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AFCI Quarterly Input: UNLV January 1 through March 31, 2007

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

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AFCI Quarterly Input – UNLV
January 1 through March 31, 2007

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:

- The new UNLV President David Ashley visited the Harry Reid Center on January 4 to meet with division directors and tour the facilities. He particularly expressed his interest in hearing about the Transmutation Research Program.
- The UNLV College of Engineering hosted an Advanced MCNPX Workshop Jan 8 to 12. Attendees included a large contingent from UNLV, plus staff members from Los Alamos, Nevada Test Site, Idaho State University, and other organizations.
- The American Nuclear Society issued “Nuclear’s Human Element: Defining the Federal Government’s Role in Sustaining a Vibrant U.S. University-Based Nuclear Science and Engineering Education System for the 21st Century.” Denis Beller from UNLV was a member of the President’s Special Committee on Federal Investment in Nuclear Education, which produced the report between August and December 2006. The report is available from the ANS website at http://www.ans.org/pi/fine.
- Todd Allen, University of Wisconsin, visited UNLV on February 1 and toured facilities as part of a User Facility study for DOE-NE.
- Anthony Hechanova was an invited panelist for “Electricity from Nuclear Energy” at the Energy Forum hosted by the Nevada Tourism Alliance on March 27.
- Nine students and faculty presented the following papers at the American Chemical Society conference, March 25-29.
  - N.A. Smith, G. Cerefice, and K. Czerwinski, “Use of UV-Vis spectroscopy and TRLFS for material accountability in solvent extraction processes.”
  - C.-M.S. Gong, F. Poineau, and K. Czerwinski, “Synthesis and characterization of the solid uranyl-acetohydroxamic acid complex.”
  - T.A. Robinson, D.R. Peterman, and R.S. Herbst, “Distribution of C-14 labeled PEG-400 in the HCCD-PEG solvent extraction system.”
  - K. Czerwinski, “Needs for americium and curium isotopes in advanced fuel cycle research.”
  - A.D. Wright and K. Czerwinski, “Nitrate effects on uranium and plutonium extractions.”

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
- Tyler Sullens was hired after a search for a Research Professor in Radiochemistry as the replacement for Thomas Hartmann who accepted a faculty position at Idaho State University.
- Three candidates were interviewed for a tenure-track faculty position in Radiochemistry.

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.

1.2.2 International Collaboration Highlights
- Vladimir Novosselov, professor from the Ural Subsidiary of Federal Government Service Academy, Chelyabinsk, Russia visited UNLV January 12 to discuss the history of the former Soviet Union nuclear fuel cycle.
- UNLV has acquired the services of Leslie Jardine to participate in the development of relationships with Russian organizations.

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 15 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 commissioned and taken into operation.
- First Cs/SiC electron spectroscopy experiments (X-ray and UV photoelectron spectroscopy) on SiC single crystal surfaces with significant oxidation were performed.
- First experiments with the new scanning probe microscope were performed on selected Cs/SiC samples.
- Cs/SiC samples were investigated with X-ray Emission Spectroscopy during the March experimental run at the Advanced Light Source, Lawrence Berkeley National Lab. Data evaluation is ongoing.

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

Highlights.

- The Soxhlet experiment continued with uranium-containing ceramics.
- A quantitative analysis was performed with a microprobe to determine the stoichiometry of phases present.
- X-ray fluorescence was used to determine the composition of an entire pellet for each composition.
- Rietveld refinement was performed on x-ray diffraction patterns to determine lattice parameter and quantify phase constitution.
- New pellets were synthesized from calcined material so that dissolution studies can be performed.

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

Highlights.

- Work continued on the visual servoing of robots inside the hot cell with focus on camera calibration and spatial range measurements from two spatial locations (stereo vision).

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

Highlights.

- Denitriding of UN2 at 1000 C was completed, and phase distributions of the samples were determined using Rietveld analysis of the XRD patterns.
- The same synthesis route was used to obtain the kinetic data at 1050 C.
- U2N3 conversion to UN at 1100 C was repeated for two different time periods using small amounts (< 15 mg) of U2N3. With these amounts the UN formation was completed before 25 minutes. These results showed that there are other physical variables that affect the rate of the UN formation from U2N3. However, for the current research this is beyond the scope of our interests since we already obtained the kinetics information of UN2 to UN reaction through U2N3.
- Results were obtained for the conversion of UN2 to UN at three different temperatures (1000, 1050, and 1100 C) and were used to determine rate coefficients and activation energy of the reaction.
• EMPA quantitative analyses of the three nitride species UN$_2$, U$_2$N$_3$, and UN showed that there are small amounts of oxygen in the first two samples. In the case of UN, the elemental distributions are close to the values that have been determined using powder XRD.
• Another batch of UN$_2$, U$_2$N$_3$, and UN were synthesized to further explore the chemistry of these compounds using EXAFS.
• Ammonolysis of ThF$_4$ at three different temperatures: 800, 1000, and 1100 °C was conducted at different time periods. Final product of the ammonolysis was identified to be ThNF which has a rhombohedral type lattice with $a = 7.13$ Å and $\alpha = 32.66^\circ$. Ammonolysis of (NH$_4$)$_4$ThF$_8$, which is the final product of ThO$_2$ reaction with NH$_4$HF$_2$, at 800 and 1000 °C also directed to the same final product (ThNF).
• Decomposition of ThNF to form thorium nitrides such as Th$_3$N$_4$ or ThN under Ar, Ar-H$_2$ (5%), or N$_2$ at 1100 °C was not successful and only led to the formation of ThO$_2$, ThN$_{0.90}$F$_{1.30}$, and some unidentified phases. At 1400 °C, ThNF was completely changed to UO$_2$ after one hour heating under N$_2$.

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

• Initial studies were conducted, including liquid ammonia generation and storage, uranium metal storage in the glove box, iodine dissolution in liquid ammonia, and test reactions between elemental iodine and U metal.
• An inventory of existing equipment and supplies was conducted, and a significant amount of synthetic glassware, supplies, and necessary gasses were ordered and received for preliminary experiments.
• Specific safety training was necessary due to the nature of the synthesis and was completed by all research personnel.
• Reviews of literature and background investigations are ongoing.

**SEPARATIONS TECHNOLOGY**

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

• Continued to explore synthetic approaches to produce MnO$_2$ suitable for the oxidation of iodide.
• Continued the measurements of iodide oxidation with various MnO$_2$ preparations at pH 4.
• Developed a method for measuring iodine production and Mn(II) formation in the same reaction mixture.
• Used the Mn(II) and iodine measurements to estimate oxidation states for various manganese oxide preparations.

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

• The first version of the interface between ASPEN-Plus and the ISOPRO system model was completed based on the modified simulation flow chart defined in the previous quarterly report.
Electrochemical Separation of Curium and Americium (Task 25) Highlights.

- Evaluated the electrochemical response of room temperature ion liquids (RTIL).
- Constructed reference electrodes for RTIL solution studies.
- Performed additional Ce/EDTA studies in aqueous solutions to clarify the redox/couple response versus background.
- Prepared complexes of Ce, Sm, Eu with trifilate ion to enhance solubility in RTIL.

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

- Crystal Structure of Uranyl-AHA: microplates were set up to explore a large variety of crystallization conditions. Crystal plates from mixtures of saturated H2O and DMSO solutions gave crystals under high-DMSO conditions, as did the DMSO stock solution of UAHA. A new grid was set up using filtered solutions, mixing the DMSO and water before saturating the solution with UAHA.
- Experiments on the effect of pH on extraction of uranyl from aqueous AHA system: 1 mM U was titrated from 1.2 to precipitation with no AHA and 2, 10, 50, 100, and 500 mM AHA at I=1.0 M (NaClO4). Experiments on the effect of AHA concentration on extraction of uranyl into organic phase: 10 x excess AHA was maintained. 1, 10, and 100 mM uranyl perchlorate were titrated; I = 1.0 M (NaClO4).
- Development of an alternate method for UAHA synthesis: Began with 100 mM uranyl nitrate, 1 M AHA. Titrated above pH 1.4. UAHA precipitated. Identical to solid-synthesis material via IR.
- The extractions were completed on the titrations of uranyl perchlorate with varying [AHA] into 100% TBP and 30% TBP/dodecane. UV-vis spectra corrected for [U] show that AHA is extracted more with increasing pH, changing the spectrum of the organic phase.
- NMR preparation: D2O constituents were exchanged for NMR studies.
- Laser Fluorescence of solids: took TRLFS of uranyl nitrate dihydrate, D2O exchanged and H2O, began freeze-drying process for uranyl nitrate H2O and D2O.
- FeU redox cycle: previously noted what appeared to be U(IV) oxide when Uranyl-AHA system was exposed to Fe3+. Microplates were set up with varying [Fe] to try to replicate.
- Uranium organic standard was prepared. It was contacted with pre-equilibrated 30% TBP/dodecane. Extraction was performed at 1M HNO3. Two different UO2(NO3)2 solutions were used to prepare two standards: 10 mL of 0.47M U and 50 mL of 0.033M U. Concentrations were measured on ICP-AES and LSC.
- Nanoparticles/self-assembling monolayers: Green gel was formed when TRLFS was taken from the organic phase of uranyl nitrate, uranyl perchlorate extractions with and without AHA. It is proposed that the green gel is from photochemical U(VI) -> U(IV) reduction using TBP as the e- donor. TEM shows that the gel self-assembles into a semi-crystalline monolayer from a methanol solution on the Cu/C slide. SEM shows that the dried/washed gel is made of green amorphous nanoparticles (150 x 300 nm). UV-vis of supernatant after gel is spun out shows only U(VI) uranyl.
• Third Phase studies: HClO₄ and NaClO₄ was mixed in varying ratios into 30% TBP; third phase formation was observed as low as 5.5m total HClO₄, 1.25M H⁺.
• Organic and aqueous phases of samples prepared in February were titrated by: Organic phase (pre-equilibrated TBP/dodecane at 1M HNO₃); Aqueous phase (1M HNO₃, 0.02 M UO₂(NO₃)₂, and LiNO₃ concentration from 0-10 M); and, Separated organic and aqueous layers.
• Samples were prepared for ICP-AES versus LSC comparisons. Samples were both aqueous and extracted organic uranium. Samples were also made by the same method except addition of ~1500 Bq²³³U for comparison. Aqueous samples were run on ICP-AES. Aqueous and organic samples were run on LSC.
• Complexation of Tc with AHA was examined including the kinetics of TcO₄⁻ reduction. Extraction of complex into TBP was evaluated.


• Determined the limits of linearity for detection of uranium by laser fluorescence (TRLFS) in aqueous process streams
• Investigation of the determination of uranium in the organic stream for the UREX process was initiated.


• Modeling of the Neutron Multiplicity Detector System (NMDS) was expanded and improved. K and t-zero values (energy-time correlation constants) were calculated for lead and carbon slowing down spectrometers for comparison to previous studies.
• Several programming and maintenance issues with the NMDS that were revealed during testing in December were repaired and/or resolved. New detector wiring that was installed on the NMDS significantly reduced background count rates (noise).

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.

• TEM analysis of Tc metal and TcO₂: Determination of lattice parameter of Tc metal was made using HRTEM, EDAX and EELS.
• Fabrication of a Tc metal electrode: Determination of corrosion potential of Tc metal (Tc → TcO₂) in (H₂O, 0.1 M NaTFMS).
• Optimization of Tc metal production by steam reforming of Dowex and Reillex resins: Work done in collaboration with LANL (Jarvinen). Pyrolysis performed at 900 C, 800 C and 700 C under nitrogen. Analysis by XRD of solid produce at 700 C indicates formation of Tc metal for both resins. Separation of U/Tc using Reillex resin on a column was also performed.
• Behavior of NH₄TcO₄ under NH₃ was examined at different temperatures (200, 350, 700, and 750 C). Analysis by XRD and TEM microscopy was conducted. At 200 C, there was no reduction of NH₄TcO₄. At 350 C, formation of amorphous phase (Tc metal) was
observed. At 700 C and 750 C, the formation of a crystalline compound was observed. TEM and EDAX indicate formation of a new metallic phase.
• Cyclic voltammetry and extraction of Tc were studied in TBP.

TRANSMUTATION SCIENCES

Corrosion Mechanisms and Kinetics of Steels in Lead-Bismuth Eutectic (Task 18) Highlights.
• Samples of D-9 steel, exposed to LBE, were investigated using nano-indentation at LANL.
• Gas Phase III experiments: exposed samples were studied by XPS, SEM, and Raman.
• Studies are continuing on the role of water oxidation of steels in the gas phase (and, by analogy, LBE) at low oxygen concentration.
• Numerous samples for LANL were analyzed

• Tensile testing was performed using T91 grade steels at 300, 400 and 550 C under strain rates of \(10^{-2}\), \(10^{-3}\) and \(10^{-4}\) sec\(^{-1}\).
• The variations of stress with strain at 300, 400 and 550 C were studied.
• Four different heats of T91 grade steel were tested for evaluation of their localized corrosion behavior. These steels contained Si levels of 0.5, 1.0, 1.5 and 2.0 wt%.
• A consistent pattern on the effect of temperature on the cracking susceptibility of two heats (1 and 2 wt% Si) in terms of percent elongation (%El), percent reduction in area (%RA), time to failure (TTF) and true failure stress (\(\sigma_f\)) was observed in slow-strain-rate testing.

Oxide Film Growth Modeling in LBE Systems (Task 21) Highlights.
• An improved cellular automation model of the oxide growth coupled with inward oxygen diffusion has been established and the benchmark of cellular automaton model for pure oxygen diffusion was completed.
• The molecular dynamics (MD) technique on modeling of corrosion and oxidation behaviors is being investigated.

Corrosion Barrier Development for LBE Corrosion Resistance (Task 23) Highlights.
• A new technique was developed for the synthesis of nanowires through the incorporation of nanoparticles, which has the potential to improve thermal recycling characteristics compared to nanowires.
• The fabrication of a new batch of samples using the new route was initiated for testing the integrity of the corrosion barrier coatings under thermal cycling.
• The process for the deposition of Cr nanowires was improved that showed increased spatial uniformity.
Reactor Physics Studies for the AFCI RACE Project (Reactor-Accelerator Coupling Experiments Project (Task 27) Highlights.

- Evaluation continued of the ISU experiments conducted in collaboration with CEA (France) during the RACE-ECATS phase of the project.
- Evaluation continued of the experimental thermal and neutron generation with the UNLV High-power RACE target (experiments were conducted at ISU).

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

- The alarm system is ready for long term operation.
- The disturbance rejection algorithm was studied and tested for the TC-1 loop.

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

- An on-line database of articles and papers related to EM pumps has been expanded and currently contains over 130 entries.
- The preliminary development of the CFD module of a coupled MHD/CFD solver was completed. Testing against analytic cases is under way.

Criticality Studies for UREX Processes (Task 35) Highlights.

- Collaboration was initiated with Georgia Tech and UNM for NERI-C.

1.3.3 Student Research Technical Reports

FUELS TECHNOLOGY

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

The focus in this quarter was on the investigation of the Cs/SiC interface. For this purpose, the Cs evaporator was commissioned and a series with Cs films of different thickness on SiC were prepared. UPS and XPS experiments were performed for each Cs film thickness.

In Figure 1, the XPS survey spectra for different Cs evaporation times (and hence different Cs film thicknesses) are shown. To clean the SiC surface, the SiC single crystal was etched in HF and subsequently heated to ca. 500 C in vacuum. As visible in the spectra, the O contamination cannot be fully removed by etching and heating. After Cs evaporation, all expected Cs lines can be found in the spectra. The intensity of the lines, which can directly be related to the film thickness, increases for increasing deposition time, as expected. In parallel, the lines of the SiC substrate, namely C 1, Si 2s, and Si 2p decrease in intensity due to the attenuation by the covering Cs layer.
Currently, a quantitative analysis of the individual XPS peaks (detailed spectra not shown) is in progress. Nevertheless, judging from the survey spectra, first trends can already be derived. The Cs 3d intensity shows a fast increase for short deposition times and only a weak increase after about 30s of deposition time. In contrast, the Si and C lines are only weakly attenuated, suggesting that the formed film does not exhibit a uniform thickness, but rather that an island-like growth is taking place.

Scanning probe microscopy pictures (not shown here) show a large number of scratches on the surface (presumably due to the polishing process applied to the samples by the vendor). This inhomogeneous surface might have a strong influence on the growth of the film (e.g. preferential deposition in the grooves at the edges next to them).

![XPS survey spectra](image.png)

**Figure 1:** XPS survey spectra of a SiC single crystal after an HF etch, after HF and heating, and after Cs evaporation for different times.

To complement the photoemission experiments of the Cs/SiC sample series, X-ray emission experiments were performed on the thickest Cs/SiC film during the last experimental run at the
Advanced Light Source, Lawrence Berkeley National Laboratory. The evaluation of the data is currently ongoing.

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

Camera Calibration and Dimensional Measurements using the CCD Camera

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

![Figure 2: Experimental Camera Setup](image-url)

![Figure 3: Calibration objects](image-url)
Estimation of the Projection Matrix

2D points in the image plane and the 3D points of the scene are connected by the projection matrix, $P$:

$$
\begin{pmatrix}
  x_i \\
  y_i \\
  1
\end{pmatrix} = P
\begin{pmatrix}
  X_w \\
  Y_w \\
  Z_w
\end{pmatrix}
$$

The 2D coordinates $x_i$ and $y_i$ in the image plane result as:

$$
x_i = \frac{p_{11}X_i + p_{12}Y_i + p_{13}Z_i + p_{14}}{p_{31}X_i + p_{32}Y_i + p_{33}Z_i + p_{34}} \quad y_i = \frac{p_{21}X_i + p_{22}Y_i + p_{23}Z_i + p_{24}}{p_{31}X_i + p_{32}Y_i + p_{33}Z_i + p_{34}}
$$

The matrix elements of $P$ can be expressed as:

$$
x_i(p_{31}X_i + p_{32}Y_i + p_{33}Z_i + p_{14}) = p_{11}X_i + p_{12}Y_i + p_{13}Z_i + p_{14} \\
y_i(p_{31}X_i + p_{32}Y_i + p_{33}Z_i + p_{14}) = p_{21}X_i + p_{22}Y_i + p_{23}Z_i + p_{24}
$$

which can also be written in matrix notation as: $Ap = 0$ with:

$$
P = (p_{11}, p_{12}, p_{13}, p_{14}, p_{21}, p_{22}, p_{23}, p_{24}, p_{31}, p_{32}, p_{33}, p_{34})^T
$$

The A-matrix contains the spatial data set describing the locations of chosen scene points.

$$A = \begin{pmatrix}
  X_1 & Y_1 & Z_1 & 1 & 0 & 0 & 0 & -x_1X_1 & -x_1Y_1 & -x_1Z_1 & -x_1 \\
  0 & 0 & 0 & 0 & X_1 & Y_1 & Z_1 & 1 & -y_1X_1 & -y_1Y_1 & -y_1Z_1 & -y_1 \\
  \vdots \\
  X_N & Y_N & Z_N & 1 & 0 & 0 & 0 & -x_NX_N & -x_NY_N & -x_NZ_N & -x_N \\
  0 & 0 & 0 & 0 & X_N & Y_N & Z_N & 1 & -y_NX_N & -y_NY_N & -y_NZ_N & -y_N
\end{pmatrix}
$$

As $P$ has rank 11, at least $N = 6$ correspondences are needed in order to solve the equation $Ap = 0$ for $p$.

Using the $N = 30$ measured correspondences from the calibration scene of Figure 3; a 60 x 12 matrix $A$ was obtained. By using more than the required minimum of 6 calibration points, errors...
are minimized. Matrix A is inverted using SVD (Single Value Decomposition) in Matlab. The camera calibration algorithm was programmed in Matlab, see Figures 4 and 5.

![Figure 4: Three different images of the calibration plane](image)

![Figure 5: Estimated 3D structure of the previous images](image)

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

For the three sample scenes of Figure 4, the spatial location of the respective calibration planes is shown in Figure 5.

**Two-View Triangulation**

Triangulation is considered the process of finding the position of a point in space given its position in a stereo image pair (Figure 6). This task might have a central matter in this project regarding the background of robot pick and place operations. In this section the Linear-Eigen method is introduced as a simple triangulation method for extracting 3D points.
Consider a calibrated stereo image pair (as seen in Figure 7) with their corresponding projective matrices $P$ and $P'$. The linear equation below describes the spatial relation between both image points:

\[
\begin{pmatrix}
  x \ p^{3T} - p^{1T} \\
  y \ p^{3T} - p^{2T} \\
  x' \ p'^{3T} - p'^{1T} \\
  y' \ p'^{3T} - p'^{2T}
\end{pmatrix}
\begin{pmatrix}
  X_w \\
  Y_w \\
  Z_w \\
  1
\end{pmatrix} = 0
\]

Again an equation of the form $Ap = 0$ was obtained. The triangulation method is known as the Linear-Eigen method.

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

Preliminary studies conducted this quarter provide a good indication for the success of synthesizing uranium(III) nitride through a low temperature, liquid ammonia-based synthesis route. The entire synthetic regime is being conducted in liquid ammonia (b.p. -34 C) cooled in a dry ice/ethanol bath (~-78 C), which could hamper the energetics of the reaction sequence. Previous syntheses of UI$_3$ were conducted at temperatures of 0 C or higher. However, difficulties in the reaction lie in the purity of the chemicals used (most notably the purity of liquid ammonia) rather than temperature regimes. Measures were taken to eliminate atmospheric contamination by purging all glassware with UHP argon, measuring reagents and sealing Shlenk
flasks in an argon filled glove box, and maintaining the inert atmosphere throughout the reaction scheme.

The dissolution of iodine in ammonia is a rapid process, resulting in a pale green solution, which does not result in any observable oxidation of iodine. This dissolution has been conducted numerous times on multiple samples, with no indication of oxidized iodine or other undesired products. The cannula transfer of dissolved iodine into the reaction vessel containing U metal has been conducted with little to no residual iodine remaining in the original flask. The metal being used for these reactions has a noticeable brown/black oxide coating that prevents the formation of UI₃(NH₃)ₓ. Stirring of U metal fragments with dissolved iodine in ammonia for 24 h revealed a thickening of the oxide coating, which presumably is a result of O₂ or H₂O contamination in the solvent. Procedures for cleaning the metal prior to the reaction are under development. Higher grade ammonia has been ordered, and procedures to dry and deoxygenate the solvent are being tested. These actions should allow the reaction to proceed without formation of the boundary oxide layer between the two reactants. There are a number of alternate synthetic routes for producing the UI₃(solv)ₓ precursor to U(III)N, which are available for successful project completion should this method be ineffective. However, it is believed that this new procedure would be most beneficial for the desired outcome and for the introduction of a novel, viable synthetic route for accessing U(III).

SEPARATIONS TECHNOLOGY

Immobilization of Fission Iodine (Task 15).

The following procedure was developed to measure iodine production from various manganese oxide preparations:

- Suspend the manganese oxide preparation (20 mg) in 50 mL of aqueous solution.
- Treat the suspensions with ultrasound for 30 minutes prior to iodine measurements.
- Mix a 50 uL aliquot of the manganese oxide suspension with 2.5 mL of water and 10 uL of concentrated sulfuric acid.
- Add a 50 uL volume of 1.0 M KI to the stirred mixture to start the reaction.

The iodine produced was measured as the triiodide complex at 350 nm. The concentration of I₃⁻ was calculated from absorbance at 350 nm using a response factor that was determined by an external calibration (KI+KIO₃ in dilute sulfuric acid).

Manganese (II) concentrations were determined using standard addition technique that utilizes a pyridylazonaphthol (PAN) colorimetric method, similar to Chiswell and O’Halloran (1991). The 0.1% PAN solution and an ammonia/ammonium chloride buffer (pH 9.2) were purchased from Lamotte. A 10 ppm Mn(II) standard was prepared by dilution of a 1000 ppm atomic adsorption standard. A 20% Tween 20 solution was prepared in distilled water. Mn(II) formation was measured as follows:

- Water (1.8 mL), ammonia/ammonium chloride buffer (0.4 mL), PAN (0.1 ml) and 0.1 mL of Tween 20 were combined in a cuvette.
- The blank spectrum (400-600) was recorded and then 0.1 mL of sample was added.
• Seven spike additions were made (10 uL of 10 ppm Mn) and blank reading at 560 nm was subtracted from each measurement.
• The results were analyzed by linear regression and the concentration of the sample was determined by the ratio of intercept to slope.
• The calculated Mn(II) concentration was corrected for dilution, an example of this type of spike addition plot is shown in Figure 8.

In a procedure similar to Murry et al. (1984) and Anschutz et al., (2005), the total yield of iodine, by these materials was compared with Mn (II) concentration to estimate the oxygen to manganese ratio (MnO_x) for the starting material. This ratio (x) is a function of the average oxidation state of the material and is given by the following equation:

\[
x = 1 + \frac{I_3^-}{Mn^{II}}
\]

Results of these analysis are presented in Table 1, where the oxidation state is tabulated along with the oxidation rate constant (KI = 0.019M) at pH 4. Results indicate that the iodide oxidation rate does not correlate with surface area; however, there does seem to be some correlation with the average oxidation state of the manganese oxide. This relationship will continue to be explored.

Table 1: Rate constants for iodide oxidation are tabulated along with the measured oxygen to manganese ratio of the manganese oxide. The mineral was identified by powder x-ray analysis.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>O/Mn Ratio</th>
<th>k(sec^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cryptomelane Type II</td>
<td>1.39</td>
<td>0.0328</td>
</tr>
<tr>
<td>Sodium Manganese Oxide Hydrate</td>
<td>1.87</td>
<td>0.0149</td>
</tr>
<tr>
<td>Black Birnessite + Crytomelane</td>
<td>1.74</td>
<td>0.0137</td>
</tr>
<tr>
<td>Cryptomelane Type II</td>
<td>2.2</td>
<td>7.97E-03</td>
</tr>
<tr>
<td>Cryptomelane Type II</td>
<td>2.47</td>
<td>1.49E-03</td>
</tr>
</tbody>
</table>

Interface to interact with ASPEN-Plus through the ISOPRO Package

This interface reads in ASPEN-Plus data file and populates data into a tabulated format. It displays the information from streams and its elements. The user can modify the input values and directly run the simulation through the interface. There are sets of standard menu items listed to provide faster access. Some changes have been made and are listed below:

GUI changes:
- Tree view of the streams was organized into “Input” and “Output”
- Streams were determined to be Input or Output based on the relation they have within the “Blocks” defined in the Aspen “b kp” file.
- More menu items were added.
- Stream information can be displayed to the table below the “Location” information, as shown in Figures 9(a) and (b), immediately after selecting a stream name.
- Output information is not initially loaded for saving reading time.
- After each simulation run of from the ASPEN-plus, input/output information is updated in the interface.
- The “Location” field is where it will indicate the Input/Output followed by the Stream name selected by the user.

Algorithm changes:
- Nested hash is used
- Hash consists of a pair, Key and Value
- Key is the Stream name
- Value consists of another hash – ASPEN information stored in hashes, one for Input streams and one for Output streams
- Determination of input or output stream type is based on checking the “connection” in the Stream Information within the ASPEN-Plus program.
- An exact copy of the hash is used for faster reloading
- Stream values changed by the user can be updated while either the “Run” button is clicked or the stream is selected to view.
Electrochemical Separation of Curium and Americium (Task 25).

This research report outlines the current status and progress associated with the electrochemical separation of curium and americium. This task has expanded its studies to include room temperature ionic liquid systems. Exploiting the 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 (hydrogen evolution)
potentials. Under non-standard state conditions the potential window can be larger based on changes in kinetics associated with the electrode material and solution conditions. However, eliminating the side reactions associated with aqueous side reactions is critical for examining lanthanide and actinide chemistry. Room temperature ionic liquids show significant promise with the electrochemistry of lanthanides and actinides.

The electrochemical window for RTIL system is based primarily on the reduction of the cation and oxidation of the anion used to make the solution. The potentials for cation reduction and anion oxidation in RTIL solutions typically occur at more positive and negative potentials than water oxidation and hydrogen reduction, respectively. Therefore, the potential window is significantly larger for RTILs ranging from approximately 4.5 to 6 V. Figure 10 illustrates the potential windows obtained in aqueous solutions of 0.1 M H₂SO₄ (blue line) and the RTIL, tri-n-butylmethylammonium bis(trifluoromethylsulfonyl)imide ([MeBu₃N][NTf₂], red line) at GC, Au, and Pt electrodes. For each electrode the positive and negative potential limits provide an absolute potential window of approximately 4.5 V for Pt, 5.0 V for Au, and 6.0 V for GC. A total of ten RTIL solutions that were examined were produced.

![Figure 10: Electrochemistry of GC, Au, and Pt electrodes in RTIL ([MeBu₃N][NTf₂]), (Red) and 0.1 M H₂SO₄, (Blue)](image)

The advantage to eliminating aqueous side reactions and expanding the potential window is that previously inaccessible electrochemical reactions may be resolved. A survey of the literature regarding the electrochemical analysis of f-elements in RTIL solutions provides an understanding of the benefits of the systems and possible applications. For example, the electrochemical analysis of f-elements has been achieved in RTIL solutions including the species Pu(IV), Np(IV), U(IV), U(VI), Th(IV), Eu(III), La(III), and Sm(III). These studies are not comprehensive in nature and examine only a small percentage of RTIL systems available for the electrochemical study of f-elements. However, they do provide the proof of principle for further studies in RTIL solutions. In fact, these studies have confirmed that it is possible to
electrochemically deposit Eu(0) and Th(0) from RTIL solutions. For example, Eu(0) was electrochemically deposited from solutions containing Eu-\([\text{NTf}_2]_3\) (\(\text{NTf}_2 = [\text{N(SO}_2\text{CF}_3]_2^-\)) using the RTIL tert-methylphosphonium bistriflimide, [Me₄P][\text{NTf}_2] at elevated temperature (160°C). The following complex, [Th(\text{NTf}_2)₄(H\text{NTf}_2)]·2\text{H}_2\text{O} has been used to electrochemically deposit as Th(0). Reaction of the Th(0) deposit with residual water from the complex resulted in the formation of ThO₂(s) at the electrode surface from the RTIL solution, [Me₃BuN][\text{NTf}_2]. Finally, there is evidence that La(III) and Sm(III) can be reduced electrochemically to their metallic state in RTIL solutions of [Me₃BuN][\text{NTf}_2] at Pt electrodes. In these studies the La and Sm were complexed with \(\text{NTf}_2^-\) prior to dissolution in the RTIL. These studies demonstrate that RTIL solutions can be used to effectively probe the oxidation/reduction of f-element complexes. In addition the potential mediated deposition of f-elements is possible indicating the controlled separation of chemical species is thermodynamically feasible.

The number of possible RTIL solutions if rather large when the number of possible cation/anion pairs is considered. For example, Figure 11 provides the total number of possible RTIL solutions for a single cation with a variety of common anions.

Cation

\[
\begin{array}{c}
\text{R}_1, \text{R}_2 \\
\text{N}^+ \\
\end{array}
\]

\(\text{R}_1 = \text{Methyl, Ethyl, Butyl, Propyl, iso Propyl}\)

\(\text{R}_2 = \text{Methyl, Ethyl, Butyl, Propyl, iso Propyl}\)

Anions

\(\text{F}^-, \text{Cl}^-, \text{Br}^-, \Gamma, \text{BF}_4^{2-}, \text{PF}_6^{3-}, \text{AsF}_6^{3-}, \text{N(CN)}_2^{2-}, \text{CF}_3\text{SO}_3^{2-}, \text{C}_4\text{F}_9\text{SO}_3^{2-}, \text{N(CFSO}_2\text{)}_2^{2-}\) etc...

165 possible combinations of Cation/Anion RTIL solutions.

*Figure 11: The number of theoretically possible combinations between a cation species (15 possible disubstituted pyrrolidinium cations) with eleven possible anions.*

The figure shows that RTILs can be systematically varied by changing the organic cation and anion pairs. Thus combinatorial approaches with anions can be used to identify RTIL systems with variable solubility and affinity for chemical species. The number of possible RTIL solutions is large when all the possible cation/anion pairs are considered. This approach is not possible in aqueous solutions where the properties of the solvent, water, are static.

This task will continue to examine RTIL solutions to determine the feasibility of using RTIL solutions rather than aqueous solutions for the potential dependent separation of actinides and lanthanides.

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

**Determination of Uranium Concentrations by Laser Fluorescence in the aqueous system**
The impact of process chemistry on the observed lifetime and fluorescence yield of uranium in the aqueous process streams was investigated.

The presence of nitrate in the system both dramatically decreases the quantum yield of the uranyl fluorescence and severely reduces its lifetime. This observation is consistent with the presence of a quenching agent, in this case the nitrate ion. The data was fitted to a Stern-Volmer relationship, $\tau_0\tau = 1 + k_q\tau_0[\text{NO}_3^-]$, and a linear fit was obtained (Figure 12).

![Figure 12: Stem-Volmer diagram](image)

The limits of detection for the technetium and raffinate streams of the UREX process were determined. Samples were prepared to match the nitrate concentrations with a range of uranyl concentrations with a fixed ionic strength. For each sample, a drift in the lifetime was noticed. The longer the sample was irradiated by the laser, the shorter the observed lifetime (Figure 13). This shift was due to the heating of the sample by the laser, which affected the lifetime. Temperature effects on the fluorescence behavior will be investigated in the next quarter.

![Figure 13: As the sample is heated by laser irradiation, the observed lifetime decreases](image)
Spectroscopy of the uranyl/organic system

Samples of uranium extracted into dodecane and TBP showed no fluorescence under laser irradiation. The reason for this is being investigated, but the leading hypothesis is that the C-H oscillators of the organic matrix are acting as quenching agents in much the same way that O-H oscillators are in a water-based system. As a result, it is unlikely that TRLFS will be useful for determination of uranium concentrations in the organic streams. UV-Visible spectroscopy, however, appears to be a viable alternative technique. Scoping studies to determine uranium concentrations by UV-Vis in the organic phase have been initiated, and will continue in the next quarter.


Development of concepts and models continued 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). Neutron slowing down spectrometers (SDS) are being modeled and plans are being developed to conduct experiments at ISU with their carbon-based SDS (CSDS). This work will be used to investigate technology for assaying fuel rods and/or complete assemblies. In preparation for these experiments, MCNPX was used to model neutron transport characteristics in LSDS and CSDS. The energy of neutrons measured in a neutron detector with an SDS can be characterized by the equation $E = K/(t+t_0)^2$, where $K$ and $t_0$ are characteristics of the SDS.

However, the detector system must be able to resolve the time dependence of the neutron signal. Because $^3$He detectors, such as those contained in the NMDS, have a slow response, the SDS configurations must be studied before conducting experiments. Those studies are currently ongoing.

Another application of NMDS to MPAC might utilize the measurement of both passive and active neutron multiplicity in very dilute concentrations of higher actinides, such as in a non-actinide waste stream. The applicability of the NMDS to measure quantities and isotopic constituents in such a stream is currently being investigated. In addition, the NMDS is being upgraded to improve its performance. The upgrade included replacement this period of standard cables with coax to reduce noise, and the mapping of detector response with data collection and analysis software.

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 have been started on the steels to determine details of the chemistry and mass transport issues surrounding the formation of protective and non-protective oxides in lead-bismuth eutectic (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 have been observed in the oxide layers produced by the gas phase experiments, discussed below.

In experiments where the steel was exposed to an oxidizing environment controlled by a Cu/CuO mixed pellet (Figure 14), the oxygen concentration is controlled by the dissociation of the CuO at a temperature set independently from the oxidizing environment of the steels (Figure 15). It was found that oxide layers formed after 100 hours at 550 C that were analogous to the oxide layers found on steel exposed to LBE (Figure 16).

Figure 14: Evacuated quartz tube with sample string and Cu/CuO oxygen source.
Figure 15. Tube furnace arrangement to allow independent control of oxidation temperature and oxygen concentration.

Figure 16. 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).
In initial work (Gas Phase 1) no effort was made to minimize water adsorbed to the evacuated quartz tube in which the experiment was performed. It was found that water was evident in the oxide layers (Figure 17) and that 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 also 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 2, etc.) efforts were made to minimize water in the vacuum, which reduced the evidence of water in the oxide layers (Figure 18).

**Figure 17:** XPS of the oxygen found in the oxide layer(s) in the wet, gas phase 1, experiments. Note the peaks at \(\sim 530\,\text{eV} \) (characteristic of metal oxides) and \(538\,\text{eV} \) (characteristic of water).
A Raman spectromicroscope was upgraded and is in 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 beam widths below 3 microns were measured. Third, the vibrational frequencies of a material are more chemically specific: While SEM can determine location of elements to micron scales; SEM cannot 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 can and has been used to determine in situ and unambiguously the presence of Fe$_3$O$_4$ as the surface species on some of the steel specimens. This task is 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.

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

Significant progress has been made during this past quarter with respect to both metallurgical and corrosion studies involving multiple heats of modified T91 grade steels. Further, studies have been performed involving martensitic alloys with higher Si content. The susceptibility of modified T91 grade steels to degradations including localized corrosion and stress-corrosion-cracking (SCC) has been determined in an acidic solution by cyclic potentiodynamic polarization.
(CPP) and slow-strain-rate (SSR) techniques, respectively. The role of applied potential on SCC behavior has also been investigated using the SSR technique. As to the metallurgical characterization of modified T91 grade steels, the roles of temperature and strain rate on dynamic strain ageing (DSA) behavior have been investigated. The magnitudes of activation energy (Q) and work hardening index (n) have been determined from the resultant analyses. The significant results obtained from the overall testing are summarized below.

Dynamic strain ageing of structural materials is known to be influenced by both temperature and strain rate \((\varepsilon^o)\). In view of this rationale, tensile testing was performed using T91 grade steels at 300, 400 and 550 \(^\circ\)C under strain rates of \(10^{-2}, 10^{-3}\) and \(10^{-4}\) sec\(^{-1}\). The DSA phenomenon, showing reduced ductility, was predominant at temperatures of 300 and 400 \(^\circ\)C in recent tensile tests. Therefore, the role of \(\varepsilon^o\) on DSA behavior was studied at these two temperatures, and a temperature of 550 \(^\circ\)C, at which the failure strain \((e_f)\) was significantly enhanced due to increased plastic flow and ease of deformation.

The variations of \(e_f\) with \(\varepsilon^o\) at 300, 400 and 550 \(^\circ\)C are illustrated in Figure 19. These data indicate that, in general, the magnitude of \(e_f\) was gradually reduced with faster \(\varepsilon^o\) irrespective of the testing temperature. However, some discrepancy on the variation of \(e_f\) with \(\varepsilon^o\) was noted with steel containing 2 wt % Si. An evaluation of Figure 19(b) reveals that, for the steel containing 2 wt% Si, the magnitude of \(e_f\) was significantly reduced at 400 \(^\circ\)C when \(\varepsilon^o\) was increased from \(10^{-3}\) to \(10^{-2}\) sec\(^{-1}\). However, insignificant variation was observed with this steel at this temperature at \(\varepsilon^o\) between \(10^{-3}\) to \(10^{-4}\) sec\(^{-1}\). At 300 \(^\circ\)C, the magnitude of \(e_f\) was at its minimum at \(\varepsilon^o\) of \(10^{-3}\) sec\(^{-1}\). It is unknown at this time as to the cause of higher \(e_f\) value for this steel at an \(\varepsilon^o\) of \(10^{-2}\) sec\(^{-1}\).

\[a\] T91 grade steel (1 wt% Si)
The effect of temperature on $e_f$ as a function of $\varepsilon^o$ is illustrated in Figure 20. As indicated earlier, the lowest value of $e_f$ was observed at 400°C under an $\varepsilon^o$ of $10^{-2}$ sec$^{-1}$. Similarly, the magnitude of $e_f$ was lower at 400°C compared to that at 300°C at an $\varepsilon^o$ of $10^{-3}$ sec$^{-1}$. Thus, the data shown in Figure 20(a) for steel with 1 wt% Si are consistent with the basic understanding of plastic deformation as functions of temperature and $\varepsilon^o$. However, at an $\varepsilon^o$ of $10^{-4}$ sec$^{-1}$, the magnitude of $e_f$ was gradually enhanced with increasing temperature for both heats of steel, suggesting that the plastic deformation occurred more readily with increasing temperature. An inconsistency on the effect of temperature on $e_f$ was, however, noted with T91 grade steel with 2 wt% Si at an $\varepsilon^o$ of $10^{-3}$ sec$^{-1}$, as shown in Figure 20(b).

(b) T91 grade steel (2 wt% Si)

Figure 19: Failure strain vs. strain rate at different temperatures

![Graph showing failure strain vs. strain rate at different temperatures](image)
The variation of $n$ with $\varepsilon^o$ is illustrated in Figure 21 as a function of the testing temperature. Based on these data, it can be concluded that the extent of work hardening, in terms of $n$, was gradually increased with faster $\varepsilon^o$. The increased values of $n$ at a specific temperature with a faster $\varepsilon^o$ can be justified since the resistance to plastic deformation is enhanced at a faster strain rate.
rate resulting from the pinning of dislocations within the matrix due to shorter testing duration. A slight inconsistency in the n value was noted for the steel with 1 wt% Si at an $\varepsilon^0$ of $10^{-3}$ sec$^{-1}$ at 400 C.

\[ \text{Figure 21: } n \text{ vs. strain rate at different temperatures} \]
Insignificant variation of yield stress (YS) with $\varepsilon^0$ was noted at 300 and 400 °C, as shown in Figure 22. However, the YS gradually increased with faster $\varepsilon^0$ at 550 °C. At the fastest $\varepsilon^0$ of $10^{-2}$ sec$^{-1}$, the resistance to plastic deformation was at a maximum, thus requiring higher strength for deformation to occur.

(a) T91 grade steel (1 wt% Si)

(b) T91 grade steel (2 wt% Si)
Figure 22: Yield stress vs. strain rate at different temperatures

Four different heats of T91 grade steel were tested for evaluation of their localized corrosion behavior using the CPP technique. These steels contained Si levels of 0.5, 1.0, 1.5 and 2.0 wt%. The results indicate that the magnitude of the corrosion potential ($E_{corr}$) gradually become more active (negative) with increasing temperature. For the steel having 2 wt% Si the magnitude of $E_{corr}$ became more active at ambient temperature and 90 C compared to that of the other three heats. The variation of $E_{corr}$ (Ag/AgCl) with temperature is illustrated in Figure 23 for all four heats. None of these materials did exhibit any well-defined slope change, thus giving no critical pitting potential values. All polarized specimens were discolored, indicating active dissolution of the specimen surface.

![Graph showing $E_{corr}$ vs. temperature for steels of different Si content]

Figure 23: $E_{corr}$ vs. temperature for steels of different Si content

A consistent pattern on the effect of temperature on the cracking susceptibility of two heats (1 and 2 wt% Si) in terms of percent elongation (%El), percent reduction in area (% RA), time to failure (TTF) and true failure stress ($\sigma_f$) was observed in SSR testing. The variation of all four parameters with temperature is illustrated in Figure 24, showing their gradual reductions with increasing temperature. The results of SSR testing under a cathodic controlled potential of -300 mV with respect to $E_{corr}$ are also illustrated in Figure 24.
The fractographic evaluations of the specimens, tested under a SSR condition with and without a controlled cathodic potential, revealed intergranular brittle failure, as illustrated in Figure 25. The extent of intergranular attack was more pronounced at 90°C whether or not controlled potential was applied during straining of these specimens.
Figure 25: SEM micrographs of the fracture surface of specimens tested under a cathodic controlled potential

Oxide Film Growth Modeling in LBE Systems (Task 21).
Cellular automaton (CA) model on the oxide growth coupled with inward oxygen diffusion

To simulate the oxide layer growth of steel in an LBE environment, a cellular automaton model was developed that considered inward oxygen diffusion. Cellular automata are mathematical idealizations that describe the discrete spatial and temporal evolution of complex systems by applying local deterministic or probabilistic transformation rules to the cells of a lattice. In the developed model, the lattice sites are occupied by metal, oxide, or LBE, while the interstitial sites are routes ways for oxygen to occupy and diffuse.

The basic rules for the current model:

- In LBE, the oxygen concentration is kept constant and the oxygen distribution is uniform (randomly distributed for each step).
- For a metal site, if none of the nearest interstitial sites (southwest, southeast, northwest, and northeast corners as shown in Figure 26) is occupied by oxygen, no oxidation will occur.
- For a metal site, if one or more of the nearest interstitial sites is occupied by oxygen, it is possible that a reaction will occur. If none of the neighbor sites is oxide or LBE, no oxidation occurs. If one or more neighbor sites are oxide or LBE, the oxidation reaction occurs immediately with a probability, p. The reaction speed is assumed to be much faster than the diffusion speed of oxygen. One of the oxygens is chosen randomly from the nearest interstitial sites for reaction and disappears. The metal site disappears and an overlapping site of oxide and ionic metal substitutes. The ionic metal site always overlaps with an oxide site and the ionic metal site can diffuse in the oxide layer and is called a “walker.”
- After each step, the atomic oxygen diffuses randomly along the interstitial edge of the lattices in the oxide layer and metal zone.
- After a few finite steps of diffusion of oxygen, the walkers diffuse one step in the oxide layer. The ratio of diffusion steps depends on the mass diffusivities of oxygen and ionic metal in oxide layer. Usually the diffusion of oxygen is faster than the diffusion of ionic metal.
- When a walker meets LBE, oxidation occurs immediately since it is assumed that oxygen diffuses very fast in LBE.
The first step of this developed CA modeling is to study the diffusion of oxygen, in which no reaction takes place. For the diffusion equation:

\[
\frac{\partial u}{\partial t} = \frac{1}{2} \frac{\partial^2 u}{\partial x^2} \quad \text{with} \quad \begin{cases} u(0, t) = 0 \\ u(1, t) = 1 \end{cases}
\]

The solution for the above equation is a transient solution and the concentration distribution approaches a steady solution with increasing time steps. As shown in Figure 27, the numerical result obtained from the developed CA model is compared with the steady-state solution and Brieger’s result. It can be found that the numerical result is in good agreement with the steady state solution and Brieger’s solution. With increasing of numbers of site in the simulation domain, the calculated concentration profile becomes smoother.

Figure 27: Comparison of numerical simulation results
The entire diffusion and reaction processes are also simulated with a domain of 500 by 500 grids. The concentration of oxygen in LBE is set at 0.2 and the reaction probability $p$ is assumed to be 0.5. The oxygen sites diffuse 2 steps after each diffusion step of ionic metal sites. After 10,000 steps, the snapshot of the simulated mesoscopic structure is shown in Figure 28. It can be found that the oxide layer grows inwardly and outwardly at the same time since the volume expansion effect is considered. The oxygen sites diffuse towards the metal and the ionic metal diffuse outwards at the same time. Figure 29 shows that the square of oxide layer thicknesses of $(\delta_{in})^2$, $(\delta_{out})^2$ and $(\delta_{tot})^2$ are close to straight lines. Therefore, the thickness of inner oxide layer, outer oxide layer and the total oxide layer grow in parabolic trends which is consistent with Wagner’s theory.

![Snapshot of simulated mesoscopic structure](image)

(a) Full view  
(b) Zoom view

*Figure 28: Snapshot of the simulated mesoscopic structure after 10,000 steps*

![Graph of oxide thickness vs time steps](image)

*Figure 29: Square of oxide thicknesses of $(\delta_{in})^2$, $(\delta_{out})^2$ and $(\delta_{tot})^2$ vs. time steps*

Corrosion Barrier Development for LBE Corrosion Resistance (Task 23).
In this project, the corrosion barrier coatings were previously developed by synthesizing Ni nanowires inside nanoporous alumina and then coating the surface with dense alumina. Ni nanowires were used instead of Cr nanowires due to the poor uniformity observed for Cr nanowires. A number of samples were created on steel substrates by incorporating Ni nanowires that were subsequently covered with dense alumina using a masking technique developed for this project. The masking technique was necessary to prevent bridging of the nanopillars to the bulk alumina. While the thermal cycling test for these samples was being waited upon, a new technique was investigated that is expected to provide improved thermal cycling characteristics of the coating. In this technique, each nanopore is filled with a number of nanoparticles instead of one solid nanowire. The nanoparticles are more flexible to move compared to solid nanowires thus allowing the coating layer to expand and contract without damage under thermal cycling. Such a coating is expected to provide improved protection under thermal cycling. An extensive investigation was carried out during the last quarter to incorporate nanoparticles inside the nanopores. A major challenge encountered in incorporating the nanoparticles was the large surface tension inside the nanopores. To address this, nanoparticles were charged through chemical functionalization and then were electrophoretically incorporated inside the nanopores. The electrical force imparted to the nanoparticles during electrophoretic deposition overcame the surface tension and helped with the incorporation of the nanoparticles inside the nanopores. A number of such samples were created that are currently being characterized by high resolution electron microscopy. The nanoporous alumina containing the nanoparticles will be covered with a thick layer of dense alumina to form the improved corrosion barrier coatings. An additional advantage of this technique is that prefabricated nanoparticles can be used for filling the nanopores, thus eliminating the non-uniformity problem encountered with the Cr nanowires. Corrosion barrier coatings are currently being implemented using this novel and improved approach. In parallel, investigation was continued in improving the spatial uniformity of the Cr nanowires and the results obtained were promising.

As reported earlier, a furnace with the capability of going up to 600 C was purchased and installed to carry out the thermal cycling tests. In addition, test procedures were identified to evaluate the adhesion properties of the corrosion barrier coatings. The furnace is currently waiting for three-phase power connection, upon completion of which it will be ready for use.

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

Results from ISU RACE experiments conducted at ISU in October are being compared with Monte Carlo radiation transport modeling using MCNP to analyze effective delayed neutron fraction ($\beta_{\text{eff}}$) in far-subcritical, under-moderated systems. 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. The statistical behavior of calculated effective delayed neutron fraction based on two independent calculations (with and without delayed neutrons) for a critical system was more stable than for the subcritical case. Calculations have been completed with and without a plutonium-beryllium neutron source. The left side of Figure 30 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. The
importance function is being used as an approximation of an adjoint weighting of the space- and velocity-dependent neutron population to calculate the effective neutron lifetime. Use of the value of a particle leaving a collision is being compared to that of a particle entering an event.

![Figure 30: Calculated effective delayed neutron fraction for a subcritical calculation (left side) versus a critical calculation (right side); without a PuBe source.](image)

Evaluation continued of experimental thermal and neutron generation with the UNLV High-power RACE target (experiments were conducted at ISU). The Target is modeled using Gambit and the CFD code FLUENT for comparison with experiments. During this reporting period, the potential complexity of the CFD modeling was upgraded with a parallel processing system. The MCNPX transport model continued to be refined to reduce statistical uncertainty and to perform parametric studies to study impacts of accelerator performance and characteristics, such as beam spread in energy or position. Figure 31 shows a comparison between calculation and experimental measurement of gold foil activation.

![Au-197 Activation Study](image)

Figure 31: Comparison of Gold Activation Calculation versus Experiment. Gold foils were placed on the HP-RACE target, and then counted using standard gamma-ray spectroscopy.

Decoupling and Disturbance Rejection Control for Target Circulation (Task 31).
In order to monitor the status of the controlling computer an additional relay was installed to send a signal to a 24-hour alarm dial-out device. The settings of the watch dog time delay relay, as well as wiring, were changed to accept the correct signal from the computer. The controlling program was modified to be able to switch from operating status to debugging status without an active alarm system.

The latest version of the alarm system can handle the alarm signals of:

- Temperature above the safety upper limitations of any heating zone
- Electromagnetic pump failure
- Power to heater failure
- Computer system suspension due to unknown reason

The alarm signals would be sent out through a phone line to any number in town by a voice message. In addition, the temperature output, lever meter reading, etc., can be reached via internet without disturbance to the primary computer for system controlling.

The alarm system will allow the TC-1 loop to operate 24 hours a day continuously without operator’s interference. This makes the TC-1 loop a reliable testing facility on campus.

The disturbance rejection algorithm was studied and tested for TC-1

The disturbance observer based control algorithm was studied to compensate modeling uncertainties as well as external disturbance (such as a heat source from other zone and EM pump). This new approach was carried out by three steps as described below.

- The simulation of the disturbance rejection algorithm. This was carried out by using software of SimuLink available in MatLab. The control system with the disturbance rejection algorithm is shown in Figure 32.
- The conversion from simulation to the real control code was carried out by using Labview software. In addition, the discrete process was performed first.
- Before applying this new approach to the TC-1 loop, the small testing furnace was applied for testing. An additional control device, a signal conditioning junction box, and a power supply were purchased and will be carried out in April 2007.
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. 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 of articles was originally set-up last quarter. Further work has continued this past quarter that expanded the number of entries and incorporated key word searches into the database.

The computational model of the TC-1 loop is currently being expanded. The model presented at the IMECE and Comsol conferences calculated 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. An in-house FORTRAN software is being developed for the calculations. The preliminary development of the CFD module of the coupled MHD/CFD solver was completed. Testing against analytic cases is under way to validate the code. The MHD module will be incorporated into the solver during the current quarter. Full testing of the completed solver began and parametric studies are ongoing.

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 were initiated. 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 scope was further defined and the appropriate focus on cross-section sensitivity studies versus design of required criticality experiments was examined. 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. The SCALE code system was acquired for processing cross sections for sensitivity studies. MCPX, MCNPX, SCALE, and data libraries were loaded for processing cross sections and conducting sensitivity studies.