AFCI Quarterly Input – UNLV January through March, 2005

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1.0 University of Nevada, Las Vegas (UNLV)

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

- The UNLV TRP hosted and facilitated a Deep Burn Reactor work package development meeting on January 26. The meeting included two NTDs and a number of research collaborators. 10 draft work packages were developed and submitted to DOE.
- The UNLV TRP hosted the joint AFCI/Gen IV Physics Working Group meeting on January 27 and 28.
- The UNLV TRP sponsored a field trip by 20 students from the UNLV Student Section of the American Nuclear Society to visit the Palo Verde Nuclear Power Plant during Spring Break on March 25.
- The UNLV College of Engineering and the UNLV TRP appointed Denis Beller as the Coordinator for the new M.S. in Materials & Nuclear Engineering Degree Program. The TRP will support this effort by funding his appointment in addition to research assistantships and course offerings.

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
- Facilities Progress Update. The TC-1 target gas vacuum system assembly started as components were finally received. A fence enclosure to limit access and provide increased safety was designed and ordered. Upon completion of the gas vacuum system (anticipated by the end of next quarter), the target complex should be ready for final testing and isothermal experiments. A LANL-designed Lead Calibration Stand (LCS) is being built in LANL for UNLV. After construction of the LCS, it will be transferred to UNLV when a facility is available. Long lead-time materials and components were ordered.
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 Khlopin Radium Institute (KRI) in St. Petersburg, Russia (Tasks 6, 15 and 16); the Institute for Physics and Power Engineering (IPPE) in Obninsk, Russia (TC-1 Loop); and, the Ben Gurion University of the Negev in Beer Sheva, Israel (Task 19).

The contract process was started for a new ISTC project entitled “Preparatory Work for the Systematic Measurements and Evaluation of Minor Actinide Nuclear Data,” project manager Leonid Ponomarev, Russian Academy of Sciences.

1.3 **Student Research**

1.3.1 **Student Research Scope**
The Student Research component is the core of the UNLV Transmutation Research Program with steadily increasing funds as the program evolves and capability expands. The milestones, schedules, and deliverables of the student research projects are detailed in the individual research proposals. UNLV currently has 27 student research tasks (including 7 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**

**Metallic Fuel Pins (Task 1) Highlights.**
- Project completed in June 2004. Theses generated:

**Remote Fuel Fabrication (Task 9) Highlights.**
- Project completed in August 2004. See Task 22 for follow-on project. Thesis generated:

**Interaction between Metal Fission Products and TRISO Coating Materials (Task 17) Highlights.**
- The reassembly of the Ultra-High Vacuum system has been completed.
- Experimental data from the summer research campaign and the Advanced Light Source
Dissolution, Reactor, and Environmental Behavior of ZrO₂-MgO Inert Fuel Matrix (Task 19) Highlights.
- Developed a new method for delivering ceramic precursors.
- Nine ceramic formulations scoping the Zr-Mg composition space were fabricated and analyzed by X-ray Diffraction and Electron Microscopy.
- Thermogravimetric analysis confirmed temperature of calcination reaction.
- Maximum temperature of the ceramics were probed using differential scanning calorimeter.
- Neutronic evaluation for LWRs on the inclusion of burnable poisons (0.5-2 % Gd, 2-3 % Hf, 4-6 % Er) was performed.
- Suitable Pu and burnable poison ratios were defined.
- Scanning electron microscope images were taken of the sintered fuel.
- Fuel samples were sized for dissolution studies.
- Fuel sample surface area was determined using BET surface area analysis.

- Design of Hot Cell robotic assembly continued, including: review of fuel manufacturing processes, control system for dispersion fuel, fuel manufacturing of sol-gel and other powder processes, and mixing and sintering techniques.

SEPARATIONS TECHNOLOGY

Systems Engineering Model (Task 8) Highlights.

Criticality and Heat Transfer Analyses of Separations Processes (Task 11) Highlights.
- None reported.

Immobilization of Fission Iodine (Task 15) Highlights.
- Synthesized modified pyridinium resin; initiated small scale testing of resin.
- Small testing methylpyridinium resin continued. Some iodine background problems are being addressed.
- Larger scale pyrolysis experiments continued using the semi-preparative GC. The recovery of iodine from pyrolyzed peat is being examined. The optimum pyrolysis temperature of the iodinated peat was addressed and it was determined that 400°C gave the best recoveries of iodine as methyl iodide.
- Some aqueous phase kinetic experiments with soluble alkali lignin, and a commercial humic acid was performed. The disappearance of iodine was monitored by UV spectroscopy. Modeling of the results is being attempted.
Fluorapatite Waste Forms (Task 16) Highlights.
- Obtained SEM/EDS, FTIR and XRD for Zn-containing samples prepared using 75, 50 and 25% Ca/Zn molar ratios and the sintered sample of Ca/Zn molar ratio 75%.
- Additionally, XPS data were obtained for these samples together with a fluorapatite and a 100% Zn sample.
- Prepared 4 different amounts of Zr-containing apatites using precipitation method and sintered these 4 samples at 1200 degrees of centigrade for one hour. SEM, XRD, FTIR and high temperature TGA/DSC data were obtained for these samples. A detailed analysis is in progress.
- Determined the dependability of the Ca/P and (Ca +Sr)/P ratios in FAP based on the amount of Sr surrogate used in synthesis.
- Prepared Cu and Ni containing fluorapatite samples and obtained powder diffraction spectra for the Cu-FAP sample.

- The following improvements were made on the TRPSEMPro package: (1) Error message will be recorded on ErrorLog if AMUSE tries to run a flowheet without section. Error message also will be recorded if aqueous and/or organic feed do not have a feed letter; (2) The updated TRPSEMPro will force to calculate flow rate prior to AMUSE simulation run. (3) A new function was added: “Show” – “Last Error Log” on top of the menu bar that allows users to open the last error log.
- A simple ASPEN PLUS flowsheet process model was created for demonstration. The demo model simulates a separation of 99% for water and heptane.
- A simple interface was created to input and output parameters from the ASPEN-PLUS.

Electrochemical Separation of Curium and Americium (Task 25) Highlights.
- Continued data collection and analysis of the Ce\(^{3+}/\text{Ce}^{4+}\) redox couple in various supporting electrolytes (0.3 M NaNO\(_3\), 0.5 M HNO\(_3\), and H\(_2\)SO\(_4\) at concentrations of 0.1 M, 1.0 M, 2.0 M, and 4.0 M).
- An investigation into ionic strength is being conducted for the Ce system, using varying concentrations of Na\(_2\)SO\(_4\) in place of the H\(_2\)SO\(_4\) supporting electrolyte solutions.
- A scan rate investigation was carried out on the Ce redox couple in 0.1 M H\(_2\)SO\(_4\) at the Pt electrode to distinguish diffusion controlled versus complex formation redox processes.
- Investigation of the Sm redox couple was initiated by employing the conditions determined as optimal for the Ce experiment.

Fundamental Chemistry of U and Pu in the TBP-Dodecane-Nitric Acid System (Task 26) Highlights.
- Uranium – TBP/Dodecane extractions performed. Samples were analyzed by ICP-AES and UV-Visible spectroscopy.
- Evaluation of the nitrate ion specific electrode for the direct analysis of nitrate concentration was initiated.
- Experiments to examine the Acetohydroxamic acid (AHA) – Uranium system were initiated.
Preparation of conditions for 3rd phase studies of nitric acid and nitrate concentration variation.

Obtained Radworker II training and XAFS safety training for work at ANL.

Compared ion specific electrode and ion chromatography method for determining nitrate concentration in organic phase.

TRANSMUTATION SCIENCES

Niobium Cavity Fabrication Optimization (Task 2) Highlights.

- Secondary electron emission data from initial experiments is being evaluated and analyzed.
- Optics used to measure electron beam diameter.
- Experimental procedures are in place for repeatability purposes.

LBE Corrosion of Steel (Task 3) Highlights.


Environment-Induced Degradation and Crack-Growth Studies in Candidate Target Materials (Task 4) Highlights.

- Project completed in December 2004. Theses generated:

Modeling Corrosion in Oxygen-Controlled LBE Systems with Coupling of Chemical Kinetics and Hydrogen Transport (Task 5) Highlights.

- Project completed in August 2004. Theses generated:

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

- Repair/modification of multiplicity detector system completed. NMDS restored to complete functionality.
• Data analysis for the dead-time measurements performed at the Remote Sensing Lab (Nevada Test Site) were completed.
• Background measurements and calibration measurements were completed.
• Experiments were conducted using a Cf-252 source to measure efficiency, dead time, and CPU losses to expand on the experiments that were conducted in January at the Remote Sensing Laboratory of the Nevada Test Site.
• A parametric radiation transport study using MCNPX was conducted to compare to the above efficiency measurements.

Development of Dose Conversion Coefficients for Radionuclides Produced in Spallation Neutron Sources (Task 7) Highlights.
• Met with researchers from Francis Marion University to examine options for experiments to produce the data needed to fill in the gaps for our radionuclides.
• All radionuclide information was sent out to the Republic of Georgia and Idaho State University for them to cross reference our results.
• Graduate student traveled to Idaho State University and completed the QA radionuclides.
• Discussed with ISU collaborators calculating DC’s for radionuclides with incomplete data.

• Project completed in August 2004. Theses generated:

Radiation Transport Modeling using Parallel Computational Techniques (Task 12) Highlights.
• None reported.

• A manuscript entitled “Enhancement of Oxygen Transfer in Liquid Lead and Lead-Bismuth Eutectic by Natural Convection” has been accepted for publication by International Journal of Heat and Mass Transfer.
• Acquired new software Pirouette for Windows for statistics analysis.
• Performed data analysis on the data collected from LANL test loop.

Use of Positron Annihilation Spectroscopy for Stress-Strain Measurements (Task 14) Highlights.
• Positron annihilation spectroscopic data obtained on cold-worked and welded specimens of austenitic and martensitic stainless steels have been analyzed.
• Calibration curves for tensile specimens subjected to different levels of plastic deformation beyond yielding have been developed.
• A proposal has been submitted to the Atomic Energy of Canada Limited (AECL) to perform additional residual stress measurements on Alloys EP-823 and HT-9 using the neutron diffraction (ND) technique.
• Transmission electron microscopic (TEM) evaluations of defects in cold-worked target structural materials are ongoing. Characterization of dislocations has been performed on Alloy EP-823, with and without cold-reduction (CR). Increased dislocation density has been noted in the TEM micrographs of Alloy EP-823, subjected to 11 percent CR.
• Additional cold-reduced and welded specimens are being machined for characterization of residual stresses by the PAS technique at the Idaho Accelerator Center of ISU.

Corrosion Mechanisms and Kinetics of Steels in Lead-Bismuth Eutectic (Task 18) Highlights.
• Started occupation of the High Temperature Materials Experimental Facility.
• Currently reviving the ion beam for implantation experiments.
• Currently analyzing 38 steel samples from the DELTA loop from LANL.

• Four vacuum-induction-melted experimental heats of T91 grade steel with variable silicon content have been received from the Timken Company, OH. Quotations for sample preparation have been received from the KAM Products of Las Vegas. Specimen fabrication will be initiated soon.
• The graduate students are being trained in related mechanical, metallurgical and corrosion testing techniques.

Oxide Film Growth Modeling in LBE Systems (Task 21) Highlights.
• An improved theoretical model for the mass transfer by corrosion/precipitation in non-isothermal LBE systems was developed. The implemented model was used to model the DELTA loop to provide data for the LANL collaborators on the task.
• Numerical analysis of the coupled natural convection and corrosion product transfer in a two dimensional circular loop were initiated to study the corrosion product under the active oxygen controlled model.
• A kinetic oxide growth model in Liquid LBE was developed for pure iron exposed to liquid LBE with oxygen controlled. The oxide \((Fe_3O_4)\) layer grows toward both in internal and external side. The following assumptions are made:
  1. The interfaces are local equilibrium and the processes do not affect the kinetics of oxidation.
  2. The growth of the oxide \((Fe_3O_4)\) is limited by the diffusion of iron
  3. The diffusion of oxygen anion is neglected.
  4. The oxide layer growth and the consumption of metal obey the Wagner’s parabolic law.
  5. The interfaces are flat surface.
Corrosion Barrier Development for LBE Corrosion Resistance (Task 23) Highlights.
- Completed apparatus design for electrodeposition of Cr.
- Completed literature search for Cr electrodeposition.
- From preliminary SEM and visual inspections, the alumina films appear to have good adhesion to the steel substrates.
- A commercial vendor is currently performing micro-scratch tests to measure exact film adhesion.
- Nickel deposition process is currently being developed.
- From present data it appears that steel substrate will require a mechanical polishing step for improved pore uniformity; this is being investigated.

Reactor Physics Studies for the AFCI RACE Project (Reactor-Accelerator Coupling Experiments Project (Task 27) Highlights.
- The newest beta test version of the MCNPX radiation transport code was acquired and installed.
- Modeling with MCNPX continued in support of subcritical experiments at the Idaho Accelerator Center and design for Texas RACE.
- In his role as national RACE Project Director, the PI visited Idaho State University (ISU), coordinated a developing project with the European EUROTRANS project, and visited University of Texas at Austin (UT-Austin), University of California Berkeley, University of Tennessee-Knoxville, Purdue University, and University of Michigan to present colloquia titled “RACE: The AFCI Reactor-Accelerator Coupling Experiments Project.”

1.3.3 Student Research Technical Summary

FUELS TECHNOLOGY

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

In this project, a combination of state-of-the-art soft X-ray spectroscopies are used to understand the chemical bonding between metal fission products (Pd and Ag) with coating layers in TRISO fuel particles (SiC and pyrocarbon). Primary focus is on an analysis of intermediate chemical phases at the interface, the intermixing/diffusion behavior, and the electronic interface structure as a function of material choice (metal and coating materials), temperature, and external stress. In the current first project year, investigations began on the Pd/SiC interface, as discussed in the previous two quarterly reports. The first experiments (both using our lab instrument as well as using high-brilliance synchrotron radiation at the Advanced Light Source (ALS) in Berkeley) indicate that the interface formation leads to three different carbon species, which are ascribed to a bulk species, an interface species, and “reacted” species due to intermixing at the interface. Furthermore, it was found that a significant charge transfer between Pd and Si, as evidenced by the synchrotron X-ray emission spectra presented in the previous report.
In the last quarter, efforts were primarily focused on completing the reassembly of a four-chamber ultra-high vacuum surface science instrument on the UNLV campus after its relocation from the University of Würzburg, Germany, at the end of 2004. Since the vacuum system as a whole and, in particular, most of its spectroscopy components are extremely sensitive instruments, the system was completely dismantled for the relocation, and hence significant work had to be done in the reassembly process. Fortunately, the damage incurred in transit was minimal – all electronic components work well and a ground-connection problem within the electron analyzer (previously encountered at the University of Würzburg) could be resolved by our careful reassembly. Large effort had to be devoted to convert the gas handling systems (ultra-high purity (6N) Argon and Helium) to American standards in order to find reliable suppliers for the required high-purity gases. While Argon is necessary for sputter-cleaning surfaces in-situ, He is required for operating the UV-lamp necessary for UV photoelectron spectroscopy (UPS).

As shown in Fig. 1, the instrument is now completely reassembled and in use on the UNLV campus. Currently, work is being conducted on a detailed and thorough optimization of the electron spectroscopy set-up (which includes the electron analyzer, the dual-anode Al/Mg X-ray source, a small-spot electron gun for local (200 nm) Auger electron spectroscopy, and the UV gas discharge source). These tasks comprise a careful alignment of all components as well as a detail electronic calibration. The latter task is currently being performed and entails the collection of reference spectra of an Ar-ion sputter-cleaned Au-foil reference sample for a variety of spectrometer settings (in order to optimize resolution vs. signal-to-noise ratio, several parameters can be tuned, including the opening angle of the spectrometer, the electron pass energy, and the slit shapes and widths within the spectrometer). As an example for the calibration spectra currently being collected, Fig. 2 shows UV- and X-ray excited photoelectron spectra of the Au foil reference sample. While these experiments are of enormous importance for the reliability and spectral quality obtained with our system in the future, they also present a unique opportunity for the graduate and undergraduate students to learn the operation (e.g.,
sample transfer) and scientific principles of our rather complicated instrument.

In parallel, all students are involved in the further analysis of two previous experimental runs at the University of Würzburg and the Advanced Light Source. This analysis is of large importance, not only to fully understand the current data set in order to gain more insight into the Pd/SiC interface, but also to optimally plan the upcoming experimental runs, both at UNLV (after completion of the calibration experiments) as well as at the ALS (May 2005). While the November 2004 and May 2005 ALS campaigns were/are conducted in experimental time granted to the PI within other projects, a separate beamtime proposal was recently submitted for the fission product/TRISO coating project and the project was awarded eight experimental shifts on a highly-competitive undulator beamline (8.0) in the Fall of 2005.

Once the calibration experiments are complete, the next steps with the project will be to reproduce the previous findings discussed in the previous reports and the introduction above, to utilize realistic SiC-layers from TRISO coaters, and to investigate the possibilities of modifying the interface properties by varying the parameters and conditions under which the Pd/SiC interface is formed in the system.

![Uncalibrated UPS spectrum and XPS survey spectrum](image)

**Figure 2.** Uncalibrated UPS spectrum (left) and XPS survey spectrum (right) of a Au-foil reference sample currently being used to calibrate the electron spectrometer for all relevant experimental settings.

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

This project examines inert matrix fuels containing ZrO₂ and MgO as the inert matrix, with the relative amount of MgO varied from 30 % to 70 % in ZrO₂. Reactor physics calculations are used to examine suitable quantities of burnable poisons from the candidate elements Gd, Er, or Hf with reactor grade Pu providing the fissile component, with up to 10 % of ²³⁹Pu. Ceramics are synthesized and characterized based on the reactor physics results. The solubility the fuel ceramics, in reactor conditions, reprocessing conditions, and repository conditions, are investigated in a manner to provide thermodynamic data necessary for modeling.
The fuel matrix is designed based on neutronic properties, repository behavior, and reprocessing characteristics. The matrix should be as neutron transparent as possible. Burnable poisons are used to maintain constant reactivity. The matrix should also act as a suitable host form for fission products and actinides in a repository environment. Finally, the matrix should be compatible with reprocessing schemes under development in the advanced fuel cycle.

In the past quarter, magnesium and zirconium ceramics were produced with erbium and cerium in the matrix by a refined precipitation method yielding large quantities of ceramics at good precision. The ceramic ratios were chosen to find the solubility point of the zirconia matrix. Analysis of the ceramic materials was performed to determine the phase structure. Studies on the neutronic properties of the inert fuel matrix were also performed.

**Ceramics Synthesis**

Nitrate salts of magnesium, zirconium, cerium, and erbium were dissolved in deionized water to form four separate solutions. The solutions were standardized to known concentrations by ICP-AES. For each of the ceramics in Table 1, a calculation sheet provided the volume of standardized solution to produce the fuel pellet in the correct ratio. The four elements mixed in each solution were all precipitated as insoluble metal hydroxides using ammonium hydroxide and an oxalate chelator. The hydroxides were filtered and rinsed using deionized water then collected and dried overnight at 85 °C. Precipitates were ground in a ball mill and placed into a furnace at 700 °C for 1.75 h, sufficient for reaction to metal oxides, confirmed by thermogravimetric analysis (TGA) and X-ray diffraction (XRD). Oxides were massed for pellet pressing and zinc stearate was added at 1.5% wt./wt. Thorough mixing of the binder and oxide power was achieved with the ball mill. Green pellets were formed into 1cm by 1cm cylinders weighing 1.5 to 2.0 grams by pressing the oxide/binder mixture in a custom pellet die at 135 MPa then sintering in a furnace at 1600°C for 6 hours (Figure 3).

<table>
<thead>
<tr>
<th>Sample #</th>
<th>ZrO₂</th>
<th>MgO</th>
<th>Er₂O₃</th>
<th>CeO₂</th>
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<td>0.598</td>
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</table>

**Phase Analysis**

Structure and phase analysis was performed on the ceramic utilizing scanning electron microscopy (SEM) (Figure 4) and XRD with Reidfield analysis. All nine ceramic SEM images show little difference between particle sizes, dimensions, and the single phase character. The
x-ray powder diffraction patterns were constructed using a Phillips instrument. The patterns were matched with Reidfield structure refinement analysis with silicon as an internal standard. The only phase found through these methods was cubic stabilized zirconia.

*Solubility Studies*

Quantities of ceramic pellets suitable for solubility studies have been produced. Solubility kinetics and high temperature liquid ceramic stability can now move forward. A pressure vessel capable of steam pressures of 180 bar and 360 °C complete with liquid sample port and stirring has been tested.

*Figure 3. Completed inert matrix ceramics.*
Figure 4. 4000x SEM image of ceramic samples 1 to 9 left to right top to bottom.

**Reactor Physics Calculations**

A design of a standard PWR and Pu loadings required for 18-month cycle was used for these calculations. The aim is to estimate performance of each design and material to address challenges of Fertile-Free Fuel (FFF) Concept. Finally, an optimal BP design will be developed and an overall feasibility of FFF concept will be determined. Basically, the main challenge encountered in neutronic design for a FFF core is to develop reactivity control system which is capable to satisfy performance and safety criteria of existing PWR plants.

Heavy Pu loadings combined with absence of fertile isotopes with capture resonances result in low reactivity worth of existing control mechanisms and inadequate temperature coefficients. The main solution adopted by several previous design efforts is based on increased content of burnable poison (BP) materials with capture resonances. The BP designs proposed and analyzed in previous designs are based on such elements as: Gd, Hf, and Er, located in fuel cell, either as a homogeneous mixture or as a thin ring (IFBA-type geometry). This approach results in a large residual reactivity penalty due to an incomplete burnup of the BP material (especially Hf and Er).

An extensive set of calculations was carried out to assess the potential of the main BP materials - B, Gd, Hf, and Er, utilized in three main geometrical arrangements: Wet Annular Burnable
Absorber (WABA) type, Integral Fuel Burnable Absorber (IFBA) type, and Homogeneous fuel-BP mixture. Heavy loadings of BP materials in non-standard geometries combined with high Pu content in a fertile-free matrix necessitated additional verification of the calculational tools.

The potential of different BP designs and BP materials to reduce the critical boron concentration (CBC) of the Pu-FFF core to below the limit of 2000 ppm was assessed. The considered BP materials (B, Gd, Hf, and Er) were utilized in three geometrical arrangements: WABA-type, IFBA-type, and Homogeneous fuel-BP mixture. For each of the BP design options several sub-cases were considered, varied by number of BP rods per assembly, volume and/or BP material density. For each case, three main performance parameters of the BP designs were evaluated:

- CBC required during the cycle,
- Residual reactivity penalty associated with incomplete depletion of the BP material,
- Assembly pin power peaking factors.

The results of calculations, performed in this task, can be summarized as follows:

1. WABA-type
   - Utilization of all BP materials in WABA-type geometry cannot significantly reduce the core CBC.
   - The residual fuel cycle length penalty is minimal because WABA absorbers are physically removed from the assembly after first out of three irradiation cycles.

2. IFBA-type
   - IFBA-type BP designs with Hf and Er can reduce maximum CBC up to 3,000 ppm.
   - IFBA-type BP design with Gd, 264 BP rods/assembly may reduce maximum CBC to 2,400 ppm. Assembly pin-power peak exceeds in this case value of 1.2.
   - IFBA design alone cannot reduce maximum CBC below 2,000 ppm even if 100% of fuel pins in the core are IFBA pins.

3. Homogeneous fuel-BP
   - Homogeneous Gd/fuel BP designs are capable of reducing the maximum CBC to less than 2,000 ppm. It was demonstrated that about 4 kg of Gd per fuel assembly distributed among 132 or 264 pins results in a relatively low penalty on fuel cycle length of 8 full power days.
   - A significant reduction of maximum CBC, below 2,000 ppm, may also be achieved by utilizing 2 - 3 v/o of Hf or 4 - 6 v/o of Er mixed in 132 or 264 fuel rods.
   - However, the major problem with using Hf and Er BP is the large residual penalty in the range of 40 to 150 full power days per cycle.
   - The possible solution to this problem is utilization of an enriched Hf or Er isotopic compositions.

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

There are three key Pu fuel types: Mixed Oxide Fuel (MOX), Thorium/plutonium mix fuels, and Inert matrix fuels (IMF). This report discusses mainly the fabrication of inert matrix fuels. There are three fabrication routes to obtain IMF. IMF is a dispersion-type fuel in which the actinide phase is distributed as a separate phase in a so called inert matrix. This concept has evolved as one of the most promising in the field of transmutation. The following section discusses each manufacturing route.
The primary advantage of IMF is the non-production of new plutonium during irradiation due to lack of uranium (U-free fuel) whose $^{238}\text{U}$ isotope is the departure nuclide for breeding $^{239}\text{Pu}$. In addition it enables nearly total destruction of fissile Pu (inherently non-proliferant fuel).

**Fuel Fabrication**

Three different routes for the fabrication of dispersion-type uranium-free fuels are being investigated. These are: Co-precipitation (CPP), Low-impact mixing of powder (LMP), and Mixing of particles and powders (MPP). Figure 5 shows the three different routes for the fabrication of dispersion-type uranium free fuels.

**CPP Scheme**

The CPP route is a relatively simple one, based on the dissolution of the starting materials in nitric acid and the precipitation of all the components from this solution after adjusting the pH by the addition of ammonia. The powder, obtained after washing, drying and calcinations of the precipitate, is directly used for the preparation of pellets. Ceramographic analysis, SEM and X-ray radiography showed that the actinide phase is present as very small (sub-micron size) particles in the matrix, uniformly distributed in the pellets.

**LMP Scheme**

The LMP route is based on the low-impact mixing of a sinter-active powder of the inert matrix and the powder of the actinide phase. The low-impact mixing is performed manually in a mortar (initial trials) or mechanically in a mixer mill. The blend thus obtained is used for the preparation of pellets. This method has been tested for matrix materials mixed with a single oxide phase or mixed with a solid solution of two or more oxides. Ceramographic analysis showed that for all mixtures of inert matrix and UO$_2$ investigated, a dispersion of the actinide phase has been obtained and randomly distributed in the matrix. However, the major part of the UO$_2$ is found in irregularly shaped inclusions whose size is in the order of 100-200 $\mu$m.

**MPP Scheme**

The MPP route is the most complex one that has been investigated. It is based on the fabrication of particles containing the actinide phase by sol-gel technique followed by mixing of the particles and matrix powder. The sol-gel technique is based on the injection of droplets of a nitrate solution in an organic phase, sphere formation in the organic phase and gelatin in the ammonia phase. After washing and drying the spheres are calcined and optionally sintered. Spherical particles with a controller and uniform size (200-300 $\mu$m) can be prepared by this method. Next, the particles are mixed with a sinter-active powder as described above for LMP route, using zinc (Zn) stearate and camphor as additives. The protruding of spheres can easily be solved by a mechanical treatment of the surface of the sintered pellets although this will lead to scrap that needs to be recycled and, moreover, the formation of dust containing the actinides. This might be acceptable for Pu fuels, but it is not preferred for americium (Am).
SEPARATIONS TECHNOLOGY

Immobilization of Fission Iodine (Task 15).

Experiments on the reaction of iodate with sphagnum peat moss were continued. It was established that iodate added to a suspension of peat moss undergoes reduction and to a significant extent is incorporated into the peat moss. It was confirmed that the incorporation of iodine into the peat matrix using pyrolysis GC/MS. In addition, a scaled-up pyrolysis was performed using the preparative GC system that was described in a previous report. This instrument consisted of a packed column gas chromatograph (SRI 8010) with a TCD detector and injector valve equipped with a thermal desorber. Pyrolysis experiments were performed in a 6” tube furnace manufactured by Carbolyte. This programmable furnace has a 0.5” diameter process tube that can hold 8-100 mg samples of peat or ion exchange resin. During sample heating helium stream sweeps products from the tube furnace to the carbosieve trap located in the thermal desorber unit. Volatile materials that are collected on the carbosieve trap can be transferred to the gas chromatograph by actuating the valve and activating the thermal desorption.
oven. Chromatography is initiated by thermally desorbing trapped volatiles from the carbosieve trap to the GC column (2mm x 2m, Porapak Q). The instrument was calibrated with by injecting methyl iodide into the thermal desorber trap. The response factor and retention time of methyl iodide were thus determined. Pyrolysis experiments with 8-12 mg of organic matter have been conducted using this experimental apparatus. Experimental results for a two series of incubations are shown in Figure 6. Results for experiments with a peat sample incubated at 40°C and pH 4.3 are shown. In addition, the results for a commercially available humic acid at pH 2 are presented. The low pH was used to prevent dissolution of the humic material.

During this last quarter, the influence of pyrolysis temperature on the yield of methyl iodide was investigated. Experiments were performed with the analytical pyrolysis unit described in previous reports and with the preparative GC. The results of these studies demonstrate optimum methyl iodide production at 400°C. The peat (350 mg) was incubated in 20 mL of 2.7*10⁻³M KIO₃. The suspension pH was established with phosphate buffer and the sample was held in a constant temperature incubator. In most cases the amount of methyl iodide produced by pyrolysis increased with an increase in heating time. Previous reports indicated that organically bound iodine went through a maximum during heating experiments and then slowly decreased. This maximum was not apparent in the pyrolysis results.

Additional kinetic experiments were conducted on the reaction of natural organic matter with iodine. These experiments were conducted in aqueous solution and the progress of the reaction was monitored by UV spectroscopy. In previous experiments iodine was added to aqueous buffers. Because of rapid reaction kinetics the rates of reaction were often difficult to follow. In this latest group of experiments a constant background of KI was included. The equilibrium constant for the formation of the $I_3^-$ (aq) species is well known.

$$I^- + I_2 \rightarrow I_3^- \quad K=740$$

The presence of $I^-$ (aq) converts $I_2$(aq) to $I_3^-$(aq) which has strong UV adsorption at 290 nm and 350 nm. Thus, the reaction of the aqueous iodine with various natural organic materials, or model compounds, can be followed by monitoring the decrease in absorbance at 290 or 350 nm. The reactive species in these experiments is still $I_2$, however, because most of the iodine is tied up as the triiodide ($I_3^-$) species reaction rates are reduced by a factor of $(1+K[I^-])^{-1}$ which makes following the reaction easier. Reactions of humic acid, soluble alkali lignin, vanillin and vanillic acid were studied. Example results for Aldrich alkali lignin are shown in Figure 7. These measurements were conducted in aqueous buffered solutions at room temperature (~20°C). The results in Figure 7 confirm previous observations an increase in reaction rate of lignin with iodine with increasing pH.

Previously it was hypothesized that iodine reacts with phenolic groups of lignin. Thus, NOM should exhibit a finite capacity for reactions. This is illustrated in Figure 8 where the reaction kinetics were monitored for three additions of iodine 3.1x10⁻⁵ M to the same solution of alkali
lignin. With each addition the rate of loss of absorbance at 350 nm is reduced (note flattening of curve). The lignin concentration was (0.008 g/mL) for these experiments.

Additional measurements of the reaction of vanillin and vanillic acid (model compounds) under these reaction conditions were conducted. The reaction of these model compounds is apparently first order in iodine and in the phenolic model compounds (modeling results not shown). The reaction is faster at higher pH for vanillin and faster for the vanillic acid than the vanillin. In the case of vanillin, the UV spectra indicated that Iodo-vanillin was the major product. The substantial adsorption of both the product and the starting material at 290 and 350 made measurements of vanillin kinetics difficult. It was found that the background adsorption at 350 and 290 nm (the adsorption maximum for triiodide) shifted substantially as a result of the formation of iodovanillin and made interpretation of measurements difficult. The reaction of I$_3^-$ with vanillin at isosbestic points (for vanillin and iodo-vanillin) where substantial I$_3^-$ absorption was still apparent was monitored. The isosbestic points have to be determined at each pH studied, as the UV spectra for ionizable compounds are pH dependent. For pH 8.1, measurements could be made at 282 nm (close to the 290 maximum for triiodide). At pH 6.9 measurements were made at 269 nm (considerably off the maximum for triiodide). This explains the difference in starting absorbance for the pH 8.1 and pH 6.9 results of Figure 9. Previously it was thought that the ionization of the phenolic proton was important for promoting the reaction. The pKa of the vanillin hydroxyl group is 7.4. Thus at pH 8.1 the phenolate is the dominant species. At pH 6.9 the concentration of the phenolate is reduced and this is reflected in the slower reaction kinetics. The pKa of the vanillic acid phenolic hydroxyl group is closer to 10. Therefore the phenolate is a minor species at pH 8.1. The oxidation of the electron withdrawing aldehyde (carbonyl) group of vanillin to the carboxylic acid (vanillic acid) seems to more than compensate low ionization of the phenolic hydroxyl in vanillic acid, as the reaction of vanillic acid with I$_3^-$ is considerable faster than with vanillin. Additional pH values for this compound will be investigated.
Figure 6. Methyl Iodide production from pyrolysis of sphagnum peat and a commercial (Flucka) humic acid exposed to a KIO$_3$ solution for various times.
Figure 7. The reaction of $I_3^-$ with commercially available alkali lignin is monitored at three different pH values. The reaction rate increases with increasing pH.
Figure 8. The finite capacity of lignin for iodine is indicated by repeated treatment of the same sample with iodine. The reaction rate decreased with each treatment. By the third treatment only small fraction of the iodine added was removed.
Figure 9. The reaction of iodine (as I3-) was examined for two lignin model compounds. Different wavelengths were used because of differences in the background absorption of the model compounds. The initial slopes indicate the reaction rates, of these compounds.

Fluorapatite Waste Forms (Task 16).

Fluorapatite, fluorinated calcium phosphate, has been identified as a potential matrix for the entombment of the zirconium fluoride fission product waste stream from the proposed FLEX process. If the efficacy of fluorapatite-based waste-storage can be demonstrated, then new and potentially more-efficient options for handling and separating high-level wastes, based on fluoride-salt extraction, will become feasible. This task is a dual-path research project to develop a process to fabricate a synthetic fluorapatite waste form for the ZrF₄, FP waste stream, characterize the waste form, examine its performance under environmental conditions, and correlate the behavior of the waste form with natural analogs. Characterization of the material will be accomplished through probing the molecular-scale electronic and geometric structure of
the materials in order to relate them to macroscopic properties, with the goal of developing techniques to evaluate and predict the performance of different waste-form materials. Time and funding permitting, other waste forms for the zirconium fluoride, fission product salt waste stream will be examined and benchmarked against the fluorapatite matrix baseline.

During last quarter, procedures were investigated to re-synthesize fluorapatite with some success. As mentioned before fluorapatite is a naturally occurring mineral with a strong crystal structure and it is an abundant mineral around the world. It is desirable to find a way to use natural apatite to synthesize nuclear waste bearing apatite rather than using the more expensive pure chemical reactants to begin with. This time re-syntheses of fluorapatite at lower temperature was tried after the first attempt at boiling temperature was partially successful. The re-synthesized sample was annealed and analyzed using the X-ray powder diffraction method and photoacoustic infra-red spectroscopy. It was found that low temperature re-synthesis of apatite results in large quantities of undesired products such as calcium phosphate, unlike the high temperature synthesis (99% apatite). The annealed product is also brittle and less dense than synthetic (or natural) fluorapatite, which makes it less suitable as storage matrix.

Experiments have been carried out to determine the change of the Ca/P ratio in fluorapatite (FAP) based on the amounts of Sr surrogates included in FAP samples. Energy Dispersive X-ray Spectra (EDS) have been obtained for various Ca:Sr ratios in synthesized FAP samples. Fluorapatite has the chemical formula $\text{Ca}_5(\text{PO}_4)_3\text{F}$ and Ca and P maintains the atomic ratio of 1.667 ($=\frac{5}{3}$) in any pure apatite sample. The accuracy of this ratio has been used as an index of composition and thermal behavior (ref.: Champion, E. \textit{et al}, Calcium phosphate apatites with variable Ca/P atomic ratio I. Synthesis, characterization and thermal stability of powders, Biomaterials, 23, 1065, (2002)). The following samples have been synthesized and analyzed:

1. Fluorapatite (FAP)
2. Ca: Sr = 4:1 FAP
3. Ca: Sr = 3:2 FAP
4. Ca: Sr = 2:3 FAP
5. Ca: Sr = 1:4 FAP

Table 2 shows the observed atomic percentages and Ca/P ratios.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ca [%]</th>
<th>Sr [%]</th>
<th>P [%]</th>
<th>(Ca+Sr)/P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca5-FAP</td>
<td>18.57</td>
<td>0.00</td>
<td>11.28</td>
<td>1.65</td>
</tr>
<tr>
<td>Ca4Sr-FAP</td>
<td>11.49</td>
<td>2.55</td>
<td>9.04</td>
<td>1.55</td>
</tr>
<tr>
<td>Ca3Sr2-FAP</td>
<td>13.21</td>
<td>8.30</td>
<td>11.63</td>
<td>1.85</td>
</tr>
<tr>
<td>Ca2Sr3-FAP</td>
<td>8.81</td>
<td>13.38</td>
<td>11.17</td>
<td>1.98</td>
</tr>
<tr>
<td>CaSr4-FAP</td>
<td>3.73</td>
<td>11.50</td>
<td>7.90</td>
<td>1.92</td>
</tr>
</tbody>
</table>

Even though the expected value for Ca/P is 1.667, only pure FAP has a value closest to the theoretical value. The ratios of Ca/P increase with increasing Sr content but starts at a lower value (1.55) when only one of the five Ca atoms is replaced by one Sr atom. This dependency is partially based on the considerable amounts of impurities ($\text{Sr}_3(\text{PO}_4)_2$ and $\text{Sr}_2\text{P}_2\text{O}_7$) formed during
the synthesis process. Another possible reason might be the replacement of fluoride ions by CO$_3^{2-}$ ions. This is a commonly found ion in fluorapatite and excessive inclusions of carbonate ions form carbonate-fluorapatite. The presence of the carbonate group was confirmed by FTIR spectra that were obtained for all the samples (2350 cm$^{-1}$). It might be necessary to use an inert atmosphere inside the synthesis flask to avoid contamination with CO$_2$ in order to get more accurate values.

Figure 10. Un-annealed Cu-apatite sample.

The third experiment performed during the last quarter was the synthesis of Cu and Ni containing fluorapatite using the same procedure as for fluorapatite and Sr-apatite (strontium containing fluorapatite). One change was made to the original procedure by not adding NH$_4$OH to keep the pH value at 9. Instead, the pH was kept at 7 in order to prevent the formation of the Cu(NH$_3$)$_2^{2+}$ complex. The Table 3 summarizes the initial compositions used for synthesis and weight load percentages.

<table>
<thead>
<tr>
<th>Ion type</th>
<th>Initial concentration (mol/L)</th>
<th>Expected formula</th>
<th>Weight load (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>0.0392 (in 0.353M Ca$^{2+}$)</td>
<td>Ca$_{9}$Cu(PO$_4$)$_6$F$_2$</td>
<td>6.16</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>0.0196 (in 0.373M Ca$^{2+}$)</td>
<td>Ca$<em>{9.5}$Ni$</em>{0.5}$(PO$_4$)$_6$F$_2$</td>
<td>3.14</td>
</tr>
</tbody>
</table>

The un-annealed Cu-apatite sample shown in Figure 10 has a light blue color and the color faded off as the temperature was increased during the annealing process. The first annealed sample became “char” when reaching the annealing temperature of 1200°C. Then the sample was heated at several lower temperatures (600°C, 700°C, 800°C and 1100°C) with similar results. A power X-ray diffraction (XRD) pattern was obtained for the Cu-apatite sample that was annealed at 600°C and is shown in Figure 11. The XRD pattern confirms the formation of an apatite structure and also shows the higher percentage of fluorite (CaF$_2$) in the product. The corresponding peaks for fluorite have been marked by arrows in the spectrum. A more refined
procedure to synthesize Cu-apatite has to be found in order to reduce the fluorite by-product formation.

![Figure 11. XRD patterns of fluorapatite before and after sintered at 1200°C](chart)

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

Major tasks can be divided into two parts: development of middleware associated with TRPSEMPro and processing modeling using ASPEN-Plus.

**Development of middleware in TRPSEMPro**

- ANL discovered several new non-fission product cations and anions needed to be added into the interface. The new component interface is shown in Figure 12. The changes involved both the code modification on the TRPSEMPro package and the AMUSE macros.
- Prior to fully utilizing the optimization module provided by ASPEN-Plus process model, the current TRPSEMPro is required to adjust D value based on each component within each section for critical simulation convergence. A new interface shown in Figure 13 was created. The modification involved more fundamental change on the TRPSEMPro code. The D value was designed as a section-related factor that sets to zero initially for simplicity.
- More error handling was implemented. Error-prompted message box contents and ErrorInfor.log file format were continuously modified for better identification of the origin of errors. Error messages will also be recorded if aqueous and/or organic feed do not have a feed letter.
- The team has added an organic flow procedure validation code for identifying a greater-than-zero organic flow rate into the first section and greater-than-zero organic flow out of the last section. Modification of the multiple-run counter was made. The updated TRPSEMPro will force to calculate flow rate prior to the AMUSE simulation run.

**Process Model using ASPEN Plus package**
• Object identification and program communication were undertaken during this quarter.
• Both the ANL and the NCACM teams are using the remote desktop connection for ASPEN-plus access. The NCACM will need more chemical process input from ANL once the basic programming components are identified.
• Several preliminary process models were created to successfully enable VB object call and manipulate processes inputs with certain given outputs.
• A simple ASPEN Plus flowsheet process model was created for demonstration. The demo model simulates a separation of 99% for water and heptane. The simulated results are shown in Figure 14 with the following conditions: \( T_{\text{feed}} = 100 \, \text{C}, \ P_{\text{feed}} = 1 \, \text{bar}, \ X_{\text{water}} = 0.5, \ \text{Stagescolumn} = 250, \ \text{Reflux Ratio} = 10. \)
• A simple interface to input and output parameters from the ASPEN-Plus was created.

![Figure 12. The updated component interface.](image-url)
Electrochemical Separation of Curium and Americium (Task 25).

Data collection and analysis of the Ce\(^{3+}/\)Ce\(^{4+}\) redox couple in various supporting electrolytes (0.3 M NaNO\(_3\), 0.5 M HNO\(_3\), and H\(_2\)SO\(_4\) at concentrations of 0.1 M, 1.0 M, 2.0 M, and 4.0 M) has continued. All electrolyte systems were investigated at Pt, Au, and Glassy Carbon working electrodes. Analysis of these data was accomplished by performing appropriate background
subtractions to reveal net peaks due to Ce redox behavior. Successful identification of the Ce redox couple was achieved with all electrolyte/electrode systems, although a decline in peak resolution was observed with increasing acid concentration. Optimal conditions in this experiment were realized with a 6.0 mM Ce concentration, 0.1 M H$_2$SO$_4$ supporting electrolyte, and scan rate of 0.02 V/s. This is in stark contrast to previously studies were the acid concentration employed was on the order of 1 to 6 Molar. The influence of acid concentration on the voltammetric response of Ce(NO$_3$)$_3$ in sulfuric acid for Au electrodes is presented in Figure 15. The same trend is observed for both Platinum and Carbon electrodes indicating that either pH or ionic strength, µ influence the ability to resolve the redox properties of Ce.

An investigation into ionic strength is being conducted for the Ce system, using varying concentrations of K$_2$SO$_4$ in place of the H$_2$SO$_4$ supporting electrolyte solutions. This is being done to determine whether the observed decline in peak resolution with increasing acid concentration is due to a decreasing pH or ionic strength. Ionic strengths were calculated and pH of all solutions will be taken in order to analyze the data obtained. Preliminary results are presented in Figure 16 for a system with an ionic strength of µ = 0.3 M. The data suggests that acidity is the key variable in the system with higher resolution and lower splitting of the Ce3+/Ce4+ redox couple.

![Figure 15. Influence of acid concentration on the redox properties of 6mM Ce(NO$_3$)$_3$. The redox couple Ce3+/Ce4+ are labeled using A and A'. The background in the supporting electrolyte is presented below the cyclic voltammetry for the solution containing Ce.](image-url)
Figure 16. Influence of acid concentration on the redox properties of 6mM Ce(NO$_3$)$_3$ with constant ionic strength $\mu = 0.3$ M.

Voltammetry will be taken at the other ionic strengths used to obtain Figure 15 to determine if the trends observed are consistent as ionic strength is increased.

Finally, the investigation of the Sm redox couple was initiated by employing the conditions determined as optimal for the Ce experiment. Successful resolution of the Sm redox couple was accomplished using this system. Future work on this species will include further experiments, similar to those conducted for Ce, which will vary the working electrode and supporting electrolyte.

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

Studies were performed the extraction of uranium from nitric acid into 30 % TBP in dodecane as a function of nitrate concentration. Stock solutions of uranyl nitrate were prepared at constant nitric acid concentration by dissolution of known quantities of UO$_2$ (NO$_3$)$_2$·62O (Merck) in nitric acid solutions. Organic extraction phases were prepared using 30 vol. % tributyl phosphate (Aldrich 97 %) with n-dodecane (Prolabo). Nitrate concentration was adjusted by the addition of concentrated LiNO$_3$. Equal volumes of 5 mL organic and aqueous phases were contacted and vigorously mixed for 5 minutes then allowed to mix on a shaker table for 5 hours. After centrifuging, samples of each phase were drawn off and spectra taken using a Cary UV-visible spectrometer with precision quartz cuvettes (1 cm path length) measured against a deionized water reference cell. Four sets of spectra were collected for each sample and the average used in analysis performed with Microsoft Excel™ software.

Improvement of the extraction methods was undertaken. The volume of aqueous and organic phase used was reduced to 1.6 mL. Spectroscopy is still possible with these volumes and waste volume is minimized. The determination of nitrate concentration in the organic phase has been measured by ion specific electrode and ion chromatography. For the ion specific electrode the
system is found to be highly dependent upon the total acid concentration. Up to 5% drift with same standards and 12% drift with variations in total acid concentration was observed. Nitrate ion chromatography shows accuracy of 5% and no acid effects are observed. UV-visible spectra were collected for a number of TBP/dodecane extractions of uranium (Figure 7).

A number of different nitrate concentrations were examined. The following conditions were found for third phase formation as measured at 18°C:

- For 1 M U, need $[\text{NO}_3]_{\text{tot}} \geq 10.2$ M, $[\text{HNO}_3] \geq 5$ M
- For 0.5 M U, need $[\text{NO}_3]_{\text{tot}} > 11$ M, $[\text{HNO}_3] > 7$ M, 
- For 10 M HNO$_3$, no nitrate need $[\text{U}] \sim 0.57$ M
- For 12 M HNO$_3$, no nitrate need $[\text{U}] \sim 0.185$ M
- For 13 M HNO$_3$, no nitrate need $[\text{U}] \sim 0.08$ M
- For 14 M HNO$_3$, no nitrate need $[\text{U}] \sim 0.022$ M
- For 14 M $[\text{NO}_3]_{\text{tot}}$ and 10 M $[\text{HNO}_3]$, need $[\text{U}] \sim 0.062$ M
- For 12 M $[\text{NO}_3]_{\text{tot}}$ and 8 M $[\text{HNO}_3]$, need $[\text{U}] \sim 0.42$ M

The results on nitrate organic concentration at 12 M HNO$_3$, 12 M total nitrate, and 14 M HNO$_3$ show that the bulk of the nitrate remains in the aqueous phase. The total nitrate extracted appears independent of initial uranium, nitrate, and nitric acid concentrations.

When the organic phase splits, the heavy phases has about 2 – 2.5 M $[\text{NO}_3]$ and the light phases have about 1-1.2 M $[\text{NO}_3]$. Single phases have about 1.3-1.5 M $[\text{NO}_3]$, similar to the light 2nd phase. High $[\text{NO}_3^{-}]$ is found to encourages complete extraction of U into a heavy phase. Kinetic effects on third phase formation were observed.

**TRANSMUTATION SCIENCES**
Niobium Cavity Fabrication Optimization (Task 2).

The Monte Carlo Back Scattering and Secondary Electron Scattering code developed by Dr. David Joy (ORNL and University of Tennessee Knoxville) has been placed on a C++ format offering fast computational speed. The architecture of the code has been modified to track multiple generations of secondary electrons. The original code only followed the secondary electrons generated by the primary electron. The model is based on Dr. David Joy’s experience in the secondary electron microscopy. The code has been modified to take into consideration four or more layers which can represent a surface contaminant. A more rigorous treatment of the elastic and inelastic process of multiple components in each layer has been carefully incorporated in the code. The current version of the code does not have a graphical user interface illustrating the particle dynamics as in the original code. As a result, a visual of the code outputs is not presented here.

Experimental Study of SEE from Niobium

Between August 2004 and January 2005, considerable effort was placed in coordinating the operation of each component of the test stand. Electronic measurements were compared against manufacture’s measurements and software output. Limitations of the test stand were also examined. Although the cryostat cold head reaches 8.5 °K, the sample itself only reaches temperatures of about 15 °K as measured by a temperature diode attached to the cryohead surface. This is due to the large thermal gradient posed to the sample and the thermal power limitations of the cryohead.

Figure 18. A long range microscope is used to examine both the electron beam diameter impinging on a phosphorescence screen and the surface structure of the piece under test.

Working within the limitations of the secondary electron emission test stand, sample studies were conducted at room temperature on a non-surfaced cleaned niobium sample. An experimental procedure was developed using the detector as a means to determine which beveled surface lies within the path of the beam. Figure 18 depicts a long range microscope used to measure the electron beam width. The same microscope is used to show the different beveled surfaces and the texture of the surfaces under test as demonstrated in Figure 19. The overall extent of the gauge in the figure measures 0.5 mm. The striations of the sample surface are very noticeable on this sample.
Figure 19. Machine cut niobium sample prior to surface conditioning as pictured in the SEE test stand. Three beveled surfaces can be seen with machine cut striations over the sample surface. A 0.5 mm reticule is also shown in the figure. All samples prior to cleaning have been machined by the same machine shop in the same manner.

Current experiments were performed with a 1 keV primary electron beam impinging on a sample surface within a 10 second acquisition time. A 100 V grid potential and a 2.4 kV MCP (micro-channel plate) potential were imposed. The sample to grid distance is 1”. Figures 20a and 20b provide typical secondary electron position data that have been conditioned for a primary beam impinging at a 15° angle to the normal of the niobium surface. Both dark noise and count levels less than five have been subtracted from the raw data. Primary beam currents are typically measured with a Faraday Cup. Although not measured for these specific shots, the beam current is on the order of 8 nA based on past measurements. Because of the striations in the unconditioned sample, one would suspect that a small change in sample position might result in a difference in the secondary electron emission pattern. It is observed in Fig. 20b that the SEE count was about twice that of Fig. 20a. The “sweet spot” of the secondary electron emission noticeably shifted.
Based on particle tracking simulations, a family of initial energies and momenta are determined for a point in the “sweet spot” of the data measured. Neglecting the effect of striations, it is assumed that the angle the beam makes with the normal of the surface is equivalent to the angle of the bevel. This assumes that the surface is smooth as should be the case in the conditioned surfaces to be tested in the future. From Fig. 20a, the (10,-30) point was translated to appropriate location on the sample surface. Figure 21 provides all of the possible initial energy and momentum angles that will lead to the final particle position location.
Figure 21. A family of initial energy and momentum conditions leading to the final condition of a electrons detected in the “sweet spot” of the secondary electron emission. This data is based on the secondary electrons being launched in the central region of the 15° bevel.

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

The Neutron Multiplicity Detector System (NMDS), which was suffering from a number of malfunctions, was completely repaired and components are performing as expected for low count rates. However, the system loses much of its data when counting high-activity neutron sources. It will not count more than two hundred counts per second. Much of the effort this quarter has been in determining the cause of this data loss and determining potential methods to improve electronic performance.

In January, a dead-time measurement experiment was conducted in collaboration with the Remote Sensing Laboratory (RSL). Data was analyzed and deadtime coefficients were determined. The measurement was conducted using a cubic configuration and 64 detectors arranged in four banks of 8. Two $^{252}$Cf neutron sources of 13,000 and 78,000 neutrons/second were used to perform two-source deadtime measurements. Figure 22 illustrates the layout of the experiment. Results indicated that the performance of individual detectors depends upon the number of detectors operating as well as the source strength (see Figure 23). The individual detector were determined to have a deadtime coefficient of a few ms, which would indicate a capability of the total system to count several thousand neutrons per second. However, more than 200 n/s have never been counted. In addition to deadtime of the individual $^3$He tubes and pre-amps, signal processing boxes which support 8 detectors each also contribute to deadtime. It was determined that 8 detectors distributed across two boxes counted at a higher rate and had less deadtime than 8 detectors in a single box. In the final analysis, though, these experiments
demonstrated that the performance of the system is critically limited because the “special computer” simply cannot handle the data throughput during high count rates. In contrast, 50 or more counts from cosmic neutrons have been measured in a single 256 µs burst, a rate of $2 \times 10^5$ counts per second, but these events never happen even once a second. As a consequence of these experiments, a plan is being formulated to acquire a modern data acquisition system that will support the maximum performance of each detector and all the detectors combined.

*Figure 22. Top view of the two-source NMDS experiment. Each “Box” represents 8 detectors stacked vertically.*
To expand on the experiments that were conducted in January at the RSL, measurements were conducted using a Cf-252 source placed at different distances from the detector system to measure efficiency, dead time, and CPU losses. A parametric radiation transport study was performed with MCNPX for comparison to the above efficiency measurements. Data is currently being analyzed.

As a result of performance limitations, future experiments at LANL were cancelled because measurements cannot be made in intense neutron fields. However, Brookhaven National Laboratory may be able to produce a low-intensity source less than 200 protons per second, so planning has been re-initiated for a Fall 2005 experiment.

**Development of Dose Conversion Coefficients for Radionuclides Produced in Spallation Neutron Sources (Task 7).**

A research consortium comprised of representatives from several universities and national laboratories has successfully generated internal and external dose conversion coefficients for 20 radionuclides produced in spallation neutron sources. In addition, the group has identified 20 radionuclides that are missing electron capture files and 18 additional radionuclides missing substantial physical data. The goal for the current year is to develop a methodology that will allow for producing the dose coefficients for these radionuclides with missing data. Methods to obtain these data are being investigated.

Investigated the requirements to produce data for radionuclides in Category 3: Several of the radionuclides first investigated lack the required nuclear data to calculate dose coefficients. The...
extension of the project has targeted investigating the feasibility of producing these rare radionuclides using the linear accelerator located on Idaho State University’s campus. A meeting with Derek Jokisch, David Peterson, and Rich Brey was conducted in January to discuss the possibility of producing the missing radionuclide data. Much concern was noted on the feasibility of this, therefore an approach that investigates the possible error associated with calculating dose coefficients without the missing electron capture files is being developed.

**Developing a Sensing System for the Measurement of Oxygen Concentrations in Liquid LBE Systems (Task 13).**

Data analysis was performed on the data collected from the LANL Delta loop to find the temperature response of the YSZ oxygen sensor under the hydrogen injection condition. The sensors based on the YSZ (solid electrolyte) /BiB$_2$O$_3$ (reference electrode) system were studied by UNLV/LANL. However, the development of this type of sensor was hindered by the some problems. First, the leakage of the liquid metal can contaminated the sensor chamber. Second, the YSZ oxygen sensor stopped functioning once the signal wire was extremely oxidized after a certain amount of running time. This negates the effort at oxygen sensor calibration, and it can be a serious problem for this type of sensor to be used in long-term monitoring of the dissolved oxygen concentration in large loops. Finally, the thermal shock of solid electrolyte can pose a serious reliability problem.

There are a few problems in the apparatus developed by TRP Task 13 team members and also the experiment. The current heating method can only heat the liquid LBE up to 480°C. Such a temperature is lower than the expected operating temperature range (> 750 °C). Even though some preliminary oxygen sensor calibration curves have been achieved and some significant improvements have been designed and taken into the practice, the comprehensive calibration curves showing the sensor characteristics and sensor response are still waiting to be addressed. Currently, a sound (pressure and vacuum) tight seal can be produced between the sensor tip and the metal body. A temperature over the melting point (780 °C) of the braze material will cause the leakage of liquid metal into the sensor chamber.

From time to time, oxygen sensors need to be replaced. As shown in Fig. 24, a thick lead oxide layer may form at the surface of the LBE liquid. The surface of the oxygen sensor will be immediately blocked by the lead oxide when the oxygen sensor is inserted into the liquid LBE again. This may cause the oxygen sensor to stop functioning.
Use of Positron Annihilation Spectroscopy for Stress-Strain Measurements (Task 14).

The purpose of this collaborative research project involving UNLV, ISU, and LANL is to evaluate the feasibility of determining residual stresses in cold-worked, plastically-deformed (bent), and welded materials using a nondestructive method based on positron annihilation spectroscopy (PAS). This technique uses $\gamma$-rays from a small MeV electron Linac to generate positrons inside the sample via pair production. This method is known to have capabilities of characterizing defects in thick specimens that could not be accomplished by conventional positron technique or other nondestructive methods.

The data generated by the PAS method has been compared to those obtained by other methods such as neutron diffraction (ND), X-ray diffraction (for thin specimens), and ring-core (destructive-for thick specimens) techniques. During the initial phase of this task residual stresses induced in experimental heats of austenitic type 304L stainless steel, and martensitic Alloy EP-823 have been determined by X-ray diffraction (XRD), PAS and ring-core (RC) techniques. More recently, residual stress measurements have been performed on Alloy HT-9 subjected to cold deformation and welding using all four techniques.

The current testing is focused on the evaluation of residual stresses in irradiated materials (welded/plastically-deformed), and welded specimens, with and without post-weld-thermal-treatment (PWTT). Measurements of residual stresses in cold-worked and welded specimens of Alloys EP-823 and HT-9 are planned to be performed at the Atomic Energy of Canada Limited (AECL) by using the ND technique. Development of calibration curves using the PAS method are also being planned at ISU involving Alloy HT-9. Cold-worked and welded specimens of Alloys EP-823 and HT-9 have been machined to measure residual stresses by ND and PAS techniques. Some tensile specimens have also been prepared for development of calibration curves for residual stress/strain by the PAS technique. TEM studies to analyze defects/imperfections in cold-worked Alloys EP-823 and HT-9 are in progress.

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

This project has four components: (1) the fabrication of a materials test apparatus with unique capabilities, (2) comparative studies of steel corrosion under gas phase conditions comparable to the Lead Bismuth Eutectic (LBE) oxygen control conditions, (3) isotope labeling studies, and (4) collaborative efforts with other workers in the field.

Materials test apparatus

The building of the High Temperature Materials Experimental Facility in room CHE 112C was started. 2-3 experiments are expected to be located there in the initial phase, and up to 6 at a later stage of the facility. The facility features a stainless steel hood for high temperature apparatus, a filtered laminar flow hood for sample manipulations and preparations, an acid work/storage area, steel bench space, gas storage, safety equipment, and space for equipment.
racks and computer workstation(s). This equipment is partially in place, and will continue to be delivered over the next month.

**Comparative gas phase studies**

An appropriate tube furnace for the gas phase experiments is being procured. Both thermal decomposition of unstable oxides (lead oxide, copper oxide) and the Oxygen Control System (built at KALLA) for atmospheric controls will be used. Access has been arranged to the quartz tube capsule fabrication station in the physics glass shop.

**Isotope labeling studies**

The isotope labeling experiments are progressing. The ion implantation facility experienced a number of control system malfunctions which have been repaired, and test experiments are planned for April.

**Collaborative work**

In collaboration with LANL, Samples are being characterized that have been exposed to LBE in the DELTA loop at a temperature of 520C and for exposure times of 267 or 400 hours. 38 samples were recently received. Mounting and SEM/EDX investigations are ongoing, and will be reported as they become available.

There was particular interest in the shot-peened 316L samples, which should be roughly comparable to the cold rolled samples exposed at IPPE and examined by us. It was found in the 267 hour DELTA loop exposed samples a very thin oxide layer, on the order of 1 micron thick (Figure 25). However, the corrosion was not uniform and in some regions pitting was found, sometimes shallow pits with oxide at the bottom and sometimes deep pits, also oxidized. In regions where the LBE was not flowing (void regions near the hold down fixtures) more significant corrosion features were found: pits, detached oxide, evidence of significant removal of metal and lead infiltration (Figure 26).

The 400 hour shot-peened specimen was similar (Figure 27). In some cases, simultaneous formation of lead, iron, and chromium oxides of porous morphology was seen. In stagnant regions, lead infiltration, breakdown of the crystal matrix of the alloy, and mixed (primarily chromium) oxides (Figure 28) was seen.

Shot-peening with smaller beads improved corrosion resistance: the smoother surface had fewer and smaller failures (Figure 29). This argues against the mechanical “keying” mechanism proposed earlier to explain the improvements in corrosion resistance observed with cold rolled 316L.

The salient feature of these specimens is the absence of any obvious healing of oxide failures in the stagnant regions during LBE exposure. This problem is less important in the flowing (non-stagnant) regions: although oxide failure do occur, evidence of healing is observed in some cases.
Aluminized 316L shows low corrosion, but a very complicated segregated surface/near surface region (Figure 30). The aluminum results suggest that a significantly different protective layer may modify the underlying near-surface region in complicated ways.

As was seen before with samples from another exposure facility (INEEL), there is evident contamination of the LBE by particulate matter, at least at cold temperatures. These particulates are not associated with observable oxygen by EDX, which argues that they were dissolved in the LBE in metallic form (i.e., not oxide particles) at the operational temperature. More detailed studies will be necessary to resolve this issue.

The purpose of this collaborative research project involving UNLV, LANL and ISU is to evaluate the effect of silicon (Si) content on the corrosion behavior and radiation-induced embrittlement of martensitic stainless steels having chemical compositions similar to that of the modified 9Cr-1Mo steel. Recent studies at LANL involving Alloy EP-823 of different Si content have demonstrated that increased Si content in this alloy may enhance the corrosion resistance in molten lead-bismuth-eutectic (LBE). Since very little data exists in the open literature on the beneficial effect of Si content on the corrosion properties, it seems appropriate to initiate a research project to address this technical issue.

This project is intended to study the effect of Si content not only on the corrosion resistance but also on the radiation-induced embrittlement of martensitic stainless steels. The susceptibility of these alloys with different Si content to stress corrosion cracking, general corrosion and localized corrosion will be evaluated in the molten LBE and aqueous environments of different pH values using state-of-the-art testing techniques. Testing in the aqueous media is intended to develop baseline data for comparison purpose. Radiation-induced embrittlement of these alloys will initially be studied by irradiating the test specimens with bremsstrahlung gamma radiation from 20-40 MeV electron beams at ISU. These gammas induce (γ, n) reactions in the giant dipole energy region. The principal radiation damage from these irradiations, in turn, stems from the recoiling residual nucleus (with average kinetic energy of approximately 20,000 eV) after the neutrons are emitted. The high penetrability of gammas, whose range is of order one meter in steel, ensures that the resulting damage will be uniform over the volume of the sample. The induced activity of these specimens will have very short half-lives (typically minutes) due the systematics of (slightly) proton-rich nuclei. The resulting radiation-induced hardening can subsequently be evaluated by proper experimental techniques. Later, similar studies can be performed using specimens radiated by neutrons at LANL.

Four experimental heats of martensitic alloys (similar to Mod9Cr-1Mo) with different Si content (0.5, 1.0, 1.5 and 2.0 weight percent) have been melted by vacuum-induction melting (VIM) practice at the Timken Research Laboratory. These heats are currently being processed by
forging and rolling, which will subsequently be thermally treated. A literature review on relevant topics is in progress.

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

**Kinetic Model**

An improved kinetic model was developed to predict the mass transfer controlled corrosion/precipitation in non-isothermal LBE pipe/loop systems.

In this mass transfer model, a turbulent core region and a laminar sub-layer region have been considered separately to the total mass transfer to the transferring corrosion product from the wall. Two sets of mass transfer equations were solved separately both in the turbulent core region and sub-layer region. Following the model development, the local corrosion/precipitation rate is calculated and a parametric study was made to illustrate the effects of the axial temperature profile in details. The obtained solutions can also be extended to the more general problems of mass transfer in the developed turbulent wall-bounded shear flows.

The improved model was applied to the DELTA loop at Los Alamos National Laboratory. The DELTA loop is a non-isothermal closed loop and is used to study the corrosion of various materials in the flowing LBE system. The temperature profile is shown in Figure 31.

![Temperature profile](image)

**Figure 31.** Corrosion rate under different axial temperature distribution

Figure 31 shows the predicted corrosion/precipitation rate by the present model in the pipe/loop flow in the DELTA Loop. From this figure, one can find that there also exists a precipitation region in the open pipe case and this precipitation region occurs beside the highest temperature region because of the large axial temperature difference.
Numerical Analyses
Numerical analysis of the coupled natural convection and corrosion product transfer in a two-dimensional circular loop was made to study the corrosion product under the active oxygen controlled model.

Figure 32 shows the distributions of velocity magnitude (Figure 32a), temperature (Figure 32b), and corrosion product concentration (Figure 32c) in the circular loop. Due to the existence of temperature difference, the liquid LBE flows clockwise due to the effect of the buoyancy. As shown in Figure 32a, the maximal velocity magnitude locates near the outer wall due the effect of curvature of circular loop. From Figure 32b, the downstream effect on temperature distribution is very evident. For the liquid LBE, the Prandtl number is very small, which makes the temperature in the bulk flow almost uniform. Since the diffusion coefficient of corrosion product (iron) in liquid LBE is very small, the Schmidt number for corrosion product becomes very large, which makes the mass diffusion boundary layer becomes very thin. To show the variation of corrosion product along the loop clearly, here we take the diffusion coefficient as $5 \times 10^{-5}$. Similar to the distribution temperature distribution, the downstream effect on corrosion product is also very evident. Figure 33 shows the corrosion/precipitation rate along the loop for the inner wall and outer wall. The figure indicates the corrosion/precipitation rate in the outer wall is larger than that in the inner wall due to effect of the curvature.

Next, the transport mechanism of oxygen in the nature convective LBE loop will be studied.
Figure 32. Distributions of velocity magnitude, temperature, and corrosion product concentration in the circular loop.
Kinetic Oxide Growth Model

A kinetic oxide growth model in Liquid LBE has been developed for the pure iron exposed liquid LBE with oxygen controlled.

A schematic plot is shown in Figure 34. The oxide (\( Fe_3O_4 \)) layer grows toward both in internal side (II surface) and external side (III surface). Assumptions have been made as follow:

- The interfaces are local equilibrium and the processes do not affect the kinetics of oxidation.
- The growth of the oxide (\( Fe_3O_4 \)) is limited by the diffusion of iron.
- The diffusion of oxygen anion is neglected.
- The oxide layer growth and the consumption of metal obey the Wagner’s parabolic law.
- The interfaces are flat plat.
Figure 34. Schematic plot of the structure of pure iron exposed to LBE with oxygen controlled. A region: Metal Fe; B region: Metal oxide Fe₂O₄; C region: Liquid LBE with oxygen; I: Original metal surface; II: Metal-oxide Interface; III: Oxide-LBE interface. X: Depth of metal consumption; Y: Width of Oxidation Layer.

Figures 35-37 show the distributions of iron in the three-phase system based on the model. As the time of holding increases, the depths of the diffusion zones in the phase A (steel) and in the phase C (liquid LBE) increases. The iron concentration in the oxide layer almost keeps the linear. From Figure 37, it can be seen that the diffusion of iron through the oxide film is very small. Figure 38 shows the time dependence of increments in the thickness of oxide layers. From Figure 38, one can see that the oxide growth toward to the inner side is considerable.

Figure 35. Iron concentration in phase A (steel).
Figure 36. Iron concentration in phase B (Oxide layer).

Figure 37. Iron concentration in phase C (Liquid LBE).
Corrosion Barrier Development for LBE Corrosion Resistance (Task 23).

Fabrication/characterization of nanoporous alumina on steel

In the last quarter, a specialized sample holder was developed for the anodization of alumina on steel. In addition, it was determined that oxalic acid was the most appropriate acid for the anodization of these structures. The steel samples obtained from LANL were first cut into a number of pieces, each measuring 11mm x 8mm x 1.6mm, to allow multiple experiments. Special care was taken to ensure that the cutting process did not damage the samples. After investigation of several techniques, including laser cutting, the samples were cut using EDM wires. The cut steel pieces did not show any damage to the surface or the edges.

The steel samples were cleaned using acetone and methanol followed by DI water rinse, and then dried in nitrogen gas. A thin layer of titanium (10 nm thick) was deposited on the surface of the steel followed by deposition of a thick layer of 99.999% aluminum (1 um thick) using e-beam evaporation. The Ti layer was deposited for improved adhesion of aluminum on steel; direct deposition of aluminum on steel showed poor adhesion. The samples were then anodized in 0.3M Oxalic acid solution maintained at 15°C using a constant current density of 20mA/cm². The voltage time relationship, monitored during anodization, and shown in Fig. 39, confirmed the formation of the porous layer of alumina. While the samples were anodized for 600 seconds, the data in Fig. 39 is shown only upto 80 seconds for clarity. Visual inspection of the samples (shown in Fig. 40) also confirmed the formation of the porous alumina layer. The samples were then coated with a thin layer of gold and characterized by SEM imaging. However, the surface of the sample was found to be very rough, which made high resolution imaging very difficult. We
believe that it will be necessary to polish the surface of the steel samples before metallization in order to perform high resolution SEM imaging, which we are currently pursuing.

An important objective of this project is to develop a coating technology that will be able to provide corrosion resistance after thermal cycling. An important requirement for this is good adhesion of the coating film on the substrate under thermal cycling. Towards this goal, the samples were subjected to thermal cycling to 300°C and 400°C. A Lindberg/BlueM oven was used for this purpose and the samples were subjected to half hour cycles. Visual inspection of the samples showed the appearance of thermally cycled samples was same as the uncycled (room temperature) samples. Also, a preliminary scratch test using a pin showed the alumina coating to have good adhesion to steel after thermal cycling.

In order to accurately characterize the adhesion properties of the alumina coatings, scratch tests were performed on the thermally cycled and uncycled samples using a nano-scratch tester instrument at microphotonics corporation. The scratch test method is done by generation of scratches using a spherical stylus (Rockwell C Diamond, tip radius 2um). The stylus is drawn at a constant speed across the sample under either constant or progressive loading at a fixed rate. For progressive loading, the critical load is defined as the smallest load at which appreciable failure occurs on the sample; for the constant loading, the critical load corresponds to the load at which a regular occurrence of such failure is observed along the track. The scratch test is basically a comparison test and the critical load depends on the mechanical strength (adhesion and cohesion) of a coating to the substrate. The critical load depends on parameters that might be directly related to the test itself like the loading rate, scratching speed and indenter tip radius and indenter material. It also depends on the coating substrate parameters that include the substrate hardness and roughness, coating thickness and roughness, friction coefficient between coating and indenter, internal stresses in the coating. A scanning force microscopy is used to obtain high resolution images in three dimensions and the quantitative lateral and depth measurements can be obtained in the scratched portions. The pre scan recording on the sample is done to include the effects of uniformity in the flatness of the sample, where the penetration depth is measured during the test. The post scan reveals the elastic recovery of the coating-substrate residue by providing the scratch path profile.

The results of the scratch tests for the thermally cycled samples (300°C and 400°C) and uncycled sample (room temperature) are summarized in Table 4. ‘Critical damage’ indicates the smallest force at which a recognisable failure occurs. ‘Delamination’ indicates the minimum force at which the film delaminates from the substrate. Fig. 41 shows a typical optical microscope image of the sample during scratch test. Fig. 42, 43 and 44 show the scratch test results for the samples 1, 2 and 3 respectively.
Figure 39. A typical voltage-time relationship obtained during anodization of aluminum steel using 20mA/cm² @ 15C.

Figure 40. Photograph of two anodized samples showing the porous alumina on steel.

Table 4. Scratch test results obtained for alumina coating on steel under different thermal cycling conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature</th>
<th>Critical Damage</th>
<th>Delamination</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Room Temp</td>
<td>1.56mN</td>
<td>5.38mN</td>
</tr>
<tr>
<td>2</td>
<td>300°C</td>
<td>1.38mN</td>
<td>2.27mN</td>
</tr>
<tr>
<td>3</td>
<td>400°C</td>
<td>1.59mN</td>
<td>3.38mN</td>
</tr>
</tbody>
</table>
The results obtained from the scratch tests are encouraging, demonstrating good adhesion of the nanoporous alumina coatings on steel for temperature cycling up to 400°C. Our next step is to subject the samples to further higher temperatures (up to 600°C) and evaluate the adhesion properties of the coatings.

Figure 41. A typical optical microscopy image obtained during scratch test.

Figure 42. Scratch test results for thermally uncycled sample.
Figure 43. Scratch test results for sample thermally cycled to 300°C.

Figure 44. Scratch test results for sample thermally cycled to 400°C.
**Synthesis of Cr nanowires**

The pores in the nanoporous alumina will be filled with Cr to provide increased corrosion resistance in LBE. These Cr nanowires will be synthesized electrochemically inside the pores. Towards this goal, a specialized sample holder was designed and fabricated that is similar to the one developed for anodization of steel. Following an extensive literature search, the following electrolytes were selected for the electrodeposition of Cr nanowires. Test runs are currently in progress to determine the suitable deposition parameters for Cr inside the pores.

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

In the RACE Project of the AFCI, a series of accelerator-driven subcritical systems experiments is being conducted at the Idaho State University’s Idaho Accelerator Center (ISU-IAC), that will be conducted at the University of Texas (UT) at Austin, and at the Texas A&M University. In these experiments, electron accelerators will be used to induce bremsstrahlung photon-neutron reactions in heavy-metal targets; this source of about $10^{12}$ to $10^{13}$ n/s will then initiate fission reactions in the subcritical systems. These systems will include a compact, transportable assembly at ISU and TRIGA reactors at UT-Austin and Texas A&M. These experiments will provide a variety of cores, fuel types and enrichments, and target/reactor configurations for many separate accelerator coupling studies. The UNLV portion of this project is a three-year, three-phase project to support computational and experimental research at the ISU and Texas universities, to integrate the UNLV Transmutation Research Project with this accelerator-driven transmutation research, and to further develop UNLV’s computational infrastructure for reactor physics research.

This past quarter, modeling with MCNPX continued in support of subcritical experiments at the Idaho Accelerator Center and target design for Texas RACE. The newest beta test version of the MCNPX radiation transport code was acquired, installed, work has started on using it.

UNLV hosted the PIs and students from the Texas universities for a meeting to discuss MCNP modeling of the RACE Project configurations at ISU, UT, and TAMU.

In his role as national RACE Project Director, the PI visited Idaho State University for RACE Project budget discussions, for a meeting with both the UT PI and a graduate student, and to conduct experiments and discuss progress. He also attended the AFCI Semianual Review Meeting where a RACE Project Technical Advisory Group meeting was held, coordinated a developing collaborative project with the European EUROTRANS project, and presented colloquia titled “RACE: The AFCI Reactor-Accelerator Coupling Experiments Project” at several universities: Texas A&M University, University of Texas at Austin (UT-Austin), University of California Berkeley, University of Tennessee-Knoxville, Purdue University, and University of Michigan.