AFCI Quarterly Input – UNLV October through December, 2004

Harry Reid Center for Environmental Studies. Nuclear Science and Technology Division
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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 the Eighth Annual IAEA Actinide and Fission Product Partitioning & Transmutation Information Exchange Meeting (Nov. 9 – 11). 120 people from 22 countries attended the meeting.
- The call for proposals for new and continuing research projects with summer starts was issued.

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. Remodeling of a high activity actinide chemistry laboratory was completed Nov. 9, 2004. The TC-1 target electrical, measurement, and control systems were connected under the direction of a delegation of six visiting Russian scientists from the Institute for Physics and Power Engineering. Upon completion of the gas vacuum system (anticipated by the end of the spring 2005 term), the target complex should be ready for final testing and isothermal experiments.

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).

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 concluded in 2004). 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.
- Evaluation of peak fitting software for further analysis of the data collected during the summer research campaign.
- Ultra-High Vacuum (UHV) experimental system transferred from laboratory in Germany to UNLV. System has arrived on campus, and installation work has been initiated.
- X-ray spectroscopy experiments conducted at the Advanced Light Source, Lawrence Berkeley National Laboratory.

Dissolution, Reactor, and Environmental Behavior of ZrO2-MgO Inert Fuel Matrix (Task 19) Highlights.
- Synthesis of MgO-ZrO2 ceramics continued.
- Evaluation of MgO-ZrO2 ceramics by X-ray diffraction initiated for the evaluation of ceramic properties and phase formation.
- Evaluation of neutronic effect on MgO-ZrO2 ratios for fuel performance.
- Installation of pressure vessel for high temperature solubility experiments completed.
- XDR evaluation of prepared samples.
- Development of data and needs for irradiation experiments.

- Two mock-up simulation sequences have been completed as avi-animations.
• Design and analysis of hot cell robotic assembly continued. Primary progress: Continuation of Pick and place dynamic simulation, including feedback control with Matlab, for dispersion Fuel manufacture.

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.
• Iodate-peat experiments continued. Work to date demonstrates IOH participates as a reaction intermediate. Iodate reduction observed to scale with amount of peat in system.
• Synthesis of the modified pyridinium resin initiated.
• Pyrolysis experiments were conducted with AG-1 Resin.
• Conducting larger scale pyrolysis experiments using the semi-preparative GC

Fluorapatite Waste Forms (Task 16) Highlights.
• Multiple samples of hydroxyapatite prepared some with surrogates (varying Ca/Zn weight ratios) and some pure samples which have then been analyzed with IR, TGA/DSC and XRD techniques.
• Fluorapatite samples synthesized using the reflux method and analyzed with SEM, XPS, XRD and single point IR.
• Experiments conducted with natural fluorapatite and hydroxyl apatite using the precipitation method to determine if procedure to synthesize fluorapatite differs based on samples used. XRD was used to analyze the synthesized samples.
• Synthesized yttrium and cesium containing FAP samples using the same method that was used for Strontium (explained in last report) and obtained XRD, SEM and DSC data for samples.

• Development of the ASPEN PLUS Windows user interface continued. A process simulation (in ASPEN PLUS) is being developed to allow work on the system interface at UNLV.
• Interface developed to allow users to view input parameters in a tree structure.
• Investigation of the system optimization package included in ASPEN PLUS initiated. The ASPEN PLUS optimization package will be compared to the TRPSEMPRO package developed previously for system optimization.
• Debugging and modification of the TRPSEMPRO package continued in coordination with ANL collaborators.
• Design of the system model in ASPEN-PLUS continued. Connecting components identified.

**Electrochemical Separation of Curium and Americium (Task 25) Highlights.**
• Preliminary polymer growth studies with existing electrochemical apparatus initiated.
• Begun electrochemical studies to examine thermodynamics of target species.

**Fundamental Chemistry of U and Pu in the TBP-Dodecane-Nitric Acid System (Task 26) Highlights.**
• Development of NMR procedures for evaluation of actinide-bearing samples continued.
• Development of ICP-AES and UV-Visible spectroscopy procedures for evaluating uranium solution phase concentration completed.
• Initial experiments examining nitrate stoichiometry at 4 M HNO₃ completed.
• Evaluated extinction coefficient for organic phase compounds for UV-Vis spectroscopy.

**TRANSMUTATION SCIENCES**

**Niobium Cavity Fabrication Optimization (Task 2) Highlights.**
• Secondary electron emission observed from oscilloscope measurements.
• Installation and modification of electron multipacting experimental system continued.
• Calibration and fine-tuning of data acquisition software for the Secondary Electron Emission (SEE) experimental system continued.
• Monte Carlo modeling of the SEE system and proposed experiments continued.

**LBE Corrosion of Steel (Task 3) Highlights.**

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

**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.
- Evaluation and repair of failed electronic components continued in collaboration with researchers from KRI.
- Further testing of the NMDS was conducted to compare daytime to nighttime background measurements, which were determined to be the same statistically.
- The NMDS “owners manual” was completed.
- Preliminary discussions for the experimental deployment of the neutron multiplicity detector at an accelerator continued with representatives from Los Alamos National Laboratory and Brookhaven National Laboratory.

Development of Dose Conversion Coefficients for Radionuclides Produced in Spallation Neutron Sources (Task 7) Highlights.
- Reviewed the radionuclides without complete data that could possibly have DC’s calculated with acceptable error.
- Feasibility of developing experiments to fill data gaps in current database, including the production of the radionuclides in question, currently under evaluation.
- Initiated discussions with Francis Marion University to evaluate the physics needs for creating radionuclides which are currently lacking data required for DC calculations.

- Project completed in August 2004. Theses generated:

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

- Analyzed data on the experimental data collected from the LANL test loop.
- Detached and removed the previous experiment setup located in LANL.
- Designed, assembled, and tested the new experiment setup. A new rocking system for oxygen mixing was fabricated. System currently undergoing shakedown testing.
Use of Positron Annihilation Spectroscopy for Stress-Strain Measurements (Task 14)

Highlights.
- Measurements of residual stresses in cold-worked and welded specimens of austenitic and martensitic stainless steels by positron annihilation spectroscopy continued at the Idaho Accelerator center of ISU. Activation of some test specimens is also in progress at the IAC.
- Calibration curves using tensile specimens subjected to different levels of loading based on the materials’ stress-strain diagrams were developed. These curves will enable the estimation of line-shape parameters (S, W and T) to determine the resultant residual stresses.
- TEM analyses of imperfections in tested specimens are ongoing.
- Additional specimens are being prepared for future residual stress measurements.

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

Highlights.
- Development of the small experiments facility continued. Final approval for the physical renovation of the Small Experiments Facility was granted. Installation of required Environmental Health and Safety upgrades for molten LBE work continued.
- Samples were analyzed for LANL from the Delta Loop.
- Lead sample preparation procedures were tested at UNLV.
- Collaborative studies with LLNL continued - samples received, analyzed, and data returned to LLNL.

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

Highlights.
- Four heats of T-91 grade stainless steel have been melted at Timken Research.
- Materials are being processed to prepare test specimens.
- Literature review is in progress.

Oxide Film Growth Modeling in LBE Systems (Task 21) Highlights.
- Analysis of experimental data from DELTA loop continued.
- Corrosion rate models for LBE loop systems compared and evaluated. Existing models found to be incomplete. A new synthesis model will be developed based on existing work incorporating known physics and transport phenomena into a single model.
- The impact of turbulence diffusion on the corrosion in the LBE Loop system has been modeled and examined.
- The numerical model has been applied to the material test loop system in Los Alamos National Laboratory. Based on model results, the impact of the turbulent diffusion term will be to increase the corrosion rate in the test region. Also, the concentration boundary layer will be thinner under turbulent diffusion conditions than in the laminar cases.

Corrosion Barrier Development for LBE Corrosion Resistance (Task 23) Highlights.
- Acquisition of steel samples for experiments.
• Design and fabrication of specialized anodization apparatus to accommodate steel samples.
• Investigation of adhesiveness of aluminum on steel.
• Investigation of effects of anodizing acids on steel to identify most appropriate acid and a suitable barrier material.

Reactor Physics Studies for the AFCI RACE Project (Reactor-Accelerator Coupling Experiments Project (Task 27) Highlights.
• Granted access to a set of export-controlled codes and databases for reactor physics studies from The Radiation Safety Information Computational Center (RSICC) at Oak Ridge National Laboratory.
• Modeling with MCNPX was initiated in support of subcritical experiments at the Idaho Accelerator Center.

1.3.3 Student Research Technical Summary

FUELS TECHNOLOGY

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

The goal of this project, is to elucidate the chemical bonding and interface formation of metal fission products with the coating materials used in state-of-the-art TRISO fuel particles. Particular emphasis is placed 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 detail, this project is devoted to studying the interface formation of Pd, Ag, and Cs with SiC and pyrolytic carbon. In order to study the properties of the relevant interfaces, such interfaces are prepared under controlled conditions in an ultra-high vacuum environment and studied with a variety of different spectroscopic methods, i.e., surface sensitive techniques (in particular photoelectron spectroscopy – XPS and UPS) and bulk sensitive methods (in particular X-ray emission spectroscopy - XES).

In the last quarter, efforts were focused on two areas, namely (1) to organize the arrival and reassembly of the four-chamber ultra-high vacuum surface science instrument on the UNLV campus and (2) to conduct first XES experiments at the Advanced Light Source, Lawrence Berkeley National Laboratory.

As shown in Fig. 1, the instrument has arrived safely on the UNLV campus after an 8 week transit from the University of Würzburg, Germany, and several weeks in customs. It appears that transit-related damage is minimal. First experiments will be conducted next quarter.

During the reporting period, initial experiments were conducted at Beamline 8.0 of the Advanced Light Source (ALS) in Berkeley. The main goal of this beamtime, apart from taking first data on Pd/SiC interfaces (see below), was to acquaint the graduate students in this project (at the time of the beamtime: G. Gajjala and V. Marepally) with the cutting-edge research environment at the ALS. This includes the operation of a soft x-ray undulator beamline, a high-end soft x-ray
spectrometer, ultra-high vacuum sample transfers, radiation safety, high-efficiency 24-hour data taking, etc.

Moreover, first X-ray emission spectroscopy (XES) data could be collected using the SiC and Pd/SiC samples produced during the summer research campaign at the University of Würzburg prior to the relocation of the instrument. As described in the previous report, it was found (using photoelectron spectroscopy) that a thin Pd overlayer induces at least two new chemical carbon species at the Pd/SiC interface. In order to shed more light on this effect, both C and Si emission spectra were analyzed for the two different samples with varying excitation energies (generally called “resonant inelastic x-ray scattering” – RIXS). Two spectra taken from these series are shown in Fig. 2. When comparing the two Si L\textsubscript{2,3} spectra at an excitation energy of 150 eV, it becomes apparent that, due to the Pd/SiC interface formation, spectral weight is lost around 91 eV (i.e., near the bottom of the valence band) and gained between 98 and 100 eV. This is more clearly shown in the difference spectrum (green) in Fig. 2. As indicated by the arrow, an increase was found in the electronic density-of-states at these energies, which, based on a thorough energy calibration (not shown here), lie close to the Fermi energy. Note that XES is a bulk sensitive probe and hence the contribution of the interface to the overall signal is rather small (but nevertheless easily discernible in the present case). The finding of an increased electronic density of states near the Fermi edge needs further confirmation and analysis, but at present suggests that the local electronic and chemical environment of the Si atoms at the interface is strongly influenced by the interface formation and now exhibits a significantly more “metallic” character. The complete analysis of the XES and RIXS data is currently in progress, both for the Si L\textsubscript{2,3} spectra as well as for the C K line. The next experiments at the ALS (May 2005) will utilize “fresh” (ideally: in-situ prepared) samples as well as sample systems involving realistic SiC-layers from the TRISO coating process, and will strongly build on the student expertise gained in the November 2004 beamtime.
**Figure 1.** Picture of the four-chamber ultra-high vacuum apparatus during set-up in the UNLV lab, showing graduate students T. Hofmann (left), V. Marepally (center), G. Gajjala (not shown), and undergraduate student J. White (right).

**Figure 2.** Si $L_{2,3}$ x-ray emission spectra of a SiC(0001) single crystal (black) and a Pd/SiC interface (red). The difference between both spectra is shown in green (magnified by a factor of five). The arrow indicates an enhanced spectral weight near the Fermi energy, suggesting an increased metallic character of the local environment of silicon atoms at the Pd/SiC interface.

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

**Manufacturing Sequence for Dispersion Fuel**

Gas Fast Reactor (GFR) dispersion fuel is a new fuel type currently under development that would be used for Generation IV applications. Dispersion fuel is basically a coated particle fuel with an individual fission product barrier layer. The major differences relate to the particle coatings and compact fabrication that encapsulate the isotopes in various morphologies of SiC. A variant of dispersion fuel is also being considered that would have coatings of ZrC rather than SiC, but this fuel is only a concept at this time. The manufacturing steps of the dispersion fuel are noted below.

1. Manufacture spherical fuel particles by wet chemical process or direct reaction and attrition.
2. Coat the particles (process not yet determined).
3. Embed fuel and matrix blend into a compact.
4. Assemble billet, Figure 3.
e) Extrude billet at ~800°C into rods about 2 m long.
f) Finish fuel rods by trimming ends.
g) Inspect the rods (radiography, dimensional, bonding, and clad defects).

Figure 3. Dispersion Fuel Element

Dispersion Fuel Hot Cell Layout

Due to software limitations, the dispersion fuel manufacturing process cannot be modeled completely. Instead, only the assembly of the billet was studied. Figure 4 shows the proposed floor layout of a hot cell manufacturing dispersion fuel. The compacts will be moved from the first table, pass through the sintering oven, ending the process of assembling the billets.
Figure 4. Schematic of the floor layout of a hot cell manufacturing dispersion fuel.

Three Wäelischmiller (GmbH) robots are used in the simulation for loading/unloading of the dispersion fuel compacts. The robots unload the completed compact from the press, place the compacts into the billets, and finalize the assembly process of the billets. Figure 5 shows a schematic of the manufacturing hot cell developed in the MSC.visualNastran® simulation environment.

Dispersion fuels originate as rectangular compacts. The first robot loads the compact onto a conveyor belt for sintering. The compacts require a custom design of the end-effector of the manipulators. An end-effector consisting of four gripper fingers was used to ensure safe and reliable grasping while moving the compacts throughout the hot cell. Figure 6 shows the modified end effector which encloses the compacts on all sides.
Figure 5. Snapshot of the hot cell developed in the MSC.visualNastran®

Figure 6. Modified end-effector utilizing four-fingered gripper

Robots 2 and 3 work together to assemble the billets, into which the sintered compacts are placed. One of the manipulators places the sintered compacts into the billet. The other manipulator covers the billet with a cladding plate, thus finalizing the process. Figure 7 shows a
manipulator placing a sintered compact in a billet. The modified end-effector can be seen with the compact secured within the four-fingered gripper.

Figure 7. Manipulator placing a sintered compact into the billet

Figure 8 shows the third manipulator in the hot cell moving the upper cover of the billet, and placing it on top of the frame containing the sintered compacts. The manipulator uses the old end-effector consisting of two gripper fingers only.

Figure 8. Manipulator finishing the billet assembly process

Analysis of Atypical Events
In the above manufacturing process atypical events can happen. For example a compact can be misplaced. In such a case, the manipulator should have the necessary path planning capabilities to correct the placing of the compact. Figure 9 shows a compact pushed into the billet frame after having been misplaced.

![Figure 9. Misplaced compact pushed in the picture frame](image)

During an compact insertion like the one depicted in Figure 9, it is desirable to know the forces and motion parameters governing the compact insertion. As an example, Figure 10 shows the friction forces between the compact and the picture frame, and between the compact and the bottom plate of the billet.
Conclusion

The deployment of remote manufacturing of transmuter fuel is a necessity for the transmutation applications. In the above reporting period, a virtual hot cell for the manufacturing of dispersion fuel was designed using MSC.visualNastran©, ProEngineer© and MATLAB©. Atypical events were successfully simulated. Relevant physical quantities arising during such events were monitored as well.

SEPARATIONS TECHNOLOGY

Immobilization of Fission Iodine (Task 15).

A large number of experiments were conducted to determine the possible reaction of iodate with sphagnum peat moss. These experiments indicate that the natural organic material reacts with iodate resulting in the formation of organically bound iodine and/or iodide in solution.

In the last quarter, a number of experiments were conducted at various pHs and several temperatures (70°C, 60°C and 40°C). The reaction of iodate with peat follows pseudo first-order kinetics, although the reaction rate does appear to decrease significantly with reaction time. As noted in a previous report organically bound iodine appears to go through a maximum with reaction time indicating that it is eventually released into the solution as iodide. The stability of the organo-iodine intermediate appears to be a function of pH and temperature, as is the reaction rate of iodate with peat.

The notion was tested that iodate was first reduced to hypoiodic acid, which either reacts with phenolic moieties in the peat matrix or is further reduced to iodide. Heating experiments were conducted in the presence of N, N-dimethylamino benzene (NNDMA). This reagent reacts rapidly with hypoiodic acid and iodine forming of p-iodo- N, N-dimethylamino benzene (I-NNDMA). This product can be extracted and identified by GC/MS. I-NNDMA was detected in several experiments confirming the formation of HOI or I₂. Results from an experiment where 350 mg of peat was exposed to 20 mL of a 100 ppm iodate solution are shown in Figure 11. The experiment was conducted at pH 5.3 and 60°C. As shown in the figure, the amount of I-NNDMA was significantly lower that the quantity of iodate lost. The calculated I-NNDMA (from iodate loss) that is shown in Figure 11 assumes that all of the iodate lost was converted to IOH that was subsequently trapped by reaction with NNDMA. The actual measurements are considerable lower. This result indicates that IOH is not the exclusive intermediate, or that the peat is competing with NNDMA for IOH. It is believed that there is a set of highly reactive functional groups that are “used up” early in the experiments. After these reactive groups are depleted the NNDMA becomes the main sink for IOH. Note that the slope of the I-NNDMA line and the slope of the I-NNMA calculated line are about the same after 120 hours.
The possible influence of oxygen on product distributions from the iodate experiments was also examined. Reactions were carried out in a continuous stirred water-jacketed batch reactor. The iodate, peat and buffer concentrations were the same as previous experiments (that were carried out in glass screw cap test tubes) that were heated in an oven. There were no special measures taken to eliminate oxygen in the test tube experiments. The batch reactor experiments were heated using a circulating water bath. The batch reactor was continuously sparged with nitrogen during the reaction. The sparge gas was passed through an impinger filled with either dilute NaOH or NaHSO₃ to determine if any iodine (I₂) was lost from the system. Initial reaction rates did seem faster in the stirred reactor, however we believe this resulted from constant stirring in the batch reactor rather than the absence of oxygen. The overall extent of iodate reduction was about the same in both systems. The results indicate that I₂ was not sparged from the system under these conditions (pH 2-9 at 60°C) so that IOH is most likely the iodinating species produced by the reduction of iodate.

The data that indicates that iodate is first converted to hypoiodic acid (or iodine), which in turn, can be further reduced to iodide, or react with peat resulting in sequestration into the organic matrix. This reaction presumably occurs as a substitution for hydrogen at phenolic rings. The reaction of iodate with peat appears to involve competition (parallel reactions) between sequestration and reduction to iodide.
Previous results demonstrated that methyl iodide was produced by pyrolysis of iodine or iodate treated peat. It was proposed that iodine could be recovered and purified chromatographically and that the purified methyl iodide could be converted to NaI for transmutation or storage. The packed column gas chromatograph that will be used for these studies was received during this last reporting period. The instrument is an SRI 8010 with a TCD detector and injector valve equipped with a thermal desorber. The thermal desorber has a trap packed with carbosieve. 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. In order to scale up the pyrolysis experiments a 6” tube furnace manufactured by Carbolyte was obtained. This programmable furnace has a 0.5” diameter process tube that can hold 8-100 mg samples of peat or ion exchange resin. The furnace is connected to a source of helium with Swagelok™ fittings. During sample heating a helium stream sweeps products from the tube furnace to the carbosieve trap located in the thermal desorber unit.

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 peat of been conducted using this experimental apparatus. The results for 10 mg of iodate treated peat (pH 2, 24 hours) was compared with the results from untreated peat. Recovery was examined from both iodine and iodate treated peat samples. Results indicate that 40-70% of the bound iodide can be recovered by this procedure.

In a previous report, it was demonstrated that ballistic heating of iodinated resin to 500°C released methyl iodide (reaction 1). The competitive reaction results in the release of trimethylamine (reaction 2).

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\text{Reaction 1: Formation of methyl iodide using AG-1 resin.}
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\text{Reaction 2: Formation of trimethylamine from AG-1 resin.}
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During this last quarter, results were obtained with resins exposed to different concentrations of iodide. The results indicate that methyl iodide yield at 500°C is a linear function of iodide concentration. It is believed this could serve as the basis for an analytical measurement of iodine. Thermal decomposition of the AG-1 anion exchange resin was also examined using the preparative gas chromatography and tube furnace. At 300 to 600°C only trimethylamine was observed. This is because of the slow heating rate of the tube furnace and the more rapid loss of
trimethylamine at lower temperatures. Therefore, the group will continuing to examine other resins for this application.

Previous reports disclosed that pyrolysis of peat moss that was used for trapping iodine produced a substantial amount of volatile and reactive methyl iodide (MeI). In addition, the reaction of peat with iodine also produces iodide that will need to be trapped and converted to NaI. The methyl iodide produced during pyrolysis can be purified chromatographically. It will need to be converted to NaI for subsequent transmutation. The Wurtz reaction will be explored for this purpose. The use of resins is being explored for two purposes: 1. Trapping of iodide from aqueous solution with subsequent pyrolysis of the resin to produce methyl iodide. 2. Capturing methyl iodide from the gas phase so that it can be converted to NaI.

Two approaches are being explored. (1) The use of poly-(4-vinylpyridine-co-divinylbenzene), PVP, to react with MeI or, in its quaternary ammonium ion form, 2 or 3, and to exchange with a counter ion, A⁻, to trap iodide ion after hydrolysis of MeI. (Scheme 1.) A key point here is the equilibrium point of the reaction $2 \leftrightarrow 3$. (2) A second approach is to employ a polymeric sulfide, 4, to trap MeI as a sulfonium salt, 5, which could then be treated with sodium hydroxide to liberate volatile methanol and form non-volatile sodium iodide and regenerate 4. The polymeric sulfide, 4, could then be recycled (Scheme 2).

At this point commercially available PVP, 1, has been obtained and quaternary ammonium ions, 2 and 3, with counter ions p-toluenesulfonate and methyl sulfate have been prepared. The sulfide resin, 4, has been synthesized.

**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 proposal will develop 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.

Technical progress

The XANES spectra that were obtained for samples including hydroxyl apatite and natural apatite near the Ca, Sr and oxygen edges at the Advanced Light Source of LBNL at beam line 6.3.1 do not indicate significant changes in the absorption edges. This is an indication that the electronic structure of apatite does not change very much after the insertion of foreign element like Sr. Further investigation is needed based on some more significant changes that were observed in the oxygen K-edge spectra.

Fluorapatite is a naturally occurring mineral with a strong crystalline structure and 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. Therefore a procedure to re-synthesizing apatite starting with natural apatite was sought. This re-synthesis of apatite using natural apatite as a starting material was partially successful. Even though, the intention was to synthesize fluorapatite but hydroxyl apatite was obtained as final product. Further experiments are necessary to refine the procedures and optimize the results.

An important property of fluorapatite is its crystallinity and the resulting tensile strength. Nuclear waste bearing apatite should have a crystalline structure to be more stable. It is therefore of interest to find methods to improve the crystallinity of waste bearing apatites. The figures below show the characteristics of fluorapatite samples that were prepared using wet methods (also called precipitation methods). Figure 12 is a SEM micrograph of a fluorapatite sample after sintering at 1200°C. This figure clearly shows that sintering of fluorapatite is creating particles of a more definite size and shape. A not sintered sample of fluorapatite was compared to the sintered sample using XRD data taken from both samples. It turns out that sintering makes the sample more crystalline based on the fact that the peaks of the XRD data shown in Figure 13 are narrower for the sintered sample. Similar experiments have been conducted with Zn-bearing fluorapatite with similar results but an overall lower crystallinity.

A project kick-off meeting was held at UNLV (10/12/05-10/14/05). During the meeting the framework of the system was proposed, discussed and finalized as shown in Figure 14. Major parts of the system are:

- TRPSEMPro (System Engineering Model System Developed by NCACM): AMUSE Simulator (connector between TRPSEMPro and AMUSE), ASPEN-PLUS Simulator (connector between TRPSEMPro and ASPEN-PLUS), and Optimization (analysis module interacts with the above connectors).
- ASPEN-PLUS (commercial process analysis software)
- AMUSE (Excel macros developed by Argonne National Laboratory)
Figure 14. The framework design for the chemical separation process

ASPEN-PLUS is a new process package for the ANL. Currently the NCACM has a few academic licenses and will provide some hands-on exercise for the ANL researchers. Meanwhile, the ANL will provide some sample cases and identify process blocks that are related to the chemical separation processing.

During the development of the system, a scenario-based database will be developed that can help decision-making on Waste Generation Management, Proliferation Resistance, Throughput Capabilities, Facility Requirements, and possibly Cost Benefit analysis. The selected database is MS ACCESS and will be interfaced through the TRPSEMPro package.

System Design – identify connecting components from the Aspen Plus package

The Aspen Plus Windows user interface provides the function using an ActiveX Automation Server. The ActiveX technology enables an external Windows application to interact with Aspen Plus through a programming interface using a language such as Microsoft’s Visual Basic. Since the TRPSEMPro was coded by MS.NET package that can be bridged to the exposed server objects through the COM object model.

Since the Aspen Plus process developed by the ANL can be sensitive in its nature, the development of the Aspen Plus Simulator (AspenSim) will be built to use those Aspen Plus components to access the inputs and outputs of the process without revealing process details.
Since the ANL is currently working on the process development. Details related to the inputs and outputs will not be available for few more months. Therefore, the NCACM is identifying useful components for handling inputs and outputs

*TRPSEMPro package improvement* – since the package will play a critical role during the system integration, more efforts were placed on modifying program bugs during this quarter. Several improvements were made such as to simplify the setup procedure, provide faster and more effective debugging.

The NCACM has allocated a workstation for housing ASPEN-PLUS and has setup up a remote desktop connection for the ANL researchers. The purpose for this connection is the following:

- The workstation will be used for familiarizing the ASPEN-plus and constructing basic system analysis cases that can be used for the testing scenarios for the NCACM team.
- Both the ANL and the NCACM teams will use this workstation to identify required parameters for connecting the ASPEN-plus to the TRPSEMPro package. Since the ASPEN-plus was designed with the object-oriented concepts. The exploration of the tree structure has been initialized and will continuously identify the parameters during the next few months.

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

The initial focus of this project involved setting up the laboratories for the studies outlined in the grant proposal. The instrumentation needed included an electrochemical work station that will perform the bulk of the electrochemical studies. In addition the required electrodes, electrochemical glassware, side apparatus including nitrogen degassers and the chemicals for the initial studies were obtained. The laboratories are up and running currently and both graduate students are actively participating in the studies.

The initial studies required that the graduate students were educated in electrochemical analysis and techniques. This was initiated the first month of the project and both students were given guidance in obtaining electrochemical data. One student was responsible for examining the nitrate salts of Cerium, Neodymium, Samarium, and Europium in 1 M HCl. These species were chosen as model species to initiate the separation studies. The initial goal is to examine the electrochemical behavior of these species to develop a complete thermodynamic picture. The next step involves the complexes formed with a variety of ligands. Electrochemical data from the complexes will be compared directly to the data from the species prior to complexation to determine how the thermodynamics can be altered. The electrochemistry of Ce, Sm, Eu, and Nd in 1 M HNO₃ is presented in Figure 15.
Figure 15. Electrochemical response of a Pt electrode in solution containing $1 \times 10^{-3}$ M Ce, Eu, Nd, and Sm in 1 M HNO$_3$. Scan rate = 100 mV/s.

The results show that the electrochemistry of Nd and Eu are closely matched. The voltammetric waves shown are for the Nd(2+/3+) and Eu (2+/3+) couples. In addition the magnitude of the current associated with the oxidation and reduction of the two species shows that the reduction to Nd$^{2+}$ and Eu$^{2+}$ is thermodynamically more favorable than the more oxidized species. In contrast the electrochemistry of Sm and Ce are not like other species. The voltammetric response for Ce shows two waves between 0.5 and 0 V vs. Ag/AgCl corresponding to the reduction of Ce(III) to Ce(II). However, under the solution conditions employed the reversible oxidation is not observed. The electrochemical response of Sm shows the reduction and reversible oxidation from Sm(III) to Sm(II) and possible Sm(I). The multi-wave oxidation for Sm suggests that a fraction of the species in solution have undergone a two-electron reduction to Sm(I). Further studies will be completed to determine the oxidation pathways of Sm.

Additional studies were initiated which examine the influence of pH on the voltammetric response. It is important to understand how pH influences the electrochemical properties of the species. The pH should influence the metal ions ability to give and receive electrons. These changes should be manifested in changing electrochemical potentials for the oxidation/reduction processes. These studies have been initiated at present and Figure 16 shows the effect of changing pH on Ce.
The electrochemical response in Figure 16 indicates that the voltammetric behavior of Ce is dramatically influenced by the pH. In the case of the pH = 0 solution two reduction waves are observed as noted previously. These voltammetric waves are absent in the pH = 9 solution. However, a new redox process is resolved at 1.5 V vs. Ag/AgCl. The emergence of both the oxidized and reduced species can be observed on the sloping background between 1.0 and 1.75 V. The initial studies confirm that pH influences the electron affinity and ionization potential of the solution species of Ce. The same trend is expected for the other species of interest. These studies will be expanded to include all of the species presented in Figure 15.

TRANSMUTATION SCIENCES

Niobium Cavity Fabrication Optimization (Task 2).
The first secondary electron emission (SEE) measurement was made from the surface of a Faraday cup in September 2004. In December, the software for the particle positioning detector was finally up and running. The integrity of the code and detector are currently being fine-tuned with the aid of the manufacturer and should be completely operational in the next quarter. Three studies in support of this last phase are being conducted in parallel. The accomplishments and directions in these three areas are presented below.

Material Secondary Electron Emission Studies:
The Monte Carlo Back Scattering and Secondary Electron Scattering code developed by Dr. David Joy (ORNL and University of Tennessee Knoxville) has been converted to a C++ language to increase its speed and allow for more flexibility in performing future modifications. The new version of the code now accepts up to four layers with a rigorous treatment of a multiple component material composition of varied thickness (machine dependent) in determining the SEE energy and trajectory. The code’s architecture has been restructured to employ both a pre-calculated look-up table and run-time generated values. Now, multiple generations of secondaries can be created AND tracked. The previous version of the code only tracked the primary electron. A batch-processing driver has also been written.
Experimental Set-up for the SEE from a Niobium Test Piece:

The experimental setup, for secondary electron emission (SEE) studies, is currently operational for some experiments. The following tasks have been completed:

- The detector is assembled and appears to be working. If the UHV chamber has been vented to air (venting is a slow process, ~5 hours), then, once UHV pressures are reached, it takes about 2.5 hours to properly prime the detector to the operating voltages required for detection. A special source regulation circuit has been designed and implemented. This device enforces voltage stability across the MCP stack.

- The electron beam generated by the electron gun is difficult to find. A phosphor coated glass disk (phosphor P43 coated on a glass substrate with charge dissipation properties and an aluminum coating for increase brightness) manufactured by Phosphor Solutions was purchased to aid in the detection of low current, low energy, electron beams and examine the electron beam profile. The glass disk was mounted on the Faraday cup attached to the moveable xyz manipulator.

- Thermally conductive greases do not seem to aid the cooling process of the sample without substantial pressure applied to the sample under test. This may preclude experimental studies hoped for in niobium’s superconducting state. Mounts needed to apply this pressure prevent for the ability to align the piece under test with the electron beam.

- Figure 17 depicts one of the preliminary secondary electron emission studies of niobium at room temperature. Currently, the software is being fine-tuned with the detector and checked for accuracy. Working with the Germans, it is anticipated that this task will be completed during the month of January.

- Course grid potential adjustments have been studied. As expected, the grid potential influences the number of secondary electrons detected.
Figure 17. Preliminary secondary electron studies with beam normally incident on the niobium sample. The detector bias conditions are: grid 250 V, MCP front voltage is 300 V, and the MCP back voltage is 2.6 kV. All voltages are referenced to ground. The niobium sample under test is grounded. The top of the niobium sample is 1 inch from the grid. The figures displayed shows (a) the spectrum dark current resulting with the electron gun is off (dark count rate ~ 3,000/s), (b) the sum of the spectrum dark current and secondary electron emission when the electron gun is in continuous mode generating 500 eV with a filament current of 1.3 A, emission current of 55 µA and a sample current of 3.15 nA (overall count rate ~ 14,000/s).
Theoretical Study for the SEE from a Niobium Test Piece:

In support of the numerical Monte Carlo and experimental studies, a particle tracking numerical/theoretical study is also underway. This study will aid in explaining experimental results. A 2-D electrostatic code and a 2-D particle tracking code are being used to map all possible secondary electron trajectories with the same termination conditions as obtained from experiment. At this time, the parameter space has been mapped for the electron beam impinging upon the surface at a 0°, 30°, and 45° angle with respect to the surface normal. This data will aid in determining what family of secondary electrons with suitable initial conditions will reach the measured position. Figure 18 yields a small sample of this data plotted for a primary beam normally incident on the sample. Electrons are tracked based on incident particle trajectory angles ranging from 0° to 90° in increments of 0.5° and initial energies typical for true secondary electrons (typically between 1 eV and 20 eV). Only select energies are displayed in Fig. 18. The jagged portion of each of the curves presented are due to the discrete presence of the wire grid. It should be noted that because this is a 2-D code, the wire grid is assumed to have only a two dimensional nature. It appears that the grid plays a significant role in backing out initial conditions based on final conditions.

![Plot of the SE Initial Angles vs Impact Point on Detector for various Energies](image)

*Figure 18. Particle trajectory mapping on the detector surface for secondary electrons released from a flat niobium surface based on a distribution of incident trajectory angles and energies.*

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

Evaluation of NMDS experiments that were conducted at the Idaho State University Idaho Accelerator Center in July continued. In these experiments, electron beams from a 30-MeV
electron linac were used to create photoneutrons in the lead-block core of the NMDS. These neutrons were then counted with the NMDS detectors.

The NMDS has experienced several failures since it was brought back to UNLV from the Idaho State University. Troubleshooting revealed that the electronic system had many loose components. This condition was probably caused by vibration during transportation from UNLV to ISU and back (one 8-detector sub-system failed at the ISU). This involved disassembling the system, packing it in its shipping crates, transporting it to ISU, reassembling it, and conducting a series of accelerator-driven experiments. Collaborators at the KRI continued to work with the UNLV team to evaluate system problems and repair failed electronic components.

In addition to background counts and performance checks, data were taken to compare daytime to nighttime background measurements, which were determined to be the same statistically. In addition, a series of counts were run to look for increased cosmic radiation during the passing of a meteorite--again with negative results.

Other work this semester has involved developing documentation of the system. This included translating many Russian schematics and preparation of a “user’s manual,” which was completed in December.

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

One graduate student conducted experiments in LANL from Nov. 8 to Dec. 21, 2004. The testing of the corrosion of different materials in LBE was performed. Delta loop experimental data analysis was performed to find the temperature response of the YSZ oxygen sensor under the hydrogen injection condition. Preliminary studies were started on the pressure-electric silicon sensor. At the same time, progress has been made in the simulation for transport in oxygen mixing.

The response time to H₂/He injection during cleaning process of DELTA Loop is shown in Figure 19. Since H₂/He injection reduces the oxygen level, such response time is to oxygen concentration change at constant temperature. The OS103 output increased at the beginning of H₂/He injection faster than the other two oxygen sensors and there is no significant time delay. The OS101 responded with a little delay. There is also a time delay for OS102. This can be explained due to the gas transport in the liquid LBE. Since the OS103 is placed near the inlet of the loop, it responded immediately after the H₂/He injection. The figure also shows that OS103 responds more sensitively than OS102, which is because the hydrogen is consumed by reacting with oxygen during its transport in the flowing LBE. After H₂/He is closed, the voltages drop suddenly and then the decreasing rates become slow. The slow rates correspond to the dissociation of the surface oxide because the oxygen activity is lower than that for oxide formation after long-term injection of H₂/He. If no new oxygen is supplied, the surface oxide will continue to dissociate until reaching a new equilibrium at the liquid/oxide surface. Such a process is long and thus more attention is needed when operating a practical lead-alloy system.
Figure 19. Sensor response time to H₂/He injection during cleaning process of DELTA Loop.

Figure 20 shows the sensor response to H₂/He injection, different sensor locations directly reflect the speed of OS response to H₂ injection.

Figure 20. Sensor response time to H₂/He injection.
The time constants (denoted by lower case t’s) are used to describe how fast the H₂ injection rate affects the sensor output. These time constants show the effects of different OS locations on the sensor output.

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

The purpose of this collaborative research project involving the University of Nevada Las Vegas (UNLV), the Idaho State University (ISU), and the Los Alamos National Laboratory (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 γ-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). Transmission electron microscopic analyses are also being performed.

The PAS method has been applied to develop calibration curves for line shape parameters (S and T) using unstressed and stressed (different magnitude) tensile specimens of martensitic stainless steels. These curves will enable the determination of residual stresses in plastically-deformed materials once the magnitude of S or T parameter is determined by the PAS technique.

The tensile and welded specimens have been irradiated by low energy photon beam at ISU to compare the residual stresses, with and without radiation. Measurements of residual stresses have been performed by the PAS technique on both welded and post-weld thermally-treated specimens to evaluate the effect of thermal treatment on the residual stresses generated due to welding. Use of transmission electron microscopy (TEM) has been initiated to analyze voids and dislocations in cold-worked/welded materials.

**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.

*Metallography test apparatus*
The physical renovation of the Small Experiments Facility for molten metal research is undergoing design and implementation (after which major pieces of the instrumentation will be located in the space). A health and safety plan was approved and power and ventilation upgrades to the facility are planned. This is a major hurdle, since it involved baseline measurements of lead release during sample preparation and review of the regulatory constraints of the facility.

**Comparative gas phase studies**

Thermal uniformity issues in the tube furnace were discovered and remedied. Tube furnace experiments are planned. Knudsen cell experiments will be performed until the experimental space becomes available and the Oxygen Control System is relocated.

**Isotope labeling studies**

Isotope labeling can be used to measure diffusion of materials under realistic conditions. Appropriate conditions have been found for electropolishing experiments and plans have been made with Dr. Gaspar of Environmental Molecular Sciences Laboratory (EMSL) in Richland WA to do the SIMS (secondary ion mass spectrometry) and NRA (nuclear reaction analysis) of the O\(^{18}\) label. Ion implantation studies will be initiated when appropriate.

**Collaborative work**

A major effort has been underway to aid efforts at LANL and INEL. Several tens of samples for LANL have been mounted, prepared, and analyzed. The data analysis of the samples is in process – several of the samples show very low levels of corrosion, as hoped.

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

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 ($\gamma$, 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) Highlights.**

For studying the oxygen distribution in non-isothermal LBE systems, experimental results from the Delta loop were analyzed. Analyses on sensor output show that the fully turbulent flow leads to a uniform oxygen concentration over the entire loop and there is no significant delay of sensor response to a change of the operating condition. Taking into account the chemical reaction at the liquid/oxide interface, the possible oxide behaviors are analyzed, providing means to achieve the optimized oxide layer thickness. At corrosion zones, the iron is removed by mass transfer corrosion. Three typical behaviors of the oxide layer at the corrosion zone can be observed: the thickness is constant if the amount of removal of corrosion products by mass transfer corrosion equals to that of diffusion through the oxide layer; the thickness decreases due to dissociation if the amount of removal by mass transfer is larger than that by diffusion through the oxide; the thickness increases due new oxide formation if the amount of removal by mass transfer corrosion is less than that by diffusion. Taking into account the mass transfer rate is propositional to the surface corrosion product (mainly iron) concentration in the liquid which is determined by the oxygen concentration at equilibrium state, it is possible to obtain an optimized oxide thickness by controlling the oxygen level, avoiding the oxidation corrosion due to the formation of very thick oxide layers and directly dissolution due to the formation of very thin oxide layers.

At precipitation zones, the iron comes from two sources: precipitation from the liquid and diffusion from the steel. Because the amount of iron by diffusion through the oxide layer decreases with the oxide thickness increasing, the oxide formation at liquid/oxide interface will be dominated by iron precipitation finally. Therefore, controlling the precipitation rate through changing the liquid flow velocity and the oxygen concentration can prevent very thick oxide formation which may result in oxide spallation or flow blockage at precipitation zones.

Corrosion of steel in flowing LBE system can be affected by hydrodynamic parameters. Available models to predict the corrosion rate in LBE loop mainly focuses on the influence of the local conditions, in particular the velocity of the liquid LBE and the local temperature and the
axial temperature profile, or the axial profile of the boundary concentration of the corrosion product, is usually neglected in the analysis of corrosion kinetics.

A new model to predict the behaviors of corrosion/precipitation in non-isothermal and multi-modular LBE loop system has been developed by others. However, according to their assumption, this model only considers very large Schmidt numbers and the variation of the corrosion product concentration is confined to a thin incompressible boundary layer, which is in the linear boundary layer of the LBE turbulent flow. This model also does not take the effect of turbulent diffusion on the corrosion into account. In fact, the Schmidt number for the corrosion product in LBE liquid is 150, and the concentration boundary layer should exist between the viscous sublayer and buffer region the corrosion transport is by both molecular conduction and eddy diffusion. So this model needs to be corrected.

The effect of turbulence diffusion on the corrosion in the LBE Loop system was checked. Based on the surface renewal concept, the diffusion of corrosion products was examined in the thin wall-layer by considering that it is periodically replenished but at a much reduced frequency than the bulk of the wall region. The model will be extended to the cases that the thickness of the concentration boundary layer is considerably greater that the thickness of the thin wall-layer.

The effect of turbulence diffusion on the corrosion in the LBE Loop system was checked numerically. A numerical model was been applied to the material test loop system at LANL. The following parameters were used in the numerical procedure: loop/pipe length L = 29.92m, hydraulic diameter d = 0.0525m, kinematic viscosity of LBE ν =1.5×10^{-7} m^2 s^{-1}, liquid LBE velocity V =0.5 ms^{-1}, oxygen concentration in LBE c_o=0.01ppm, difference between maximum and minimum temperature ΔT =350K. Figure 21 (a) and (b) show the distribution of the concentration for the whole loop. Figure 22 shows the corrosion rate in along the pipe. From the figure, it can be found that the effect of the turbulent diffusion term will increase the corrosion rate evidently in the test region and the concentration boundary layer becomes thinner than that in the laminar cases.
Figure 21. Distribution of Concentration of Corrosion product (a) with turbulent diffusion term and (b) without turbulent diffusion term.
Corrosion Barier Development for LBE Corrosion Resistance (Task 23) Highlights.

Acquisition of steel samples for experiments

Four HT-9 Martensitic steel samples were obtained from collaborators at LANL. The average dimensions of the samples are 1.25 inches in length, 5/16 inches in width and 1/32 inches in thickness. Based on the shape of the sample, it was decided that it will be the most beneficial to use square pieces for experiments, which will provide approximately four experimental samples from each steel sample.

Design and fabrication of specialized anodization apparatus

A specialized anodization apparatus was designed and fabricated to accommodate the particular shape and thickness of the steel samples. The schematic diagram of the sample holder is shown in Figure 23 (1). The apparatus consists of three main parts: the stopper shown in Figure 23 (3A), the sample chamber shown in Figure 23 (3B), and the threaded rod (threads not shown) running through the stopper and the sample chamber. The square portion of the sample chamber, the stopper, and the sample holder threaded screw (threads not shown) are made of Teflon. A metal contact, labeled in Figure 23 (1), is placed inside the sample chamber. The rod is a continuous piece of metal that touches this metal contact (see Figure 23 (3B)). An acid-resistant stopper is placed inside the chamber to prevent solution from leaking in. The sample is then placed inside the chamber. A metal backing is placed on top of the sample, followed by a round contact whose diameter is equivalent to the inner diameter of the metal contact with a spring attached. The sample holder screw is fastened securely; this entire procedure both prevents solution from
leaking in and creates a contact so voltage/current readings can be taken on the sample. The sample holder is the anode. The sample holder is then placed inside a specially designed container and immersed in the acidic solution. The stopper prevents the sample holder from falling into the apparatus.

Figure 23. Schematic layout of the sample holder for anodization of aluminum coated steel samples.

Investigation of adhesiveness of aluminum on steel

An extensive literature search was carried out to investigate the adhesiveness of aluminum on steel; however no data was available in this field. It was decided that the adhesiveness of aluminum on steel will be determined experimentally using scratch tests, and one of the test samples will be dedicated for this purpose. The need for any barrier metal will be determined based on the scratch tests.

Investigation of the effects of anodizing acids on steel

Anodization of aluminum is carried out in either sulfuric, phosphoric or oxalic acids. However, it is well known that acidic environments corrode steel; the rate of corrosion depends on factors such as the pH and the temperature. Based on a review of the literature, it was decided that oxalic acid will be used to carry out the anodization of aluminum on steel.

With the research group functioning well, and with completion of the above tasks, the project is now ready for the next step of aluminum deposition and anodization, which will be carried out during the next few months.

Reactor Physics Studies for the AFCI RACE Project (Reactor-Accelerator Coupling Experiments Project (Task 27) Highlights.
In the RACE Project of the U.S. Advanced Fuel Cycle Initiative (AFCI), a series of accelerator-driven subcritical systems (ADSS) experiments will be conducted at the Idaho State University’s Idaho Accelerator Center (ISU-IAC), at the University of Texas (UT) at Austin, and at the Texas A&M University. In these experiments we will use electron accelerators 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 Radiation Safety Information Computational Center (RSICC) at Oak Ridge National Laboratory granted UNLV graduate student Evgeny Stankovskiy access to a set of export-controlled codes and databases for reactor physics studies.

Modeling with MCNPX was initiated in support of subcritical experiments at the Idaho Accelerator Center. Electron beam/target interactions were studied for maximizing and characterizing photoneutron production from accelerated neutrons.

Collaborations were begun with Texas RACE Project participants to develop a plan to conduct an accelerator-driven subcritical experiment at UT-Austin or Texas A&M University.