UNLV, 2005.
Figure 53. Temperature profiles of all zones after algorithm modification at UNLV in 2006. Temperatures were within the desired range of 190°C-200°C.

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

The goal of this new 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 nuclear applications. The main effort for this year lies in the following subtasks:

- A literature review will be conducted in order to collect information on topics pertinent to EM pump design. These topics will include the equations governing the physical phenomena occurring in EM pumps and mathematical algorithms used in modeling these physical phenomena, different EM pump configurations, and the effects of materials properties on pump performance. The information gathered in this literature review will be consolidated into an overview report and the individual papers will be available in an online database.
- Computational models of the TC-1 loop at UNLV will be developed using the information gathered from the literature review.
- The results from the computational models will be evaluated by comparing them with experimental data taken on the TC-1 loop.
- A parametric study of the TC-1 loop will be conducted. Operating conditions, materials properties, and geometric parameters will be varied to gain an understanding of those conditions that have the greatest impact on pump efficiency.

Although this project is just getting started, significant work has begun. Approximately 100 papers have been reviewed and they are being organized into an online database for easy access by the other researchers involved in the project.
Work is being performed to expand the initial computational model. One of the biggest assumptions made in the initial model was to treat the discrete, source current coils as an idealized current sheet. Although this assumption was sufficient to validate the numerical aspects of the model, there is some question of how well it reflects coil configurations with either high coil aspect ratios, and/or large coil pitch. A variety of commercial and in-house software packages are being evaluating to address this issue.

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

The project was initiated in September 2006 with discussions with LANL, ORNL, and ANL regarding project scope and direction. The appropriate division of effort between cross-section sensitivity studies and design of required criticality experiments, such as measurement of thermal feedback coefficients in dilute mixtures of plutonium with varying isotopic constituents, needs to be determined. The project will likely focus on sensitivity studies similar to those that ANS is conducting for several types of reactors within the AFCI. At UNLV, separations processing facilities and components as opposed to critical cores will be concentrated upon. Students began to collect references on criticality and sensitivity studies.

**Deep Burn Separations and Repository Behavior.**

*Fluorination studies*

The fluorination studies on SiC with NH₄FHF were performed by the UNLV team. No degradation of the SiC was observed.

*XAFS studies*

The SRNL team provided assistance to Dr. Frederic Poineau with the U- and Tc-EXAFS data collection and data analyses while at the APS during the August 2006 experiment. The SRNL team arranged for the safety aspects and assisted with the experiments. Actinide Sample Boxes were developed and produced for future XAFS experiments. The UNLV team performed further data analysis from the August 2006 XAFS experiments and will incorporate the data into a publication. The SRNL team provided a final report on its activities.

*Ligand Development*

The goal of this research is to develop a rational, scalable method to separate Am from 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 Am³⁺ from Cm³⁺. The proposed ligand groups exploit the principal 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.
DTPA dianhydride was reacted with per-6-(2-amino(ethylamino))-β-cyclodextrin to yield a tri-functionalized cyclodextrin which is observable via mass spectrometry (m/z = 2497). However, the purification of this derivatized cyclodextrin has proven difficult. Additional attempts at purification or new synthetic routes will be carried out in the near future.

Acid-base titrations of the sodium salt of per-6-thiopropionate-β-cyclodextrin with the lanthanides have been completed. The $\log \beta_{110}$ for the ligand with each lanthanide are shown in the Figures 54 and 55 and Tables 3 and 4. For comparison to the sodium salt of per-6-thiopropionate-β-cyclodextrin, the data for the sodium salt of per-6-thiopropionate-β-cyclodextrin has been included.

![Figure 54. $\log \beta_{110}$ for ligand with each lanthanide.](image-url)
Table 3. $\log \beta_{110}$ for ligand in Figure 54 with each lanthanide.

<table>
<thead>
<tr>
<th>Lanthanide</th>
<th>$\log K_{110}$</th>
<th>Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
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<td>0.48</td>
</tr>
<tr>
<td>Ce</td>
<td>27.12</td>
<td>2.61</td>
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<tr>
<td>Pr</td>
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<tr>
<td>Nd</td>
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<tr>
<td>Eu</td>
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<tr>
<td>Tb</td>
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<tr>
<td>Dy</td>
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<tr>
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<tr>
<td>Yb</td>
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<td>0.97</td>
</tr>
<tr>
<td>Lu</td>
<td>19.13</td>
<td>0.76</td>
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</table>

Figure 55. $\log \beta_{110}$ for ligand with each lanthanide.
Table 4. log $\beta_{110}$ for ligand in Figure 55 with each lanthanide.

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<th>Lanthanide</th>
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<th>Std. Dev.</th>
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<tr>
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<tr>
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<td>1.55</td>
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