AFCI Quarterly Input – UNLV April through June, 2005

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

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AFCI Quarterly Input – UNLV
April through June, 2005

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:

- FY05 funding was received from DOE in June and continuing and new graduate student research tasks received allocations.
- Thirteen students from the TRP presented papers at the ANS Student Conference in Columbus, Ohio, April 14-16, 2005. Three of these students were given session awards (one first place and two second places).
- UNLV was represented at a meeting of the Western Nuclear Science Alliance at Oregon State University on May 3, 2005.
- Incoming graduate student Amber Wright received an AFCI graduate student fellowship.
- The UNLV Health Physics Department has opened a search for a new radiochemistry professor in Health Physics.
- The following three new tasks were approved for funding starting summer and fall terms 2005 and their accounts have been set up: Task 28 “Impact of the Synthesis Process on Structure Properties for AFCI Fuel Candidates” PI Thomas Hartmann; Task 29 “Investigation of Optical Spectroscopy Techniques for On-Line Materials Accountability in the Solvent Extraction Process” PI Gary Cerefice; and, Task 30 “Combined Radiation Detection Methods for Assay of Higher Actinides in Separation Processes” PI Denis Beller.

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
2.0 Facilities Progress Update. The assembly of the TC-1 target gas vacuum system is nearing completion and the TC-1 loop will be ready for final installation in September by visiting Russian scientists. Purchase orders for all parts requested from Keith Woloshun for the Lead Calibration Stand were prepared and submitted. After construction of the LCS, it will be transferred to UNLV when a facility is available. The TEM User laboratory was officially approved as a University laboratory center by the Nevada System for Higher Education as a stand-alone, self-supporting user facility.

2.1 International Collaboration
2.1.1 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).

2.2 Student Research

2.2.1 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 currently has 30 student research tasks (including 7 that have concluded). The tasks are divided below in terms of their research area: fuels, separations, and transmutation sciences.

2.2.2 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 experimental set-up was further optimized including commissioning and optimization of the UPS mode, installation of a low-energy ion source, and optimization of communication between electron spectrometer and measurement electronics.
- An experimental campaign was carried out at the Advanced Light Source, Lawrence Berkeley National Laboratory (3 graduate students, one undergraduate student, and PI).
- Fit routines were implemented for data analysis, in particular the Doniach-Sunjic line profile for metal photoemission peaks.
Dissolution, Reactor, and Environmental Behavior of ZrO$_2$-MgO Inert Fuel Matrix (Task 19) Highlights.
- Dissolution studies of ZrO$_2$-MgO matrix were initiated.
- Acid and environmental solubility test procedures were developed.
- Pellets were fabricated.
- Acid dissolution studies were initiated.
- Reactivity feedback coefficients in Fertile-Free Fuel lattices were evaluated.

- Continued work on a hot cell robotic assembly including pick and place dynamic simulation with feedback control using Matlab for dispersion fuel manufacture.
- A systematic study was started seeking to arrive at an optimized plant configuration using value engineering techniques.

Impact of the Synthesis Process on Structure Properties for AFCI Fuel Candidates (Task 28) Highlights
- Sample preparation equipment for surrogate and radioactive fuel samples were set up.
- Sample preparation equipment for performing high-resolution electron microscopy (TEM) including ultrasonic disk cutter and ultra-microtome was purchased and installed.
- Sample preparation equipment for optical microscopy and electron microscopy (SEM, TEM) including low speed saw, vacuum impregnation, polisher/grinder, multi-sample preparation station, and environmental filtering and recirculation system was purchased and installed.
- Sample preparation procedure for radioactive SEM samples was developed and optimized on surrogate and radioactive ceramic fuel pellets as well as for metal oxide powders and students were trained.
- Radioactive test samples in the system ZrO$_2$ – Er$_2$O$_3$ – UO$_2$ were synthesized applying the dry chemical route in order to understand the solid state reaction kinetics in the oxide system at 1600°C under reducing atmospheres.

SEPARATIONS TECHNOLOGY

Systems Engineering Model (Task 8) Highlights.

Immobilization of Fission Iodine (Task 15) Highlights.
- Established first order dependence for the reaction of a lignin analog and iodine in the iodine substitution reaction.
- Established a 1:1 reaction stoichiometry for the reaction of iodine and a lignin analog.
- Established Arrhenius type temperature response for both lignin analogs and natural organic matter.
- Established the relative importance of I$_2$ and IOH in the iodination reaction.
Fluorapatite Waste Forms (Task 16) Highlights.

- The FT-IR spectra for samples annealed Ca$_5$Fap, Ca$_4$SrFap and Ca$_3$Sr$_2$Fap (synthesized at UNLV) has shown an unidentified peak at 3640 cm$^{-1}$. It has been determined that this peak results from trapped water molecules (interstitial water) in the apatite structure.
- A high resolution SEM analysis was done on Ca$_4$SrFap samples before and after annealing. Long crystals about 10µm long can be seen for the annealed sample, whereas the un-annealed sample of the same material showed an amorphous phase.
- Data obtained for the Zn and Zr samples has been analyzed. The data include XRD, XPS, FTIR, TGA/DSC and SEM/EDS spectroscopy.


- Based on the discussion with Argonne National Laboratory personnel (April 2005), the TRPSEM package includes new reporting features that exports new report format into MS Excel spreadsheet.
- Fundamental separation flowsheets were constructed using ASPEN-PLUS. The chemical separation information passed from the ANL has been converted into flowsheets.

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

- The electrochemical investigation in of the Ce$^{5+}$/Ce$^{4+}$ redox couple was completed and the optimum experimental conditions were determined.
- Computer modeling of the cerium using the JChess speciation-modeling program has been completed for the Ce redox couple. Traditional complexing ligands such as EDTA, oxalate, NTA, phosphate, acetate, and sulfate have been purchased and will be used to initiate the complexation and electrochemical characterization.
- Electrochemical investigations have continued on the Eu$^{2+}$/Eu$^{3+}$ redox system in HClO$_4$ supporting electrolyte at a glassy carbon working electrode. The redox couple has been electrochemically resolved using cyclic voltammetry and square wave voltammetry. The data suggests that the couple is stable with reversible oxidation/reduction occurring.
- Complex formation has been initiated and theoretical calculations regarding the stability of species has been used to target the solution conditions required to view the oxidation/reduction processes.

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

- Data analysis of XAFS data from experiments on U-TBP system including third phase obtained at ANL is ongoing.
- Waste recovery and alternate disposal methods were investigated.
- A method to prevent the undesirable formation of diammonium urinate was investigated.
- The maximum concentration of U that can be measured using UV-vis of extraction samples (aqueous and organic phases) was determined.
- Duplicates of samples of [U] and [NO3] were sent to Argonne for determination.
- Liquid chromatography was used for the detection of nitrate.

TRANSMUTATION SCIENCES
Niobium Cavity Fabrication Optimization (Task 2) Highlights.
- Secondary electron emission experiments on seven LANL cleaned niobium samples at 23 degrees K have been completed yielding 170 shots worth of data.
- Experimentation has been completed for this task. The graduate student successfully defended his thesis.

LBE Corrosion of Steel (Task 3) Highlights.
- Project completed in May 2004. See Task 18 for follow-on project. Thesis generated:

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.
- The NMDS was disassembled and placed into storage pending determination of a suitable laboratory space at UNLV.
- A new method based on a LANL report on the Nuclear Weapons Inspection System was investigated for measuring deadtime.
- A new data acquisition system incorporating a multi-component digital input/output board and Labview software was received. Work was initiated to interface the system with the NMDS.
- Modeling of the NMDS in alternate configurations, such as for monitoring actinides in a processing pipe, was initiated.
Development of Dose Conversion Coefficients for Radionuclides Produced in Spallation Neutron Sources (Task 7) Highlights.

- The ten example radionuclides missing e-files were investigated in order to determine the best way to address these.
- Graduate student recalculated the 84 radionuclide chains that have a Q-value discrepancy.
- The biggest concern is still a lack of radionuclide data. Time has been spent in developing a method to produce these data, but that has become a much bigger project. Prof. Rich Brey (ISU) started to develop the white sheet for calculating the missing radionuclide data.
- A second paper sent to the Journal of Health Physics was accepted for publication.


- Project completed in August 2004. Theses generated:

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

- Analyses of defects (dislocations) in martensitic Alloy EP-823, cold-reduced to different levels, have been performed by using transmission electron microscopy. The dislocation density has been related to the degree of cold-reduction and residual stress in terms of a line-shape parameter determined by the positron annihilation spectroscopy (PAS).
- Additional PAS measurements are ongoing on tensile, welded and cold-worked specimens of Alloys EP-823 and HT-9 at the Idaho Accelerator Center of ISU.
- A graduate student is performing neutron diffraction (ND) measurements at the Atomic Energy of Canada Limited (AECL), Chalk River Laboratory using Cold-worked and welded specimens of Alloys EP-823 and HT-9.
- TEM studies involving welded specimens of Type 304L stainless steel and Alloy EP-823 are being performed by a second graduate student to characterize defects at the fusion line, heat-affected-zone and base metal.

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

- Took delivery of system for laminar flow filtered air work surface for use in High Temperature Experimental Facility. Existing hood renovation completed. Facility almost ready for operation.
- Received pipe pieces from DELTA loop, SEM and XPS examination started.
- Ion current to sample area in mass selective ion beam machine attained.
- Studies of DELTA loop samples by SEM/EDX and XPS/SDP were continued.
- Machining of tensile and polarization specimens of T91 grade steel with different silicon content are in progress. Tensile, stress corrosion cracking and polarization experiments will be initiated soon.
- A fixture to hold Charpy V-notch specimens for impact testing was installed in the existing instrumented impact tester. This type of testing enables the determination of impact energy and ductile-to-brittle transition temperature.
- All three graduate students have been trained in high-temperature tensile testing using the MTS machine. They were also trained in using the newly-installed Instron testing equipment to perform tensile and fracture-mechanics related experiments.
- Literature review on relevant topics is ongoing.

Oxide Film Growth Modeling in LBE Systems (Task 21) Highlights.
- 2-D and 3-D lattice Boltzmann method (LBM) codes have been developed to simulate the oxygen transport and oxide layer growth in the LBE pipe/loop systems.
- The Lattice Boltzmann method was applied to simulate the oxygen transport for the nature convection in the 2-D enclosure.
- Using LBM for simulation of corrosion behavior in a coupled natural convection of lead bismuth eutectic (LBE) flow in a two-dimensional container using different operating conditions has been studied.

Corrosion Barrier Development for LBE Corrosion Resistance (Task 23) Highlights.
- Thermal cycling experiments up to 400 C were performed on the nanoporous alumina coating on steel. Visual inspection confirmed good adhesiveness of coating under thermal cycling.
- Scratch tests carried out on the thermally cycled samples using a Nanoscratch tester confirmed and provided quantitative values of adhesiveness.
- Higher temperature thermal cycling experiments were conducted.

Reactor Physics Studies for the AFCI RACE Project (Reactor-Accelerator Coupling Experiments Project (Task 27) Highlights.
- Prepared to use FLUENT to analyze the thermal performance of high-power targets for future Texas RACE.
- Modeling was begun on the use of the UNLV Neutron Multiplicity Measurements System to measure time-dependent neutron production in the Idaho State University full-core RACE.
- The PI and both students participated in the Third Annual Idaho Workshop on Accelerator-Driven Subcritical System experiments which was held at Idaho State University on June 1 & 2. Participation included ISU, UT-Austin, Texas A&M, U of Michigan, UNLV, U.S. DOE, ANL, LANL, CEA, ENEA, FZK, and MUCATEX (Russia).
- The PI and students also participated in a meeting at ISU between the RACE Project and the ECATS Project (Experimental activities on the Coupling of an Accelerator, a spallation Target and a Sub-critical blanket, Domain 2 of EUROTRANS). A RACE-ECATS work package was discussed and a statement of cooperation was signed.
Combined Radiation Detection Methods for Assay of Higher Actinides in Separation Processes (Task 30) Highlights

- The project was initiated in June following receipt of funds from DOE-ID.
- A literature search was initiated to accumulate information on actinide characteristics (e.g. decay schemes) and modeling of radiation detector systems.
- Modeling of the NMDS in alternate configurations, such as for monitoring actinides in a processing pipe, was initiated.

2.2.3 Student Research Technical Summary

FUELS TECHNOLOGY

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

The goal of this project is to investigate interface corrosion processes in TRISO nuclear fuel particles. For this purpose, a detailed study was undertaken of the interface formation between potential candidates for metallic fission products (Pd, Ag, and Cs), likely to diffuse from the kernel of the TRISO particles, with the TRISO coating layers. As a starting point, the Pd/SiC interface is being investigated and will be extended to Ag/SiC during the current summer research campaign. The experimental approach comprises the preparation of metal/SiC interfaces in-situ in an ultra-high vacuum system by electron-beam deposition. In order to understand the impact of the SiC surface on the interface formation properties, a variety of surface preparation and modification schemes are employed. In the past quarter, a specialized low-energy ion source was obtained as a long-term loan from the Hahn-Meitner-Institute, Berlin, Germany. This source (see Fig. 1), which was successfully installed and commissioned in our ultra-high vacuum system, allows us to clean surfaces from ambient contamination by using a low-energy (50 eV) Ar ion beam, which desorbs the surface contaminants with a minimal amount of structural damage. The group of the PI has pioneered this approach for chalcopyrite materials, and first tests on other semiconductors, including SiC, are currently under way.

Figure 1: Picture of the newly-installed low-energy ion source for surface modification.
After preparation of the interface, a variety of spectroscopic methods were used to analyze the chemical and electronic properties of the interface and the metal overlayer. The primary “work horse” is photoelectron spectroscopy, both with X-ray (XPS) and UV (UPS) excitation. In addition, X-ray emission spectroscopy was performed at the Advanced Light Source, Lawrence Berkeley National Lab. Examples from these experiments were presented in previous quarterly reports. In the current quarter, a significant emphasis was placed on a further detailed analysis of XPS spectra. As shown in Fig. 2, various routines were implemented for fitting experimental data with different lineshape profiles. The Voigt profile (top fit in Fig. 2) is generally the profile of choice for semiconductor materials (such as SiC), because it involves a symmetric convolution of Gaussian (i.e., experimental broadening) and Lorentzian (i.e., lifetime broadening) contributions. Metals, in contrast, are generally best described by an asymmetric Doniach-Sunjic profile (bottom fit in Fig. 2), which takes electronic excitation into account. At this point of the analysis, it was found that both profiles require the assumption of two different Pd species (for each spin-orbit split peak in Fig. 2) to achieve a satisfactory description. Furthermore, the (nominally metallic) Pd monolayer on SiC is best described by Voigt profiles, which indicates a reduced metallicity of the Pd atoms. This corroborates earlier-reported XES results which show a significant charge transfer to the Si atoms of the SiC substrate near the Fermi edge. The next experiments will thus focus on a thickness-dependent series to investigate at what Pd layer thickness one begins to observe a purely metallic behavior.

Figure. 2: Pd 3d XPS spectrum for a thin (approx. 1 monolayer) Pd film on a SiC(0001) single crystal substrate. The experimental spectrum (black line) is shown twice, once analyzed with a
Doniach-Sunjic line profile representative of a metal environment (bottom), and once analyzed with a Voigt profile lineshape (top).

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

This project examines inert matrix fuels containing ZrO$_2$ and MgO as the inert matrix, with the relative amount of MgO varied from 30 % to 70 % in ZrO$_2$. Reactor physics calculations 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 $^{239}$Pu. Ceramics are synthesized and characterized based on the reactor physics results. The solubility of the fuel ceramics in reactor conditions, reprocessing conditions, and repository conditions is 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.

The synthesis of ceramics for further studies is ongoing. The development and finalization of methods and equipment for conducting dissolution experiments have been achieved in the current quarter.

Zirconium Ceramic Fuel

Prototype zirconium ceramic fuel was produced through several reproducible steps. Initially, nitrate salts of zirconium, magnesium, erbium, and cerium were dissolved in deionized water and treated with ammonium hydroxide to precipitate metal hydroxides. The resulting precipitate was dried at 80$^\circ$C before being ground to a fine powder using a planetary ball mill. Metal oxides were formed upon calcination of these fine powders at 700$^\circ$C for 1.5 hours (as shown by amorphous XRD patterns). Zirconium based fuel pellets were then formed after removing calcined powders, which were ground and pressed into cylindrical shapes. XRD patterns were taken from these powders confirming that the crystal structure is cubic zirconia.

Pressure Vessel Sampling Method

A pressure vessel was purchased from Parr and fitted with a custom sample draw tube constructed from stainless steel components (Figure 3). The sample extraction system allows 5-10 mL liquid samples to be drawn while the vessel is under pressure. Following each sample extraction the tube is cleaned with an Argon flush and allowed to cool. The Argon line is fitted to a custom high pressure 6000 psi regulator and commercially available tank, that allows pressure testing of the vessel before heat is applied. Full sealing does not occur until the Teflon gasket has been thoroughly heated thus expanding into the vessels mating surfaces.
Ceramic Solubility in Reprocessing Conditions

Two systems were constructed for the purpose of simultaneous studies of ceramic fuel pellet solubility (Figure 4). The apparatus is designed to reflux nitric acid for extended periods of time without harm to most components. Samples can be extracted from the system using a glass syringe with Teflon plunger or a disposable plastic syringe, depending on the acid concentration. Future studies involving this apparatus can include elemental analysis of the ceramic constituents.

Reactor Physics Calculations

One of the major design challenges associated with utilization of inert matrix is deterioration of the temperature coefficients and control materials reactivity worth caused by high thermal cross-section of Pu and consequent hardening of the neutron spectrum. The purpose of the investigation reported in this section is to estimate the potential of addition of different burnable poison (BP) materials to improve reactivity feedback coefficients without significant deterioration of control materials worth. Therefore, each parameter was evaluated for all BP design options. For each design option, i.e., BP material and geometrical arrangement, one design was selected, that with sufficient loading of BP material to ensure operationally acceptable maximum soluble boron concentration. These BP loading values were determined previously in the current project.

Main design parameters are summarized in Table 1 for WABA (1.A), IFBA (1.B), and Homogeneous (1.C) design options. Additional details may be found in previous progress reports.
In addition to cases with practical BP loading for each design option and selected from the previous work the same set of reactivity coefficients for cases with BP loading reduced roughly by 20% was calculated. This is in order estimate the sensitivity of the reactivity coefficients to the BP concentrations and by that to evaluate the potential of each BP material and design to improve these coefficients. In Tables 1.A – 1.C, the cases with the reduced BP loading are designated as “x.1”, where x denotes the case number.

Table 1.A: WABA cases

<table>
<thead>
<tr>
<th>Case #</th>
<th>Case designation</th>
<th>Inner / outer radii of BP ring (cm)</th>
<th>BP material in BP region (vol./o)</th>
<th>Number of BP rods per assembly</th>
<th>Total weight of BP (kg/assembly)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>No BP</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>0.00</td>
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<tr>
<td>13</td>
<td>WABA-Gd-9</td>
<td>0.33379 / 0.46895</td>
<td>100</td>
<td>24</td>
<td>21.08</td>
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<tr>
<td>13.1</td>
<td>WABA-Gd-9.1</td>
<td>0.33379 / 0.46895</td>
<td>80</td>
<td>24</td>
<td>16.86</td>
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<tr>
<td>16</td>
<td>WABA-Hf-3</td>
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<td>27.24</td>
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<td>16.1</td>
<td>WABA-Hf-3.1</td>
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<td>21.79</td>
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<td>19</td>
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<td>24.32</td>
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Table 1.B: IFBA cases

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<th>Case #</th>
<th>Case designation</th>
<th>IFBA coating thickness (mm)</th>
<th>BP material in BP region (vol./o)</th>
<th>Number of BP rods per assembly</th>
<th>Total weight of BP (kg/assembly)</th>
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<td>25.1</td>
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<td>26</td>
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<td>27</td>
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Table 1.C: Homogeneous cases
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<th>Case #</th>
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<th>IFBA coating thickness (mm)</th>
<th>BP material in BP region (vol./o)</th>
<th>Number of BP rods per assembly</th>
<th>Total weight of BP (kg/assembly)</th>
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<td>46.1</td>
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</table>

The potential of different burnable poison materials and geometrical arrangements to improve the reactivity coefficients of fertile free fuels was calculated with BOXER corresponding to 18 months fuel cycle length. The main design challenges of fertile free fuel (FFF) include:

- Positive Moderator Temperature Coefficient (MTC)
- Significantly reduced Doppler Coefficient (DC)
- Significantly reduced Soluble Boron Worth (BW)

Two reservations must be made regarding applicability of the results presented in this report.

1. All reactivity coefficients have large sensitivity to the soluble boron concentration in the coolant. The calculations in this task were performed by “guessing” soluble boron concentration to approximate the real conditions. The boron concentration in the actual core may be different. Therefore, values obtained in this task may serve only as a guideline for comparing different fuel options on the consistent basis.

2. The used computation methods themselves may introduce significant uncertainties in evaluation of FFF reactivity coefficients as concluded from the series of computational benchmarks for various Fertile Free Fuel unit cells (J.-M. Paratte, H. Akie, R. Chawla, M. Delpech, J. L. Kloosterman, C. Lombardi, A. Mazzola, S. Pelloni, Y. Pénéliau, H.Takano, “Comparisons of Cell Calculations for Uranium-Free Light Water Reactor Fuels,” Nuclear Technology, 130, 159- 176, 2000). However, the most important findings in the current research task were verified by Monte Carlo neutronic simulations and found to be in good agreement with BOXER results.

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

Moderator Temperature Coefficient:

1. FFF for a No BP case shows small and positive MTC at beginning of life (BOL).
2. WABA-Gd shows a negative MTC of a reasonable value close to a standard LWR core.
3. IFBA-Gd and HOMO-Gd cases show unacceptably large and positive MTC values.
4. Hf and Er BP materials show a potential to improve MTC, where all Er designs seem more efficient in "correcting" the MTC value.
5. For all BP materials and geometries simultaneous burnout of Pu and BP results in acceptable MTC values at middle of life (MOL) and end of life (EOL) time-points.
Doppler Coefficient:
1. As expected, the DC of Pu loaded FFF is reduced to ~1.0 pcm/°C as compared with ~2.0pcm/°C for conventional All-U fuel.
2. No dramatic influence of BP on DC is found, with exception of a modest improvement for Er cases (up to -1.6 pcm/°C)
3. DC value is becoming more negative with burnup reaching -1.5 – 2.0 at EOL.

Boron Worth:
1. The well-known effect of BW reduction was also observed. In comparison with the reference All-U fuel, the BW is reduced by approximately a factor of 2 to 3 due to the presence of Pu.
2. Hf and Er in Homogeneous and IFBA configurations show modest potential of increasing the BW. Otherwise, addition of Gd burnable poison slightly reduces the BW.
3. The effect of increasing BW towards the fuel EOL as a result of fissile isotopes depletion was found to be much more pronounced in FFF than in All-U fuel, which may potentially cause power peaking problem in FFF core.

In conclusion, Pu loaded FFF showed potential feasibility to be used in existing PWRs. All FFF problems may be significantly mitigated through the correct choice of BP material and configuration. Based on the performed analysis, it was found that a combination of BP materials and geometries may be required to meet all FFF design goals. The use of enriched (in most effective isotope) burnable poisons, such as Er-167 and Gd-157, will further improve the BP effectiveness and reduce the fuel cycle length penalty associated with their use. However, these findings can be confirmed only by performing a full core 3-dimensional neutronic analysis. The final result of the next stage of this research will be the choice of acceptable FFF core fraction with appropriate mix of BP designs. This result will be obtained and verified by a full core 3-dimensional simulation and fuel cycle analysis.

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

Value Engineering Analysis of Hot Cell Manufacturing Plant

Value Engineering (VE) is used to maximize the product of a process while utilizing the minimum amount of resources. In previous reporting periods a powder processing hot cell was designed and simulated. A VE study will be initiated for this work cell. A manipulator reliability study and a workspace study are performed in this work period. The above noted studies can be combined and improvements can be made in the operations of the work cell.

The functionality of the powder processing work cell can be divided into different subjects to be studied separately. Estimates of manipulator reliability and a workspace study are presented below.

The powder processing hot cell uses two robotic manipulators. A separate value analysis study is performed for each robot. The results will be combined later and recommendations to improve operations will be presented.
**Manipulator Reliability**

The robotic manipulator must be as safe and reliable as technically possible. The difficulties of applying robotics in a hot cell environment include limited access for service and maintenance, possible radiation damage to electronics and insulators, and abrasion damage to bearings and sliding surfaces. Robots may contain electrical, mechanical, pneumatic, electronic and hydraulic parts. Their complexity compounds the reliability problem because of the many different sources of failures. According to Dhillon (*Robot Reliability and Safety*, Springer-Verlag, New York, NY, 1991), the best mean time between failures (MTBF) achieved by robots is only 2,500 hours. There is definite room for further improvement in robot reliability.

Dhillon and Yang (“Reliability Analysis of A Repairable Robot System,” *Journal of Quality in Maintenance Engineering*, Vol. 2, No. 2, pp. 30-37, 1996) presented a Markov model, which allows the integration of robot reliability, safety, and probabilistic analyses. A basic system transition diagram for both the models is shown in Figure 5. It is assumed that the robot system is composed of a robotic manipulator and an associated safety system. The inclusion of safety systems with robots is widely practiced in the industry, and would be a necessity for manipulators operating in hot cells. Let $i$ be the state of the system (see Figure 5), then the probability that the robot system is in state $i$ can be expressed as $P_i(t)$. $\lambda_s$, $\lambda_r$, $\lambda_{vs}$, and $\lambda_{rs}$ are assumed to be constant failure rates.

Using the Markov approach, a system of initial-value differential equations defines the failure dynamics.

![Figure 5: Basic Reliability Diagram](image)

The reliability of the both robot and the safety system is denoted as $P_r(t)$ and $P_s(t)$, respectively. The reliability of the robot with safety system is the sum of both reliability values:

$$R_r = P_r(t) + P_s(t)$$
Figure 6 shows the reliability of the manipulator alone, and the reliability of the manipulator with the safety system added. The failure rates of the robotic system states are assumed to be constant. Their numerical values are expressed below:

\[ \lambda_s = 0.0001 \]
\[ \lambda_r = 0.0002 \]
\[ \lambda_{ri} = 0.00005 \]
\[ \lambda_{rs} = 0.00004 \]

![Comparison of Manipulator Reliability with and without Safety System](image)

Figure 6: Comparison of Manipulator Reliability with and without Safety System.

The failure rates listed above are common failure rates of industrial robots. Specific experience ratings for the Wäelischmiller TELBOT manipulator are not available.

SEPARATIONS TECHNOLOGY

Immobilization of Fission Iodine (Task 15).

Additional kinetic experiments were conducted on the reaction of iodine with lignin and various low molecular weight analogs. These experiments were conducted in the aqueous phase. The objectives of these experiments were to measure temperature responses and to probe the mechanism of the iodination of lignin.

Previous work by other investigators on the reaction of phenolic compounds with iodine indicated that the reaction was first order in iodine and the phenolic compound. The effect of
vanillic acid concentration was examined on the pseudo first order reaction rate constant by measuring $k$ as a function of phenol concentration. The results are shown in Figure 7. The best-fit value of $n$ (at pH 8.5) was 1.05, which is sufficiently close to 1.0 to indicate that the reaction is first order in the phenol (vanillic acid) as well as iodine (as indicated by $I_3^-$ concentration). The stoichiometry of the reaction between iodine and phenol was also examined by looking at the production of iodinated product against the loss of iodine. In these experiments, iodine concentration was measured by examining the loss of $I_3^-$ by UV spectroscopy in the presence of a p-hydroxybenzoic acid (PHBA). These experiments were conducted at pH 8.5 and 31°C. The loss of PHBA and the appearance of the iodination product were measured by GC/MS. The PHBA and its iodination product were extracted from the reaction mixture after acidification and silanated before analysis. The results of this study are shown in Figure 8 and indicates 1:1 stoichiometry for the loss of the PHBA and the formation of the single iodination product (presumably 5-iodo-p-hydroxybenzoic acid) observed and the loss of active iodine (as indicated by $I_3^-$).

It is of interest to investigate the temperature dependence of the iodination of natural organic matter because of its environmental importance and its potential for binding radioiodine. Using a temperature regulated UV/Vis spectrophotometer, temperature kinetics were investigated for several simple NOM analogs as well as a sample of humic acid and lignin. Some of these results are shown below.

For the humic acid and lignin experiments the pseudo first order plots were observed to give two or more linear regions. The loss of iodine from experiments with lignin and humic acid could be fit to equations of the form:

$$[I_3^-] = A_1 e^{-k_{1}t} + A_2 e^{-k_{2}t}$$  \hspace{1cm} (1a)

$$[I_3^-] = A_1 e^{-k_{1}t} + A_2 e^{-k_{2}t} + A_3 e^{-k_{3}t}$$  \hspace{1cm} (1b)

Only two exponential terms were required for the humic (Equation 1a), while three were used to represent the lignin experiments (Equation 1b). In the case of humic acid, the first exponential term was very fast and often difficult to estimate accurately. Temperature dependencies for all three terms were discernable for lignin.

Although it is clear that iodination (ring substitution) is a complex process and is dependent on the speciation of the phenol and iodine, surprisingly the reactions for vanillic acid and p-hydroxybenzoic acid have a simple Arrhenius type temperature dependence. A similar dependence, although not quite as clear, is followed for the various $k$’s for humic acid and lignin.

The two likely reactive species of iodine in these experiments are $I_2$ and IOH. The species $I_3^-$ is in rapid equilibrium with both of these species, and is easily detected by a distinctive UV adsorption (360 nm) but is thought not to be reactive.

For the reaction of iodine there are potential two reactions corresponding to each species. Thus the rate constant can be represented by
\[ k = \frac{k_1}{K_1[I^-]} + \frac{k_2K_2}{[H^+][I^-]^2} \]  \hspace{1cm} (2)

This relationship can more simply be represented by

\[ k = \frac{A}{[I^-]} + \frac{B}{[I^-]^2} \]  \hspace{1cm} (3)

The rate of reaction of iodine with vanillic acid and the Flucka (brand) humic acid was examined as a function of iodine concentration. The results of these studies are shown in Figures 9 and 10. In the case of vanillic acid (at pH 8.5) \( I_2 \) and \( IOH \) contribute significantly to the iodination process. The relative contribution will depend on the iodide (I\(^-\)) concentration. At a \([I^-]\) concentration of 0.01M, 88% of the iodine substitution was a result of the reaction of \( IOH \). In the case of humic acid a different result was apparent. The fit of equation 3 to iodination data indicated \( IOH \) did not make a significant contribution to iodination and that the entire reaction could be accounted for by the reaction of \( I_2 \). This result is illustrated in Figure 10 where a plot of \( k \) against \( 1/[I^-] \) was linear.

In addition to these mechanistic experiments, experiments were conducted with the conversion of methyl iodide to sodium iodide using the sodium naphthalide through the Wüst reaction. At this time a stable solution of the naphthalide was produced and its reaction with methyl iodide was measured.

Experiments with the pyridinium resin continued although no new results are reported at this time.

A new set of experiments were initiated aimed at verifying the intermediacy of \( IOH \) (or \( I_2 \)) in the reduction of iodate. These experiments involve the use of leuco crystal violet to trap the intermediate. The results of these experiments will be reported in the next quarterly report.
Figure 7: Iodine loss as I\textsubscript{3} is plotted against the disappearance of PHBA. The linear relationship indicates a 1:1 stoichiometry.
Figure 8: The rate of iodination of vanillic acid follows a simple Arrhenius relationship.
Effect of \( I^- \) on the Rate of Vanillic Acid/I\(_3^-\) Reaction

\( pH \) 8.5

Figure 9: The effect of \([I^-]\) concentration on the loss of \(I_3^-\) from vanillic acid iodination experiments. The \(pH\) was 8.5 and the temperature was 31°C. The results indicate that both \(I_2\) and \(IOH\) are potentially iodinating species under these conditions. At low \(pH\) and higher \([I^-]\) the \(I_2\) will dominate. At high \(pH\) and low \([I^-]\), \(IOH\) will be the major iodinating species.
Humic Acid
KI influence on Reaction Rate
pH 8.5

Figure 10: These results indicate that at pH 8.5, IOH is not an important species for the reaction of iodine with humic materials.


Refinement of the TRPSEMPro Software Package
The original design of AMUSE database stores results into excel-formatted file after each AMUSE simulation. Flowsheet information, such as type of solvent, solvent extraction type, process temperature, CMPO concentration, TMP concentration, Crown concentration, recycle organics, are not included in this report file. The current TRPSEMPPro package preserves all flowsheet information as well as simulation results into the database.

Per request from the ANL, a report generator needs to be modified. The process requires the user identify interested flowsheet ID and the system can generate a query results that are importable to the MS Excel spreadsheet. More detail selection flow can be reviewed in Figure 11.

Figure 11. Schematic data flow for the new reporting module.

Simulation of Acetic Acid (HC₂H₃O₂) Removal

The Objectives are to understand if a simple distillation column could be used for this process and to study how varying the molar concentration of nitric acid would affect the post separation compositions.

The flowsheet uses an initial distillation block of the “DSTWU” (calculations using Winn-Underwood-Gillan method) as shown in Figure 12. Currently the designed separation parameters were set to 99% nitric acid recovery in tops and 01% acetic acid recovery in tops. A single feed stream consisting of water, acetic acid and nitric acid enters the distillation at a user-defined
temperature of 60 °F. The selected tower has 100 stages with the pressure at 1 atm for both the reboiler and condenser.

Approach on varying distillation method may provide more valuable information on the effect of nitric acid molar concentration. This new block is the “Distl”. Edmister method is used for separation calculations. While applying this method, the separation compositions are not specified and are solved for. The defined number of stages, the feed stage, the reflux ratio, the distillate to feed mole ratio, and the pressures of the reboiler and condenser are 25, 5, 5, 0.5, 14.7 and 14.7 psi, respectively.

It can be seen that increasing the molarity of the nitric acid in the feed plays no effect on the percentage of recovery of the nitric acid. However, it does have an effect on the percentage of recovery of the acetic acid and water as shown in Tables 2 and 3. Increasing the molarity of the feed nitric acid leads to a decrease in the recovery of the other components in the top stream and an increase in the bottoms stream. The role of the optimum stage number and feed stage placement is currently under investigation.

![Acetic Acid/Nitric Acid Separation Process](image)

**Figure 12: The initial design for the case 1 - acetic acid removal.**

<table>
<thead>
<tr>
<th>Feed composition (mol/L)</th>
<th>Tops composition (mols)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitric</td>
<td>Acetic</td>
</tr>
<tr>
<td>0.6</td>
<td>1</td>
</tr>
<tr>
<td>1.0</td>
<td>1</td>
</tr>
<tr>
<td>1.5</td>
<td>1</td>
</tr>
<tr>
<td>2.0</td>
<td>1</td>
</tr>
<tr>
<td>2.5</td>
<td>1</td>
</tr>
<tr>
<td>3.0</td>
<td>1</td>
</tr>
<tr>
<td>3.5</td>
<td>1</td>
</tr>
<tr>
<td>4.0</td>
<td>1</td>
</tr>
<tr>
<td>4.5</td>
<td>1</td>
</tr>
</tbody>
</table>
Table 3. Effects on the percentage of recovery of the acetic acid and water by varying molar concentration of the nitric acid

<table>
<thead>
<tr>
<th>Nitric composition (mols)</th>
<th>Bottoms % Recovery</th>
<th>Tops % Recovery</th>
<th>Bottoms % Recovery</th>
<th>Tops % Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitric</td>
<td>Acetic</td>
<td>Water</td>
<td>Nitric</td>
<td>Acetic</td>
</tr>
<tr>
<td>trace</td>
<td>1.902</td>
<td>48.098</td>
<td>100%</td>
<td>0.68%</td>
</tr>
<tr>
<td>trace</td>
<td>1.926</td>
<td>48.074</td>
<td>100%</td>
<td>0.67%</td>
</tr>
<tr>
<td>trace</td>
<td>1.956</td>
<td>48.044</td>
<td>100%</td>
<td>0.61%</td>
</tr>
<tr>
<td>trace</td>
<td>1.986</td>
<td>48.014</td>
<td>100%</td>
<td>0.60%</td>
</tr>
<tr>
<td>trace</td>
<td>2.018</td>
<td>47.982</td>
<td>100%</td>
<td>0.54%</td>
</tr>
<tr>
<td>trace</td>
<td>2.050</td>
<td>47.95</td>
<td>100%</td>
<td>0.53%</td>
</tr>
<tr>
<td>trace</td>
<td>2.084</td>
<td>47.916</td>
<td>100%</td>
<td>0.48%</td>
</tr>
<tr>
<td>trace</td>
<td>2.118</td>
<td>47.882</td>
<td>100%</td>
<td>0.47%</td>
</tr>
<tr>
<td>trace</td>
<td>2.153</td>
<td>47.847</td>
<td>100%</td>
<td>0.46%</td>
</tr>
</tbody>
</table>

Plutonium Separation Process (from the PUREX plant)

As shown in Figure 13, the Pu separation process is broken up into four sub-processes.

![Overall Plutonium Extraction Process](image)

Figure 13: The Pu separation process.

The overall desired process is the conversion of plutonium nitrate (Pu-HNO₃) to plutonium tetrafluoride (Pu-F₄). After the plutonium tetrafluoride is produced, it is reduced to plutonium metal and shipped offsite for further processing (beyond the scope of this investigation). Currently being studied is the first of the four sub-processes; conversion of plutonium nitrate to plutonium oxalate. This is performed by the reacting of plutonium nitrate with oxalic acid (H₂C₂O₄). The product is brown cake, plutonium oxalate [Pu (C₂O₄)₂] solid. The ASPEN Plus flowsheet for this reaction is shown in Figure 14.
Figure 14: A preliminary flowsheet design for plutonium nitrate conversion.

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

The electrochemical characterization of the Ce$^{3+}$/Ce$^{4+}$ redox couple as a function of working electrode material, pH and ionic strength has been completed. A manuscript outlining the data and results will be submitted in August. The work has shown that the choice of electrode material determines the ability to resolve the redox couple under very different solution conditions. In the study, optimum conditions for redox couple resolution at all three electrodes were realized in 0.1 M sulfuric acid solution. A decline in redox peak resolution, magnitude, and reversibility was observed as acid concentration was increased. The substitution of nitric acid for sulfuric acid yielded similar, though less resolved results. The influence of pH on the redox properties was illustrated using buffered solutions of incrementally increasing pH, while holding ionic strength constant. The results indicate that a pH greater than 2 was detrimental to the resolution of the cerium redox couple. Experimental results at the glassy carbon electrode differed significantly from those obtained at either Au or Pt, and revealed that glassy carbon was least affected by changes in pH. Glassy carbon also allowed successful resolution of the cerium redox couple in solution conditions that precluded its observation at either Au or Pt. Figures 15 through 21 are presented below.

Progress was also made on the Eu$^{2+}$/Eu$^{3+}$ system and a figure of the cyclic voltammetry and square wave voltammetry for the redox couple is provided in Figure 22.
Figure 15: Cyclic voltammetry performed on the Ce(III)/Ce(IV) redox couple in 0.1, 1.0, and 2.0 M (top) H₂SO₄ concentration at the glassy carbon working electrode (ν = 100 mV/s).
Figure 16: Cyclic voltammetry showing Ce(III)/Ce(IV) redox behavior at Au (left column) and Pt working electrodes. These experiments were conducted at 0.1 M (lower figure in both columns) and 2.0 M H₂SO₄ concentration (ν = 100 mV/s).
Figure 17: Comparison of the Ce(III)/Ce(IV) redox couple in 0.1 M HNO₃ at GC (top), Au, and Pt working electrodes (ν = 100 mV/s).
Figure 18: The Ce(III)/Ce(IV) redox behavior examined by cyclic voltammetry at GC (top), Au, and Pt working electrodes in 0.1 M $K_2SO_4$ supporting electrolyte ($v = 100$ mV/s).
Figure 19: Ce(III)/Ce(IV) electrochemistry at Au (left column) and Pt working electrodes. pH was controlled by means of HSO₄⁻/SO₄²⁻ buffered solutions. The figure at the top of each column shows cyclic voltammetry conducted at pH 4.7, followed by pH 3.4, compared to 0.1 M H₂SO₄ (lower figure in each column) at pH 1.0. (ν = 100 mV/s).
Figure 20: Cyclic voltammetry showing cerium redox behavior at a GC electrode at pH 4.7 (top), 3.4 (middle), and in 0.1 M H₂SO₄ (v = 100 mV/s).
Figure 21: Cyclic voltammetry showing cerium redox couple at a GC electrode in pH 4.7 acetate buffer (top) compared to pH = 4.7 in sulfate buffer (ν = 100 mV/s). Apart from the nature of the buffer system, both voltammograms were obtained under the same experimental conditions.
Figure 22: Cyclic voltammetry showing Europium redox couple at a GC electrode in 1M HClO₄ (top) containing 5mM Eu³⁺ (ν = 100 mV/s). Square wave voltammetry for the forward and reverse scan (bottom) obtained under the same experimental conditions.

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

Work in this quarter focused on third phase formation studies with the uranyl system, which happens when the organic phase spontaneously splits into a light and a heavy phase. This
phenomenon occurs when the uranium and nitric acid concentrations exceed a certain threshold. Current theories include that the third phase forms gradually in small reverse micelles when uranyl and nitric acid reach a certain limiting organic concentration (LOC) that makes it thermodynamically favorable to separate and form a different structure. This is analogous to the critical micelle concentration (cmc) in surfactant micelle formation. The third phase formation is quite dependent on temperature. There has been some work indicating that the UV-visible spectrum changes at certain wavelengths as the system approaches third phase, indicating a variation in the uranyl electronic structure as this third phase begins to form.

One theory about the mechanism of formation is that the uranyl begins to gather excess nitrate or nitric acid around itself. The third phase only forms at high [U] and/or high [HNO3]. One question is whether the complex formed is dependent on [H+], [NO3⁻], or [HNO3]. The current prevailing theory is that the complex formed is \([\text{UO}_2(\text{NO}_3)_2] \bullet \text{HNO}_3 \bullet 2 \text{TBP}\) as opposed to the “normal phase” or “single phase” complex, which is purported to be \([\text{UO}_2(\text{NO}_3)_2] \bullet 2 \text{TBP}\). What this formula indicates is that the uranyl pulls in nitrate and TBP and an additional nitrate that is itself still coordinated to a proton. Further research using the aforementioned SANS technique, among others, seemed to indicate a slightly different structure \(\text{H}[\text{UO}_2(\text{NO}_3)_3] \bullet 2 \text{TBP}\).

Previous work in this project found that at 12 M HNO3, the organic phase split with an initial [U] around 0.16 M U, and afterwards the concentration of U in the light phase stayed constant around 10 M while the concentration of U in the heavy phase increased fairly linearly with increasing initial [U]; this split decreased to 0.05 M [U]i for 13 M HNO3 and all the way down to 0.01 M [U]i for 14 M HNO3. Using the scaled down method in the plastic tubes, similar results were found at 17-18 °C, validating the method.

Furthermore, the role of nitrate vs. nitric acid in third phase formation was evaluated. To this end, hundreds of samples were generated over a spectrum of concentrations for U, LiNO3, and HNO3. The raw data are condensed in Table 4.

### Table 4. Concentrations used in investigate the role of nitrate vs. nitric acid in third phase formation.

<table>
<thead>
<tr>
<th>Conc. [U]i</th>
<th>Conc. HNO3</th>
<th>Total NO₃⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6 M</td>
<td>≥ 5 M</td>
<td>≥ 8.2 M</td>
</tr>
<tr>
<td>0.8 M</td>
<td>≥ 5 M</td>
<td>≥ 10.2 M</td>
</tr>
<tr>
<td>0.4 M</td>
<td>≥ 8 M</td>
<td>≥ 11.8 M</td>
</tr>
<tr>
<td>0 M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>≥ 0.32 M</td>
<td>8</td>
<td>12 M</td>
</tr>
<tr>
<td>≥ 0.056 M</td>
<td>10</td>
<td>14 M</td>
</tr>
</tbody>
</table>

A catalytic amount of acid is needed to form the third phase with uranium. Acid can even form third phase on its own without uranium, but much higher concentrations are needed. As the concentration of U decreases, the amount of acid and nitrate needed for third phase formation increases. Conversely, as the concentration of HNO3 increases, the amount of U necessary for third phase formation decreases. XAFS experiments on third phase were preformed and data analysis initiated. Data analysis should be complete by the next quarter.
A definite kinetic component was observed in third phase formation. This was especially true for material near the cusp of the third phase; often material just above the putative LAC would not separate for several hours, or material just below will separate after waiting for several hours. Part of this is due to the exquisite sensitivity of third phase to small changes in temperature as shown in Table 5.

Table 5. Data showing the sensitivity of third phase to small changes in temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>17 C</th>
<th>30 C</th>
<th>40 C</th>
<th>60 C</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 M HNO3</td>
<td>0.472 M U</td>
<td>0.800 M U</td>
<td>≥ 1 M U</td>
<td>≥ 1 M U</td>
</tr>
<tr>
<td>12 M HNO3</td>
<td>0.162 M U</td>
<td>0.400 M U</td>
<td>0.6 M U</td>
<td>0.8 M U</td>
</tr>
<tr>
<td>12N/8H</td>
<td>0.320 M U</td>
<td>0.630 M U</td>
<td>0.8 M U</td>
<td>1 M U</td>
</tr>
<tr>
<td>13 M HNO3</td>
<td>0.065 M U</td>
<td>0.10 M U</td>
<td>0.1 M U</td>
<td>&gt; 0.2 M U</td>
</tr>
<tr>
<td>14 M HNO3</td>
<td>0.020 M U</td>
<td>&gt; 0.2 M U</td>
<td>&gt; 0.2 M U</td>
<td>&gt; 0.2 M U</td>
</tr>
<tr>
<td>14N/10H</td>
<td>0.056 M U</td>
<td>0.20 M U</td>
<td>0.2 M U</td>
<td>0.3 M U</td>
</tr>
<tr>
<td>0.4 M U</td>
<td>H &gt; 8 N &gt; 11.8</td>
<td>H &gt; 9 N &gt; 13</td>
<td>H &gt; 11 N &gt; 13</td>
<td>H &gt; 12 N &gt; 13</td>
</tr>
</tbody>
</table>

Above and below, 12N/8H means 12 M total nitrate, 8 M acid; 14N/10H is defined similarly.

The kinetics problem may easily be seen in the change in aqueous concentration over time. Initially, more U is extracted than ultimately ends up after equilibrium is reached; these numbers were reached by making duplicate samples and separating the organic and aqueous after about 1 hour and then after over 24 hours.

Table 6. The ratio of the concentrations of sample before and after separation.

<table>
<thead>
<tr>
<th>Sample:</th>
<th>12 M HNO3</th>
<th>12N/8H</th>
<th>14 M HNO3</th>
<th>14N/10H</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2/A1</td>
<td>1.117</td>
<td>1.169</td>
<td>1.087</td>
<td>N/A</td>
</tr>
<tr>
<td>L2/L1</td>
<td>0.958</td>
<td>0.997</td>
<td>0.958</td>
<td>N/A</td>
</tr>
<tr>
<td>H2/H1</td>
<td>1.090</td>
<td>1.081</td>
<td>1.054</td>
<td>N/A</td>
</tr>
</tbody>
</table>

The ratios shown in Table 6 reflect the ratio of the concentrations of sample before and after separation. With this quick and dirty experiment, one can see that the concentrations in the aqueous phase generally increase by about 10% over time (U is extracted quickly, then re-equilibrates as water is taken up into the organic system) while the concentrations in the organic phases hold fairly steady. It has already seen that the concentration in the light and single phases does not change much with changes in nitrate, uranium, or acid concentration, but the heavy phase is affected in both volume and concentration. A more systematic study of the kinetics of the solutions on the cusp is needed.

**Liquid Scintillation Counting**

A liquid scintillation counter was used with known aqueous standards of U and organic samples that were counted on the ICP-AES. Since there are at least four daughter products in secular equilibrium with $^{238}U$ including $^{234}U$ one can only expect about half of the activity to be due to uranium. In addition, the solvent extraction purifies the U from the daughter products; the ~250
keV $^{234}$Th beta peak takes about 170 days to grow into secular equilibrium with U, so the amount of time between the extraction and liquid scintillation counting will affect the overall radiation; after purification and seven Th half-lives (170 days), Th will be in secular equilibrium with the U; however, since the U-234 daughter is long-lived, it will not contribute significantly to the radiation. Thus the uranium can be expected to contribute to two thirds of the activity. By knowing the time and counting the spectrum, one may then figure out what of the activity is due to the uranium and the daughter products. However, since the U has a much higher energy than the Th daughter, an easier route would be to gate the LSC so that it only integrates under the U peak, around 40-110 keV for the aqueous and about 50-105 keV for the cleaner organic. Gating on this peak only yields a calibration curve of $y = 6.8x$ with an $R^2$ value of 0.990, where $y =$ concentration (in µM) and $x =$ counts per minute (cpm). The detection limit will be about 1 ppm (about 8 cpm above background).

**TRANSMUTATION SCIENCES**

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

This project was developed to test a Russian-built Neutron Multiplicity Detector System (NMDS) shown in Figure 23 for measuring neutrons generated in a central target by a variety of accelerators. To assist in experiment design and evaluation MCNPX was used to model experiments. Experimental results are compared to computational predictions and discrepancies are investigated. Initial plans were to conduct experiments using a 70-MeV proton cyclotron at the Crocker Nuclear Laboratory at the University of California at Davis and/or a 20 to 40 MeV electron linac (linear accelerator) at the Idaho Accelerator Center (IAC) at Idaho State University (ISU). Finally, the current plan is to use the 800-MeV linac at the Los Alamos Neutron Science Center at Los Alamos National Laboratory.

![Figure 23: NMDS in the cubic configuration for cosmic radiation measurements.](image)

37
Dead time appears to be extremely high, with a resolving time constant for a single detector, many detectors, or the whole system on the order of 5 to 10 ms, which limits the count rate of the NMDS to less than 200 counts per second, and reduces its efficiency to a few percent when counting high-activity sources. It appears the problem is simply a limitation of the processing capability of the CPU in the “special computer.” One CPU is simply trying to process too much information when count rates are high. Thus, the NMDS is only useful for sources between a few hundred to a thousand neutrons per second.

The NMDS, which was repaired and tested in the previous quarter, was determined to need a hardware and software upgrade to reduce data losses from count-rate limitations (dead time).

The NMDS was disassembled and placed into storage pending determination of a suitable laboratory space at UNLV.

During this quarter various solutions were investigated and a decision was made to purchase a digital data acquisition board and software. Much of the effort this quarter was dedicated to selecting the optimum combination of hardware and software to support the full 64-element NMDS while providing much faster detection capabilities. A new data acquisition system incorporating a multi-component digital input/output board and LabView® software was purchased. The new equipment was interfaced with one bank of eight detectors and testing was begun. When this system is successfully implemented on the NMDS it will eliminate the count-rate limitation, which will allow the NMDS to be used with a high-energy spallation source.

Other activities during the quarter included investigating a new method for measuring deadtime that is based on a LANL report on the Nuclear Weapons Inspection System. The undergraduate student on this task began modeling of the NMDS in alternate configurations, such as for monitoring actinides in separations processes for upcoming materials protection, control, and accounting research.

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

The research consortium comprised of representatives from several universities and national laboratories has successfully generated internal and external dose conversion coefficients for twenty radionuclides produced in spallation neutron sources. These dose coefficients fill data gaps that exist in Federal Guide Report No. 11 and in Publications 68 and 72 of the International Commission on Radiological Protection (ICRP), and two articles containing the data have been accepted for publication in the *Journal of Health Physics*. Currently, more nuclear data is needed for the rare radionuclides produced from a mercury target. While attempting to develop a workable plan to acquire this missing data, Q-value discrepancies are being investigated.

Eighty-three radionuclides have a Q-value discrepancy between the two nuclear data sets used in this task. This equates to 54 decay chains. The Q-value using both data bases have been recalculated and compared to determine the magnitude of the difference. Previous work relied on the Q-value obtained from ENSDF.
**Corrosion Mechanisms and Kinetics of Steels in Lead-Bismuth Eutectic (Task 18).**

Approximately 30 samples of steel, corroded by LBE, exposed at the DELTA loop at Los Alamos were analyzed. In addition, analyzing samples exposed at the IPPE composed of D-9 steel was continued.

Continuing studies of samples exposed at other facilities yield new insights on the mechanisms of LBE corrosion of steel. A paper published by the research group in JNM indicated the importance of surface preparation of 316L stainless for LBE service. Recent results on D9 (a polished and etched 316L formulation) show more details of the corrosion of 316L (Figure 24).

![Figure 24: Images of corrosion of a D-9 steel sample (polished and etched 316L formulation).](image)

Corrosion at low times (1000 hours) shows massive corrosion being initiated at localized regions to form pits/bumps of mixed oxides. Examination of the atom maps (in particular the Fe, Cr, and O maps) show that Fe and O are mobile whereas Cr is not.

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

2-D and 3-D lattice Boltzmann method (LBM) codes have been developed to simulate the oxygen transport and oxide layer growth in the LBE pipe/loop systems.

Benchmark has been made for a steady diffusion problem between two parallel porous walls. Figure 25 shows the comparison between the analytical solutions and LBM numerical solutions. From the figure, one can see that the numerical results from the LBE code agree with the analytical solution very well. The LBM code has been extended to 3-D dimension geometry. Figure 26 shows isothermal surface for the natural convection of liquid LBE in a 3-D cube cavity (Rayleigh number is $10^5$ and Prandtl number is $1.7624 \times 10^{-2}$).
Figure 25: Calculated concentration profile of a binary fluid diffusion problem between parallel walls.

(a) Temperature contours  (b) Temperature iso-surface

Figure 26: Temperature contour and iso-surface for natural convection of liquid LBE in a 3-D cube cavity

Lattice Boltzmann method has been applied to simulate the oxygen transport for the nature convection in the 2-D enclosure.

Active oxygen control is an important method to mitigate corrosion and coolant contamination in lead and lead-bismuth eutectic systems. A well-controlled extremely low oxygen concentration level (as low as $10^{-7}$ wt.\% in liquid Pb and $10^{-10}$ wt.\% in liquid LBE) is crucial in avoiding the
corrosion of lead-alloy carriers as well as in avoiding the formation of lead oxide contaminations. Available publication indicated that how to uniformly and quickly mix the low concentration oxygen in liquid lead or LBE under the high temperature is very important. Hence, a numerical analysis of the natural convection of liquid metal flow, as well as the oxygen transport is carried out by the Lattice Boltzmann method in simplified two-dimensional geometry. The motivation is to examine the characteristic of oxygen transport in the high temperature liquid lead or LBE system.

Figure 27(a) shows the vector graphs for the velocity and Figure 27(b) shows contours of temperature in the steady state with the $125 \times 125$ lattice. As shown in Figure 27, due to existence of temperature difference, the circulating flow driven by the buoyancy force can be found in the cross-section and the temperature field is distorted by the flow. Figure 28 shows the instantaneous oxygen concentration distributions at several time periods. Here the time step is taken as $\Delta t = 0.03333$ s. From these figures, it can be found oxygen is carried by the convection flow to the left sidewall first and then towards the right sidewall. As time increases, the oxygen distribution will be similar like the velocity field and becomes uniform gradually.

Figure 27: Numerical results for steady velocity and temperature fields (Temperature is normalized by $(T - T_{\text{cold}})/(T_{\text{hot}} - T_{\text{cold}})$).
Using LBM for simulation of corrosion behavior in a coupled natural convection of lead bismuth eutectic (LBE) flow in a two-dimensional container using different operating conditions has been studied.

Figure 29 shows the transition of corrosion product (iron) transport for different times under controlled oxygen concentration for different heating cases. Since the diffusivity of iron in LBE is very small, the transport of iron is mainly controlled by the nature convection. As shown in Figure 29, the iron is transported away from the wall to LBE as time increases and the averaged iron concentration in the LBE increases gradually. Finally, the value of averaged iron concentration reaches that on the wall and the distribution of iron is similar to that of stream function gradually. Figure 30 shows the variation of bulk iron concentration with the time. From the figure, it can be found the diffusion time for iron to LBE in case C is the slowest, which indicates the corrosion behavior in case C is the weakest in the three different heating cases. Figure 31 shows the variation of average Sherwood number with time for different cases. It can be found that the averaged Sherwood numbers in the wall for different case first decreases
sharply in the initial period and almost reach the constant value after about 5 hours. In these heating conditions, the iron transport form wall to LBE in case A is the slowest.

Figure 29: Transition of corrosion product (iron) transport for different time under controlled oxygen concentration for different heating cases.

(a) Case A

(b) Case B

(c) Case C
Figure 30: Variation of the bulk iron concentration with time.
Figure 31: The variation of average Sherwood number with time for different cases.

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

Synthesis of Cr nanowires inside alumina template pores

With the demonstration of formation of nanoporous alumina on steel and its good adhesion to substrate under thermal cycling, the next project task was to synthesize Chromium nanowires inside the alumina pores. During the previous quarter, a specialized sample holder was
developed towards this goal. Various techniques for the deposition of Chromium were investigated and electrodeposition was determined to be the most suitable approach due to the large aspect ratio of the pores. A challenge in using electrodeposition for porous alumina is the potential sealing of the pores in aqueous solutions at higher temperatures. To avoid this problem, a search was carried out for recipes for the deposition of Cr using non-aqueous or low temperature deposition schemes. Two such recipes were identified and experimentally tried out, the one selected is described below.

The process for the Cr wire nanodeposition was developed on silicon substrates using the following procedure. Silicon substrates were first degreased and cleaned using standard cleaning techniques. A back contact was next formed on the back of the silicon wafer by depositing 500 nm of aluminum followed by annealing at 250 degrees C for 30 minutes. Next, Pt/Al layers of thicknesses 10nm/900nm were formed on the top of the silicon wafers. The Pt layer was deposited to provide improved adhesion to the substrate as well as to act as a protective layer for silicon from the anodization process. The top Al layer was then anodized in 0.3M oxalic acid at 22 degrees C using a current density of 40mA/cm². The voltage time relationship monitored during anodization, shown in Fig. 32, confirmed the formation of the porous alumina all the way down to the Pt layer. After this the samples were pore widened in 6% phosphoric acid solution for 7 minutes to clean up the residues from the anodization process. The samples were then thoroughly rinsed in DI water and dried in nitrogen gas. Following this, the samples were imaged in a Field Emission SEM; the top and cross-sectional views are shown in Figures 33 and 34 respectively. The irregularity of the pore structures in Fig. 33 is due to the single step anodization used for the test runs; the pore regularity can be significantly improved by using the two-step anodization process as demonstrated earlier.

Next the pores in the alumina layer were filled with Cr using the following procedure. A fresh chemical solution was prepared using 100 g/l Chromic acid solution, 5g/l of sulfuric acid solution and 1 liter of water. A specialized sample holder was designed and fabricated to carry out the electrodeposition of Cr. For electrodeposition, the back of the silicon substrate was used as the cathode and a platinum mesh was used as the anode (note that this configuration is opposite of that of anodization). A current density of 20 mA (60mA/cm²) was then applied and the process continued for 1 to 5 mins. Fig. 35 shows the voltage time characteristics monitored during the process for 5 minutes of electrodeposition. Next the samples were scribed and cross-sectional images were taken in a Field Emission SEM. Figure 36 shows the cross-sectional image of a sample showing complete filling of the pores demonstrating the feasibility of this technique. This process will be next transferred to steel substrates using a similar procedure.
Figure 32: Voltage time relationship monitored during anodization.

Figure 33: Top view of porous alumina sample.
Figure 34: Cross sectional view of porous alumina sample.

Figure 35: Voltage time characteristics monitored during chromium deposition.
Reactor Physics Studies for the AFCI RACE Project (Reactor-Accelerator Coupling Experiments Project (Task 27)).

In the RACE Project of the U.S. Advanced Fuel Cycle Initiative (AFCI), a series of accelerator-driven subcritical systems (ADSS) experiments is being conducted at the Idaho State University’s Idaho Accelerator Center (ISU-IAC) and will be conducted at the University of Texas (UT) at Austin and 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.

An expansion of RACE into an international project was coordinated this quarter, focusing on high-power experiments using Texas TRIGA reactors with thermal feedback, which will impact the level of subcriticality, start-up and shut-down ADS reactor operations, and measurements of subcriticality. This will prove to be an extremely challenging expansion of the RACE Project. Design codes were investigated for modeling thermal feedback in reactors. INL was contacted to obtain a license for a reactor thermal-hydraulic analysis code, RELAP, which may be modified to calculate TRIGA reactor transients. Discussions were initiated with members of EUROTRANS (EUROpean Research Programme for the TRANSmutation of High Level Nuclear Waste in an ADS) at FZK (Germany) and ENEA (Italy) on thermal-hydraulic analyses of source-driven TRIGA reactors (e.g. the ENEA TRIGA at Cassachia).

In his role as national RACE Project Director, the PI visited Idaho State University (ISU) and participated in an international meeting in Brussels to begin integrating the EUROTRANS
ECATS (Experimental activities on the Coupling of an Accelerator, a spallation Target and a Sub-critical blanket) project with the RACE Project.

Preparations were started to use a thermal code, FLUENT, to analyze the thermal performance of high-power targets for future Texas RACE. Deposition of accelerator beam power is being computed, which will be used as the heat source in the FLUENT calculations, by simulating the target with MCNPX, a Los Alamos neutron transport code. Modeling was also begun on the use of the UNLV Neutron Multiplicity Measurements System to measure time-dependent neutron production in the Idaho State University full-core RACE.

The PI and both students participated in the Third Annual Idaho Workshop on Accelerator-Driven Subcritical System (ADSS) Experiments which was held at Idaho State University on June 1 & 2, see Figure 37. Other participants included faculty and students from ISU, UT-Austin, Texas A&M, and the U of Michigan, advisors from the U.S. DOE, ANL, and LANL, and collaborating scientists and engineers from CEA, ENEA, and FZK. The PI and students also participated in an organizing meeting at ISU between the RACE Project and the ECATS Project (Experimental activities on the Coupling of an Accelerator, a spallation Target and a Sub-critical blanket, Domain 2 of EUROTRANS). A RACE-ECATS work package was discussed and a statement of cooperation was signed.

Figure 37: UNLV students Evgeny Stankovskiy (far left) and Timothy Beller (kneeling far right) with other participants in the RACE and ECATS projects after the joint RACE-ECATS.