AFCI Quarterly Input: UNLV July through September, 2004

Harry Reid Center for Environmental Studies. Nuclear Science and Technology Division
AFCI Quarterly Input – UNLV
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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.

- The following 11 new graduate student research tasks were started in 2004:
  Task 17 (Fuels): “Interaction between metal fission products and TRISO coating materials: A study of chemical bonding and interdiffusion,” C. Heske, Chemistry Department. Summer 2004 start date.
  Task 26 (Separations): “Fundamental Chemistry of U and Pu in the TBP-Dodecane-Nitric Acid System,” K. Czerwinski, Chemistry Department. Fall 2004 start date.


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**
- **Academic Programs.** 4 students enrolled in the inaugural class (Fall term 2004) of the Ph.D. program in Radiochemistry.
- **Facilities Progress Update.** Remodeling of MSM 173 for the actinide chemistry laboratory is scheduled to be completed in October 2004. The electron microscopy sample preparation facility and transmission electron microscope facility are complete and the first research images were taken in July 2004.

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; the Institute for Physics and Power Engineering (IPPE) in Obninsk, Russia; and members of the International Molten Metal Advisory Committee (from Sweden, Germany, Belgium, and Italy).

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**

Remote Fuel Fabrication (Task 9) Highlights.
- Control system development and modeling of the hot cell robotic assembly work focused on the continuation of the pick and place dynamic simulation, including feedback control with Matlab, for metallic fuel manufacture.
- Development of the Vision-Based object recognition continued, including work on the Matlab image processing, recognition of cylindrical objects, and adaptive threshold for edge detection.

Interaction Between Metal Fission Products and TRISO Coating Materials (Task 17) Highlights.
• Student was taught about advanced aspects of operating the ultra-high vacuum apparatus and its spectroscopic techniques and about elemental line analysis in XPS spectra.
• Work conducted on optimization of experimental setup (ion sputter gun, Pd evaporator operation and water cooling, spectrometer parameters for low-energy electron detection).
• Sample surface cleaning experiments were performed by repeated Ar ion sputter – annealing cycles.
• The first XPS experiments were performed on Pd layers on commercial SiC-6H(0001) single crystal surfaces.
• Completed lab renovation (CHE112). Ordered chiller for cooling water.
• Preparation of laboratory for installation of equipment initiated.

Dissolution, Reactor, and Environmental Behavior of ZrO2-MgO Inert Fuel Matrix (Task 19) Highlights.
• Initial reactor fuels calculations performed by partner at Ben-Gurion University.
• Laboratory was organized and prepared for fuel synthesis.
• Tested dies and press for pellet fabrication.
• Precipitated and sintered a range of ZrO2-MgO ceramics for testing.

• This is a new task starting August 2004 that is a follow-on study of Task 9.
• Continued pick and place dynamic simulation for dispersion fuel manufacturing by hot lab robotic systems, including feedback control with Matlab.

SEPARATIONS TECHNOLOGY

Systems Engineering Model (Task 8) Highlights.
• Per request from Argonne National Laboratory (ANL), the NCACM is transferring database storage from SQL Server to the MS ACCESS. Currently multiple run data are saved into MS ACCESS.
• Multiple-run option has been added to the system engineering model. Since the system engineering model program is complicated, Version 1 of the User Manual will focus on procedures related to the new AMUSE interface that considers single and multiple simulations.

Criticality and Heat Transfer Analyses of Separations Processes (Task 11) Highlights.
Collaboration was initiated with Prof. Chen on AMUSE Light software to determine whether to move forward with possible PhD project of incorporating AMUSE Light software with Excel criticality and heat transfer programs.

An article for Nuclear Technology was completed.

**Immobilization of Fission Iodine (Task 15) Highlights.**
- Additional fuel rod simulation experiments on NOM were conducted and the effect of NOx was reexamined.
- Continued study of the reaction of peat with iodine and iodate.
- Continued work with additional model compound reactions at low pH to gain more insight into the reaction mechanism.
- Continued experiments on the pyrolysis of anion resin.

**Fluorapatite Waste Forms (Task 16) Highlights.**
- Measured DSC and TGA data for four samples and verification of DSC/TGA data of previous samples based on the fact that the instrument has been upgraded.
- Eight Fluorapatite samples synthesized and 6 of them were annealed at 1200 C.
- Powder diffraction patterns were obtained for all samples. All samples shows basic P6_3/m hexagonal structure with slight unit-cell parameter changes.
- XPS spectra were obtained for 6 of the samples.
- Obtained X-ray diffraction data (XRD) for previously prepared 8 samples.
- Prepared two final Apatite samples with Zn.
- Obtained XRD data for these two samples.
- Obtained Raman spectra and NEXAFS data for the synthesized apatite.

**Development of Integrated Process Simulation System Model for Spent Fuel Treatment Facility Design (Task 24) Highlights.**
- The kickoff meeting has been scheduled on October 13 and 14 at UNLV. Dr. George Vandergrift and Ms. Jacqueline Copple of Argonne National Laboratory (ANL) will attend the meeting.
- Graduate student has started compiling the needed parameter tables used by the TRPSEMPro package generated by the NCACM. Meanwhile, the system administrator was setting up the required database (MS SQL Server/ACCESS) for later use.
- Literature search on the ASPEN-PLUS specification and detail documentation was initialized.

**Fundamental Chemistry of U and Pu in the TBP-Dodecane-Nitric Acid System (Task 26) Highlights.**
- Submission of paper on 3rd phase formation.
- Initiation of NMR techniques for speciation.

**TRANSMUTATION SCIENCES**

**Niobium Cavity Fabrication Optimization (Task 2) Highlights.**
- Installed software to operate gun and detector.
• Placed phosphorescence paint on manipulator to detect beam.
• Both a Faraday cup and a phosphorescent paint (toy paint) have observed electron beam.
• New temperature diode received to monitor temperature through conductive gel that sample will be mounted in.
• Secondary electron emission observed off of surface of Faraday cup based on Faraday cup measurements. SEM simulation software has been modified and placed on a C platform.
• Website showcasing the experiment has been developed and is available for viewing: http://EEandPPLabs.nscee.edu

Modeling Corrosion in Oxygen-Controlled LBE Systems with Coupling of Chemical Kinetics and Hydrogen Transport (Task 5) Highlights.
• Simulations for several pipe arrangements were run using STAR-CD in the turbulent regime. All these runs used the k-ε Chen model useful for high Re numbers. Calculations for the concentration gradients at different inner surfaces of the fittings were manually calculated to indicate corrosion/precipitation locations in these typical fittings. These cases include the following geometries: sudden expansion, sudden contraction, elbow, T-joint flow with flow coming from central leg, and T-joint flow with flow coming from side leg.
• The chemical kinetics modeling continued, focusing on liquidized reactant iron involved in surface chemical reactions at LBE temperatures of more than 1400 K. The homogeneous chemical reaction between liquidized Fe and O₂ is used to be an approximate substitute for their surface chemical reaction.
• The Chemical Reaction Subroutine dealing with surface chemistry was modified slightly. These original constants and coefficients were replaced by the updated constants.

Neutron Multiplicity Measurements of Target/Blanket Materials (Task 6) Highlights.
• Irradiation/counting experiments were conducted with 3 NMDS configurations including a cubic arrangement and two different elongated arrangements (e.g. for high-energy proton-accelerator targets).
• Limitations of the system, such as flux levels and accelerator pulse frequencies, were determined during the experiments. The system was not sensitive to gamma-ray flash from the accelerator.
• Evaluated NMDS experiments conducted at the Idaho State University Idaho Accelerator Center in July. In these experiments, neutrons created in lead by electron beams from a 30-MeV electron linac were measured.
• Previously reported system lockups returned after the NMDS was reassembled at UNLV following the IAC experiments. Colleagues at the Khlopin Radium Institute are continuing to work on this problem. Because of extremely short run times at ISU, these lockups did not present a problem, and they are not expected to be a problem when the system is taken to LANSCE next year.

Development of Dose Conversion Coefficients for Radionuclides Produced in Spallation Neutron Sources (Task 7) Highlights.
• Categorized radionuclides that the consortium may want to produce in order to study their behavior.
• Began investigating the equipment needs and methods to produce the radionuclides in Category 3.
• Resubmitted two revised articles to the Health Physics Journal.

• Bhagath Yarlagadda and Venkata Potluri successfully defended their M.S. thesis July 2004.

• Students extracted some useful information for oxygen sensor from the raw data obtained from experiments conducted over the first two months of the quarter.
• Literature was surveyed.
• Design work for a new testing apparatus with better mixing was initiated.
• Analysis of data from LANL test loop initiated.

Use of Positron Annihilation Spectroscopy for Stress-Strain Measurements (Task 14) Highlights.
• PAS tests using welded specimens of Alloy HT-9 are also ongoing at ISU.
• Residual stress measurements on welded specimens consisting of similar (EP-823/EP-823 and 304L SS/304L SS) and dissimilar (EP-823/304L SS) materials by positron annihilation spectroscopy (PAS) were performed at ISU.
• Tensile specimens of Type 304L SS were subjected to plastic deformation by applying loads beyond yielding. Data analyses are in progress to determine the line shape parameters (S and T) based on the 511 keV spectrum.
• Data analysis of tensile specimens of 304L SS experiments are underway.
• TEM analyses on tested specimens have been initiated.

Corrosion Mechanisms and Kinetics of Steels in Lead-Bismuth Eutectic (Task 18) Highlights.
• FeSi studies completed in collaboration with Dr. Loewen of INEEL.
• FeSi and FeCrSi studies continued with LANL. Met with Stuart Malloy of LANL.
• Materials for gas phase experiments obtained.
• Reported results to LANL collaborators from DELTA loop samples previously analyzed (30+ samples).
• Started preparation of new DELTA loop samples for SEM investigation
• Ion beam system under vacuum in preparation for isotope labeling studies. Materials for isotope labeling studies obtained, contacts with EMSL initiated for this work.
• Initiated IR studies of corrosion products.
• Delays in receiving estimates from Planning and Construction are delaying progress on the development of the small experiments laboratory.

Oxide Film Growth Modeling in LBE Systems (Task 21) Highlights.
  • Dr. Zhang from LANL visited UNLV twice in September. He provided several references on the oxidation of steels.
  • Analysis of experimental results on several U.S. steels (D-9, HT-9, 316, 316L and T410) initiated.

Corrosion Barrier Development for LBE Corrosion Resistance (Task 23) Highlights.
  • Established research group, hired one graduate student and two part-time undergraduate students.
  • Apparatus design performed.

1.3.3 Student Research Technical Summary

FUELS TECHNOLOGY

Remote Fuel Fabrication (Task 9).
  Dynamics of Hot cell Operations

Robot Control and Kinematics
In order to perform the required tasks by the robot in a hot cell, the kinematics and dynamics of the manipulator should be carefully studied. The kinematical study insures that the manipulator’s end effector will be in the right position with the right orientation to pick, place or insert a fuel pellet.

A closed form of the inverse kinematics of the Wäelischmiller was determined. Despite the fact that eight solutions exist for a particular position and orientation, one solution is picked and that’s the solution closest to the current configuration of the manipulator.

A thorough study and modeling of the manipulator allows achieving the best control on the manipulator’s motion. The Wäelischmiller has six rotary joints, each driven by a motor. The command trajectories can either be given in the joint space or in the Cartesian space. The joint space is usually easier to control, but the manipulator’s motion can’t be guaranteed.

In the case of brittle fuels (powder pressed fuel prior to sintering), the motion characteristics (velocity and acceleration) of the end effector is of interest. The fuel pellet handled will tend to depart from the end effector grippers in the case of high or sluggish accelerations. Insuring the smoothness of the end effectors motion profile guarantees that such departure does not happen.

Metallic Fuel Hot Cell Layout
Figure 1 shows a schematic of a hot cell that would manufacture metallic fuel pellets. The hot cell includes two manipulators that would move the fuel pins around in the hot cell. The hot cell supervision will be accomplished by using CCD cameras.
Due to software limitations, the casting process, the addition of the bond phase (Na), and the welding process could not be modeled in the MSC.visualNastran© environment. The simulation postulates that the metallic pins have already been cast.

Figure 1. Schematic of Metallic Fuel Cell as modeled in MSC.visualNastran©.

A Wäelischmiller (GmbH) robot was used for loading-unloading of the cast fuel slugs. The Wäelischmiller (GmbH) robot will insert the fuel pins in the cladding tube as well. Figure 2 shows a snapshot of the hot cell developed in the MSC.visualNastran© environment.

Cast Slug Storage
The cast fuel pins are scattered on a storage table, and the Wäelischmiller (GmbH) robot will move then individually to the grinder. After being grinded, the pellets will be inspected by the camera through the shielded glass. Finally, the pins will be placed on a V-Tray, to be inserted in the cladding tube.

Feature-Based Pattern Recognition and Object Identification for Telerobotics

A method to efficiently recognize 3D objects from 2D images based on feature-based indexing was developed. Object recognition is the identification of correspondences between parts of a current scene and stored views of known objects, using chains of segments or indexing vectors. To create indexed object models, characteristic model image features are extracted during preprocessing. To overcome 3D viewing effect, feature vectors representing model object contours are acquired from several points of view around each object and stored. Recognition is the process of matching stored views with features or patterns detected in a test scene. At recognition time, those indexing vectors with the highest match probability are retrieved from the model image database, using a search strategy that employs knowledge-base search criteria. The knowledge-based system simplifies the recognition process and minimizes the number of iterations and memory usage. In case of 3D viewing effect, probabilistic viewing interpolation is employed. The experimental results indicate that feature-based indexing in combination with a knowledge-based system will be a useful methodology for automatic target recognition.
Interaction Between Metal Fission Products and TRISO Coating Materials (Task 17).

The goal of this project, which started in May 2004, 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. Using the TRISO coating materials and single crystal references as substrates, interfaces are prepared under controlled conditions in an ultra-high vacuum environment and studied with a variety of different spectroscopic methods. The combination of surface sensitive techniques (e.g., photoelectron spectroscopy) with bulk sensitive methods (e.g., X-ray emission spectroscopy) probes the chemical properties as well as the diffusion behavior in several complementary ways. A variety of surface modification methods is and will be applied ex-situ (e.g., for stressed coating layers) or in-situ (e.g., by ion bombardment or plasma surface treatment) prior to or after the interface formation to study the dependence of the interface properties on the surface/interface morphology and quality of the coating material.

The project utilizes a four-chamber ultra-high vacuum surface science instrument (shown in Figure 3), which combines several experimental techniques, including X-ray and UV photoelectron spectroscopy (XPS and UPS), X-ray and small-spot-electron-excited Auger spectroscopy (XAES and AES), low-energy electron diffraction (LEED), and in-situ ellipsometry. It allows the modification of surfaces by ion bombardment, plasma etching, annealing, and metal evaporation under strictly controlled conditions. The instrument is currently in transit from the University of Würzburg, Germany, to UNLV. First experiments on the Pd/SiC interface could be conducted in Würzburg during the summer of 2004 before dismantling the system for shipment (see results below).
A second line of experiments is being conducted at the Advanced Light Source, Lawrence Berkeley National Laboratory (Beamline 8.0, SXF endstation). The first experimental campaign, in which the Pd/SiC interface will be studied by soft X-ray emission spectroscopy, is scheduled for the end of November.

First Results
After getting all researchers acquainted with the operation of the ultra-high vacuum equipment, several experimental runs were conducted to optimize the surface cleaning procedures for commercial SiC(0001) single crystal substrates. Figure 4, bottom, shows an XPS survey spectrum taken after a series of ion-sputter/annealing cycles to remove surface contaminants from the surface polishing process and the air exposure (in particular Ca, O, and water). As can be seen, only a small residual signal of oxygen is present, while all other prominent peaks are associated with the SiC bulk material. This surface was used to collect first data on the room temperature Pd/SiC interface formation by depositing a thin (less than 1 nm) layer of Pd (top spectrum in Figure 4). This leads to the observation of Pd-related lines and an attenuation of the SiC peaks. In order to gain insight into the chemical interaction at the Pd/SiC interface, a detailed analysis of the individual XPS peaks is currently being conducted. As an example, Figure 5 shows a close-up of the Carbon 1s peak. Again, the bottom spectrum pertains to the clean SiC surface, while the upper spectrum was derived from the carbon atoms at and near the Pd/SiC interface. Even without a detailed peak-fitting analysis, which is currently in progress, it is evident that at least two additional chemical carbon species exist after Pd deposition. In an initial-state picture, the fact that the new species appear at higher binding energies indicates a charge transfer away from the carbon atoms. This effect is currently being further analyzed (e.g., by investigating the Si 2p spectra) and will be further studied after the reassembly of the instrument at UNLV is completed.

Figure 4. X-ray photoelectron survey spectrum of a SiC(0001) single crystal before (bottom, black) and after (top, red) Pd deposition.
Dissolution, Reactor, and Environmental Behavior of ZrO$_2$-MgO Inert Fuel Matrix (Task 19).

This project examines inert 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 will be 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 will be synthesized and characterized based on the reactor physics results. The solubility of the fuel ceramics, in reactor conditions, reprocessing conditions, and repository conditions, will be investigated in a manner to provide thermodynamic data necessary for modeling.

In this quarter work was performed on synthesis of ceramics and reactor physics calculation.

Ceramic Pellet Synthesis
The inert fuel matrix project is underway with progress in ceramic synthesis and pellet assembly. Zirconium oxide and magnesium oxide ceramics in varying ratios are synthesized from aqueous Zr$^{4+}$ and Mg$^{2+}$ ions prepared from zirconium chloride (ZrCl$_4$) and magnesium chloride hexahydrate (MgCl$_2$•6H$_2$O), respectively. From this solution, hydroxides of these two metals are precipitated using ammonium hydroxide. The precipitate is filtered, ground to a powder, and calcined at 700 °C for one hour to drive off the water of hydration. The product is zirconium oxide (ZrO$_2$) and magnesium oxide (MgO). Starting with ions in solution, precipitating out together will yield a higher probability of the final product being a zirconium oxide and magnesium oxide solid solution.

A pellet die was developed from a similar design used at Argonne National Laboratory – West. Powdered ceramics are pressed into pellets at pressures around 100 MPa using a laboratory
The formed pellets are sintered at 1500 °C for 4 hours under an argon atmosphere. Finished pellets are 1 cm by 1 cm diameter cylinders resembling nuclear fuel pellets. Near term efforts will focus on characterization of existing pellets, synthesis of pellets with differing Zr:Mg ratios, and initial synthesis of uranium containing pellets.

Figure 6. MgO-ZrO₂ pellets synthesized from precipitation of metal salts

**Reactor Physics Calculations**

A number of benchmark calculations for a standard PWR unit cell and 17x17 fuel assembly were performed with the code BOXER. BOXER is a modular code for two-dimensional neutron transport calculation of LWR fuel lattices. The main modules of the code are:

**Cell calculation module:**
In every configuration to be treated, the most important cell from the point of view of the neutron spectrum is chosen as the "principal cell type". It is calculated with white boundary conditions. Its outgoing partial currents can be used as boundary conditions for other cell types and for the homogeneous materials. The cell calculation begins with the resonance calculation in two material zones and about 8000 lethargy points depending on the composition of the material, employing collision probability method. The resulting ultra fine spectrum is used as weighting function to condense the pointwise cross sections into groups. Afterwards, a one-dimensional flux calculation is done with a transport theory in cylindrical or slab geometry and in 70 energy groups, in all zones of the cell. Then the cross sections of the cell are condensed spatially as well as energetically. The cross section library is primarily based on JEF-1 evaluated data file.

**Two-dimensional modules:**
The configuration is represented by a X-Y mesh grid. Fuel and water cells are represented explicitly. The flux distribution can be calculated by either diffusion or a transport module. The results are the multiplication factor - keff, neutron flux, power distribution, and reaction rates.

**Burnup module:**
The evolution of isotopic densities for each material is calculated using reaction rates collapsed to one group by weighting with the multigroup fluxes from the cell- and the two-dimensional calculations. The time dependence of the nuclide densities is described by Taylor series. The
nuclide densities with high destruction rates are assumed to be asymptotic. An iterative correction adjusts the fluxes within the time step in order to keep the power constant. The effect of the changing spectrum on the reaction rates is taken into account by a predictor-corrector method and by density dependent one-group cross sections within the time step for $^{239}\text{Pu}$ and $^{240}\text{Pu}$ (approximated by a rational function). In the predictor-corrector method, the depletion is performed twice – using the spectrum at the beginning and at the end of the timestep. Average isotope number densities between these two calculations are then used as initial values for the subsequent burnup step. A time step can be divided into several micro-steps without recalculating the reaction rates in order to improve the numerical accuracy of the depletion calculation.

The results of the BOXER computer code, suggested for use in the analysis of fertile free matrix fuels, were compared with MCNP results for different Pu loadings and cross section libraries. The criticality prediction difference between BOXER and MCNP ranges between 0.13 and 0.37% depending on the cross section library and Pu loading. The absorption rates in Zr, $^{240}\text{Pu}$ and $^{242}\text{Pu}$ isotopes were identified as major contributors to the discrepancy in criticality prediction. Relatively large Zr contribution to the total k-infinity prediction difference is due to the large Zr concentration in the fuel matrix as compared to a typical UO$_2$ fuel where Zr presents only in the cladding. The relative error introduced by the Zr cross section data uncertainty decreases with an increase of Pu v/o and related hardening of the neutron spectrum (Error! Reference source not found.). This is expected to introduce additional uncertainty in evaluation of Moderator Temperature and Void reactivity feedback coefficients. Validation of BOXER computer code with respect to the accuracy of reactivity coefficients evaluation necessary for performing Task 3 of this program will be performed in the next stage. Analysis of the energy dependent differences for major isotopes presented in this report will provide a starting point for these studies.

The fuel assembly benchmark case tested the capabilities of 2D transport module of the BOXER code. We observed reasonable agreement in criticality prediction of the standard 17x17 PWR fuel assembly between BOXER and MCNP - on the order of 0.2% $\Delta\rho$. The fuel assembly local pin power distribution predicted by the two codes is within 2% discrepancy.

In conclusion, the performed benchmark calculations confirmed that the BOXER code is suitable for the scoping studies of plutonium in fertile free matrix fuel designs. The BOXER code predicts criticality, reaction rates and power distribution in fuel assembly with accuracy sufficient for the purposes of this study.
Figure 7. Absorption rates in Zr in 70 energy groups.

SEPARATIONS TECHNOLOGY

Systems Engineering Model (Task 8).

The whole chemical separation process is complex to the point that definitely requires certain level of systematic coordination. To perform smoothly and meet the target extraction rates among those processes, this research proposed a general-purpose systems engineering model. Since constructing a system model is generally complex, requiring intensive communication and in-depth understanding, a carefully designed model can be more flexible and useful in the long term. This research project considered the design concepts from requirements definition and conceptual design to system partitioning, and finally system validation. Lengthy pre-coding of the design process and recursive modification provides a system with high degree of flexibility and robustness.

A general purposed systems engineering model, Transmutation Research Program System Engineering Model Project (TRPSEMPro), was developed based on the above design concept. The system model includes four main parts: System Manager, Model Integration, Study Plan, and Solution Viewer. System Manager supervises all the case (problem) creation, and functionality definition. Model Integration identifies chemical extraction processes and their execution sequence. Study Plan is the key to define modeling scenarios, such as Optimization, Design of Experiments, single-set parameter and multiple parameter-set. No system can be completed without a visualization tool. Solution Viewer provides a visual means to monitor the optimization process during and after model execution. TRPSEMPro can apply not only to chemical separation process, but also a general system model. TRPSEMPro allows industries to
model their process quantitatively and to study the interactions between subsystems and performance of the model under the influence of various design parameters.

Software engineering and Object Oriented Analysis and Design (OOA&D) play a critical role during our software development. Through the application of OOA&D, the user can define objects and concepts from our problem domain that is quantitatively described by Unified Modeling Language (UML). The logical software objects were created from the previous definition. Meanwhile, different design patterns were also applied during the detailed design phase. Finally, those designed components were implemented by using MicrosoftTM.Net, the most up-to-date object-oriented programming language framework from Microsoft.

Currently, only the UREX process module is available and ready to be implemented. Since extraction modules can be developed from various agencies with different development concepts and programming conventions, an intermediate bridge or interpreter is generally required. The system connects the only available process, UREX and with the TRPSEMPro system model from the AMUSESimulator interface. The AMUSESimulator communicates with the calculation engine AMUSE macros designed for the UREX process. A user-friendly GUI in AMUSESimulator allows the user to efficiently define the UREX process: flowsheet, input streams, sections, and stages.

The combination of several up-to-date techniques makes this research unique and robust. Those include Microsoft.NET framework, MS SQL Server database, MS ACCESS, extensible Markup Language (XML), Design of Experiment and System Optimization. The design and implementation of database provide an effective way to manipulate and store all the input and output data generated during the system design run. To analyze the system in an optimum way, several optimization technologies have been studied and correspondent algorithms have been developed and implemented into the system model. A universal XML file format is applied for data storage and transport among modules. While waiting more chemical processes to be developed, more improvement will be made to enhance the TRPSEMPro package for solving complex chemical separation process.

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

During first year of the project, iodine sorption by a sphagnum peat and Ca(OH)$_2$ mixture were demonstrated. The ratio of Ca(OH)$_2$ to sphagnum on the retention of iodine in both the iodine generator experiments and the fuel rod simulator experiments were explored. Both of these experiments were described in earlier reports.

Figure 8 illustrates the effect of Ca(OH)$_2$: sphagnum ratio on iodine sorption by natural organic matter. These experiments are conducted with our iodine generator device at iodine concentrations of about $\sim 10^{-5}$ mol/L in the presence of nitric acid fumes. In all of these experiments, the traps were packed with about 0.5 g of the sphagnum and Ca(OH)$_2$ mixture. The results indicate that the 30% Ca(OH)$_2$ mixture was most effective for sequestering iodine under these conditions.
Figure 8. The breakthrough of iodine using the iodine generator apparatus described in earlier reports. The trap consisted of 0.5 g of Ca(OH)$_2$: sphagnum mixtures. Three ratios were tested: 10, 30, 60%. The flow rates were 20.0 mL/min and the concentration of iodine was $\sim 10^{-5}$ mol/L. The carrier was 50% saturated with nitric acid vapor.

A device for simulating the dissolution of fuel rods was constructed. Both FCC and the sphagnum were retested using this device. In these experiments a known quantity of iodine (3 – 6 mg) is placed into the system and nitric acid is added. The system is sparged with nitrogen through trap materials and through bisulfite filled impingers. Results for various Ca(OH)$_2$/sphagnum ratios are shown in Figure 9 and again indicate that the 30% mixture resulted in the smallest breakthrough. These experiments were conducted with very small quantities of sorbent (0.02 g) so that breakthrough could be observed in a reasonable amount of time. With larger amounts of material (~0.5 g) breakthrough was not observed under these conditions. Additional fuel rod simulation experiments were conducted on FCC and NOM to examine the effect of NOx. Results are presently being evaluated.
Additional data was obtained on the reaction of peat with iodine and iodate in aqueous suspension. Results indicate that peat reacts with both iodate and iodine and for both species, reduction to iodide and incorporation into the organic matter occurs. Experiments over a range of pH values were conducted.

Experiments with iodine were conducted in aqueous buffered solution. All of the experiments were conducted with 350 mg of sphagnum suspended in 20 mL of solution with an initial iodine concentration of ~10^{-4}M. The reaction was modeled with a simple kinetic scheme. Additional model reactions of compound at low pH were conducted to gain more insight into the reaction mechanism.

The kinetics of the reaction of iodine with peat is presented in Figure 10. These data were obtained by a combination of ion chromatography and the N,N-dimethylaniline method described in earlier reports. The reaction of peat with iodine obeys pseudo first order kinetics in the iodine concentration. The overall rate of reaction with the peat is increases with pH. The loss of iodine and the appearance of iodide can be modeled using the simple reaction scheme (P represents the reactive sphagnum and Pox has been oxidized by iodine). This scheme assumes two parallel reactions. The first is a reduction of iodine to iodide, while the second reaction is a substitution reaction (incorporation).

\[ \text{I}_2 + \text{P} \rightarrow 2\text{I}^- + \text{Pox} \]
\[ \text{I}_2 + \text{P} \rightarrow \text{I}^- + \text{PI} \]

This reaction scheme can be modeled as two parallel first order equations (1 and 2).

\[ \frac{dI^-}{dt} = -(k_{\text{red}} + k_{\text{sub}}) \cdot [\text{I}_2] \]  \hspace{1cm} (1)
\[ \frac{d\text{I}^-}{dt} = 2 \cdot k_{\text{red}} \cdot [\text{I}_2] + k_{\text{sub}} \cdot [\text{I}_2] \]  \hspace{1cm} (2)

The rate constant \( k_{\text{red}} \) and \( k_{\text{sub}} \) are pseudo first order rate constants for the reduction of iodine and incorporation into the organic matrix (ring substitution?). The contribution of the two reactions can be calculated from the best-fit rate constants. These constants can be obtained by a numerical fit of 1 and 2 to time series data. Results indicate that in the pH range of 6-8, these experiments indicate that 60-75% of the iodine reacted by incorporation (electrophillic substitution) into the organic matter.

During the first year of this study it became apparent that iodine could be oxidized to iodate in the presence of nitric oxide and nitrogen dioxide. 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 and result in the formation of bound iodine (organo iodine) and/or iodide. The kinetics of this process is illustrated in Figure 11. This experiment was conducted at 60°C. The reaction of iodate follows pseudo first-order kinetics. Iodide is formed by reduction of iodate in addition to organically bound iodine. The organically bound iodine appears to go through a maximum with reaction time indicating that it is eventually released into the solution as iodide. The reaction rate of peat with iodate decreases with increasing pH. The reaction rate of iodate is about one order of magnitude slower than that of iodine. Some data that indicates that iodate is first converted to
hypoiodic acid was also obtained, 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. Work is being done on a model for this process.

For both iodine and iodate experiments, the incorporation of iodine into the peat using the pyrolysis technique was verified. Pyrolysis of sphagnum peat (at 500°C) from either type of experiment results in the release of methyl iodide.

The formation of iodide from iodine during fuel rod dissolution would result in reduced fugitive iodine during fuel dissolution. However this iodide is also water soluble and highly mobile in the environment. The potential use of ion exchange resins for temporarily sequestering this iodide is being explored, as are exploring several different types of resin for iodide sequestration. As noted in previous reports, after pyrolysis at 500°C, iodide can be recovered from both ion exchange resins and sphagnum peat as methyl iodide. During the next year, this phenomenon will be explored as well as developing a technique for converting methyl iodide to NaI. The equipment necessary to begin the next phase of experiments has been ordered.
Figure 9. The breakthrough of iodine on 0.02 g of Ca(OH)$_2$:sphagnum mixtures using the fuel rod simulator experiment described in earlier reports. The flow rates were 20.0 ml/min.
Figure 10. Pseudo first order kinetics for the batch reaction of iodine with suspensions of sphagnum peat. The reactions were carried out in buffered solutions with initial iodine concentrations of \(~10^{-4}\) M (20 mL volume) and 350 mg of sphagnum.
Iodate-Peat pH 4.5

Figure 11. Reaction of iodate with a suspension of sphagnum peat. The reactions were carried out in buffered solutions with initial iodine concentrations of ~3*10^{-3} M (20 mL volume) and 350 mg of sphagnum.

TRANSMUTATION SCIENCES

Niobium Cavity Fabrication Optimization (Task 2).

Designing the experimental setup of secondary electron emission was well underway in early summer of 2003 when funding was made available for this portion the study. By March 2004, many of the components of the experimental study reached UNLV with some assembly accomplished. The first secondary electron emission (SEE) measurement was made from the surface of a Faraday cup in September 2004. At a particular beam energy, the current measured with the Faraday cup and electrometer changed sign over a range of energies. 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) is being translated into C++ by a third student and Dr. Kant (volunteer) not associated with this research project but both part of the Electromagnetics and Pulsed Power Laboratories. The code now accepts up to ten layers of varied thickness of material composition in determining the SEE energy and trajectory. The code is fast and agrees with earlier versions.

Thoughtful code inputs are required. With the use of an RGA and time, we will estimate the formation of gas layers on the sample (partial pressures). After appreciable pumping at around 1e-9 Torr, RGA measurements will be monitored as the sample is brought down to cryogenic temperatures from room temperature. Keeping in mind that cold surfaces act as pumps, the change in the background environment will be noted. Since only the sample and cold heads of the cryostat will be cold, changes in partial pressures will be attributed to these surfaces. This will allow for one to estimate the layers of material deposited on the sample surface and in what order. The sequential layer composition and thickness may be determined and implemented into the SEE code for evaluation.

Experimental Set-up for the SEE from a Niobium Test Piece:

The completion of the experimental setup for the secondary electron emission (SEE) studies from niobium is nearing completion. Refer to Figures 12 and 13. The following tasks have been completed:
- The experimental setup with electronics has been assembled.
- The electron gun is functional and appears to work as advertised.
- The detector is assembled and connected to computer. The last check in the sequence of checks for the detector failed. A special source regulation circuit is being designed to correct for the inability of the voltage supplies to reach the required potentials across the MCP stack.
- About 2x10^{-9} Torr pressures has been demonstrated with the current system without baking.
- The Faraday cup and tungsten lamp work.
- The cryostat (insides of a cryopump used) is operational. Measured temperatures between 8.5 to 9.5 °K have been achieved.
- A good thermally conductive grease has been identified and purchased to attach the niobium sample to the cold head. The InGa material used acted as a thermal insulator at cold temperatures. Although In is a good thermal conductor, it appears that separation between the two metals resulted in the Ga to act as a good insulator as far as the test sample is concerned.
- Secondary electron emission has been observed from the Faraday cup detector. A Keithley electrometer was employed to measure the low currents.
- A website has been developed to display some of our efforts regarding this research. Please refer to http://EMandPPLabs.nscee.edu
- LANL and Cornell cleaned niobium samples have been received and are currently stored in a Ni environment in its original packaging awaiting for test.
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. An electrostatic code and a particle tracking code are being used to map all possible
Modeling Corrosion in Oxygen-Controlled LBE Systems with Coupling of Chemical Kinetics and Hydrogen Transport (Task 5).

Several CFD runs have been made to simulate flow in pipe fittings. These include sudden contraction, sudden expansion and a T-joint. Testing of a new turbulent model is also being made namely the k-e Chen model which will work a little better with high Re number flows and will be able to predict some of the peculiar flow features relevant to sudden expansions where eventually vortex generation is expected at the backward step (i.e. sudden expansion location) in that flow. It is important to try to predict that because it may have a bearing on the behavior of the chemical kinetics model when it is completed.

Development continued of a user subroutine that will simulate the corrosion/precipitation processes and predict their maximum/minimum location in a typical LBE loop.

Sudden Expansion

The results of the sudden expansion model is shown in Figure 14. The diffusion of the temperature into the fluid was clearly visualized. The diffusivity of iron into LBE is as low as $10^{-8} \text{m}^2/\text{s}$, which makes the diffusion very slow. Figure 15 shows the graph of concentration gradient v/s distance from the inlet. These gradients represent corrosion/precipitation on these locations. The decrease in the concentration gradient is due to the flow reversal, which takes place after the sudden expansion followed by an increase and then a decrease at further distances downstream. This is due to the formation of new boundary layers after the sudden expansion region. It is observed that the change in concentration is proportional to the change in temperature.

Figure 14. Concentration profile for sudden expansion at Re = 200,000
Figure 15. Concentration Gradient at the Wall v/s Distance from Inlet

**T-joint Model**

Results obtained from the inlet from straight arm are shown in Figure 16. The wall concentration is a function of wall temperature. The diffusion is more prominent in the flow reversal region in the branch of the T-joint. Figure 17 shows the graph of concentration gradient along the straight wall. Point A in the graph is the area where the branching starts. In this region there is an increase in the concentration gradient because of the regeneration of the boundary layers after the branching. At the elbow of the T-joint, there is a decrease in the concentration gradient because of the flow reversal.

Figure 16. Concentration profile for T-joint at Re = 200,000
Figure 17. Concentration gradient v/s distance from the inlet for the straight wall

Results were also obtained for the inlet from the branched arm. The flow pattern indicates that there is a stagnation region as expected. The velocity vectors right outside that region show a larger magnitude and connect to the outer wall of the tee intersection on both sides. Two reversal flow zones are noticed on the inner wall of the T-joint right downstream of the right-angled intersection of the two T-sections.

Sudden Contraction

The model created for the sudden expansion was used, but the inlet and outlet are changed accordingly. The concentration gradient decreases as the fluid enters the fitting and as the fluid encounters the sudden contraction region the concentration gradient increases as new boundary layers are being formed and then it evens out.

Study of Surface Chemical Reactions

The original straight pipe 3-D model was modified. Specifically, the CFD domain, material, fluid zones, each species’ inlet concentration, etc, were kept the same while the boundary conditions of 2 sides of the baffle cells are changed to constant heat flux boundary conditions. In addition, the temperature of interface between outer fluid zone and wall was changed to 1400 k. This liquidized the iron adjacent to the inner surface. This way, the homogeneous chemical reaction between liquidized Fe and O2 took place and was used to be an approximate substitute for surface chemical reaction.

The chemical reaction subroutine dealing with surface chemistry was updated. The Arrhenius Equation was still used to calculate the reactant reaction rate but some constants and coefficients
used in calculating chemical reaction rate were updated using some empirical data found in chemical reaction research papers and textbooks. The species’ molecular weights, the initial species’ concentration, iterations, etc., did not change.

Several runs with and without the subroutine connected were made. The area with the highest concentration occurs in the baffle cell which is adjacent to the iron surface while the area with lowest concentration occurs around the central line of the pipe. It can be inferred that after Fe₃O₄ is formed, it diffuses to the fluid area close to the central line of pipe. But, overall, the concentration value is very low.

Similar to the concentration gradient, the area with the highest temperature occurs in the baffle cell which is adjacent to iron surface while the area with lowest temperature occurs around the central line of the pipe. It is obvious, based on the model, that heat was transferred from inner wall to central area of the pipe due to the setting of constant heat flux boundary conditions of baffle cells.

The chemical reaction model subroutine worked well and this simple CFD model roughly simulated the chemical reaction, diffusion, and heat transfer condition inside the LBE piping. Since the subroutine works well, it can be used in much more complex model.

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

The NMDS was used in conjunction with an accelerator at the IAC to determine it’s performance. 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. After the experiments were completed, the system was returned to UNLV and reassembled there.

**ISU-IAC Experiments**

In preparation for experiments at the Idaho State University (ISU) Idaho Accelerator Center (IAC), several different configurations were designed to determine how the detectors would perform: three cubic configurations—BCube (see Figure 18), BCube2 and BCube3—and two rectangular accelerator target configurations—AT-1 and AT-2. All five configurations were modeled in MCNPX prior to the experiments. The AT-1 and AT-2 configurations were created in anticipation of conducting neutron multiplicity experiments on the 800 MeV proton linear accelerator (linac) at the Los Alamos Neutron Science Center.
The system was transported to the IAC, where a linear accelerator (linac) was used to place an electron beam on the front face of the Pb. Initial background readings at the IAC showed that, overall, the system was still performing properly after being transported. The average background reading was less than 1 count/s inside the IAC, which is shielded from cosmic radiation by several feet of earth.

**NMDS Performance**

An AmBe source with a neutron production rate of $2500 \pm 10\%$ n/s was placed against the face of the Pb in all 5 configurations to measure the overall efficiency of the system. The system measured an average of 88 counts/s from all configurations, giving us an average efficiency of $3.5\%$.

Testing commenced with the electron beam using the BCube configuration. During this time, the beam was adjusted so that it worked within the boundaries of the detectors. The system was tested with frequencies of 15, 30, and 120 Hz. At 120 Hz, the dead time of the detectors caused the system to acquire data for only 20-25% of the pulses. After the initial test runs, the frequencies were restricted to 15 Hz and 30 Hz for data acquisition, which allowed data to be acquired for 82-99% of the pulses received from the accelerator. All beam results presented herein are from a 15 MeV beam at a frequency of ~200 µA, and a pulse width of ~2 ns.

Several parameters and results are examined and compared to radiation transport predictions in these studies. These parameters include the neutron absorption time or lifetime, efficiencies of the systems and individual detectors, and multiplicity distributions. All results from the ISU-IAC accelerator-driven experiments were influenced by a count-rate limitation that is inherent in the NMDS hardware and software.
Efficiency: Calculations using MCNPX produced far greater efficiencies than were generated in the experiments. Efficiencies for BCube, BCube2, and BCube3 in MCNPX were 17%, 19% and 27%, respectively, while experimental efficiencies were 2.9%, 1.3% and 3.2%. These values are similar to the low efficiency measured with the AmBe source, and about an order of magnitude less than that measured with a $^{252}$Cf source at UNLV.

Neutron Lifetime: In the BCube configuration, the average lifetime for absorbed neutrons was 71 µs. MCNPX modeling for this configuration produced average lifetimes of 44 µs. Lifetimes were lower in BCube2 (see Figure 19) because the electron beam contacted the Pb in the center of the configuration. This caused the neutrons to reach the detectors more quickly, with an average lifetime of 59 µs experimentally and 43 µs in MCNPX. In BCube3, there were a total of 23 detectors that were moved 5 cm closer to the Pb and were no longer blocked by a layer of polyethylene. As expected, the lifetimes further decreased to around 55 µs experimentally and 39 µs in MCNPX.

![Figure 19. BCube2 Lifetime. A numerical fit of neutron capture times for BCube2. Calculated lifetimes from experimental data and from MCNPX are also shown.](image)

<table>
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<td>59</td>
</tr>
<tr>
<td>BCube2</td>
<td>0.0163</td>
<td>43</td>
</tr>
</tbody>
</table>

Neutron Multiplicity Distribution: Neutron multiplicity distributions were corrupted because of the 256-µs data acquisition window of the NMDS. It was determined that “events” with few counts were recorded that should have been part of the immediately previous event. This produced a skewed multiplicity distribution. Data manipulation is under investigation to combine multiple events into one, which may also impact the calculated neutron lifetimes.
**Individual Detector Performance:** A comparison of the measured versus predicted count rates in the AT-1 configuration is illustrative of detector performance. Figure 20 shows the measured and predicted fraction of total neutrons absorbed by each detector. The fraction of total neutrons absorbed in the left-side detectors (43-54) was very close to that of the right-side detectors (13-24). The same was true for a comparison between the top (1-12) and bottom (31-42) detectors. In the experiment the bottom and top detectors performed nearly the same, with the bottom counts being slightly lower because at the bottom neutrons are reflected from the steel frame. MCNPX calculations, however, had more extreme variations. While the left and right sides were very similar in the experiments, in MCNPX the top and bottom absorptions were not. In MCNPX calculations, the top row of detectors absorbed a much greater fraction of neutrons than the bottom row. For example, detector 3 on the top row absorbed 7.7% of the total neutrons, but detector 33, which occupies the same position on the bottom row, only absorbed 4.9%.

![Figure 20. AT-1, Fraction of Total Counts by Detector Number, MCNPX vs. Experiment. Side detectors are 13-24 and 31-42, top detectors are 1-12, bottom detectors are 31-42.](image)

It was also noted that the ratio between absorptions in the inside detectors and their corresponding outside detectors was much larger in MCNPX than in the experiments. For example, in MCNP, detectors 31 and 32 measured 4.6% and 2.0%, respectively, a ratio of 2.3. Experimentally, they measured 5.0% and 4.2%, a ratio of only 1.2. This was true for all of the detectors at the front of the system (nearest the beam impact point). Due to the length of the Pb in this configuration, counts at the back of the system are so low and the statistics so poor that comparisons are only qualitative.

**Conclusions and Future Plans**

The experiments conducted at the ISU IAC provided a much better understanding of the capabilities and limitations of the NMDS. The system is severely limited by source rate. At
moderate frequencies, the percentage of events recorded begins to decrease significantly. During the analysis of the data from ISU, it was also noted that the 256 µs data acquisition window is not sufficient to record all of the neutrons in the system. Attempts will be made to alter the software to provide a longer timeframe for recording counts.

The NMDS is also limited by dead time. In the future, attempts will be made to develop the capability to calculate an accurate value for the average dead time in the system. Once the effect it has on the results is determined, then progress can be made on reducing it. It is believed that the 15 MeV electron beam was too strong relative to the current dead time. If the dead time can be decreased, better results may be seen with the same beam. Future plans include using the NMDS to measure neutron multiplicity with an 800 MeV proton beam.

**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 exist in Federal Guide Report No. 11 and in Publications 68 and 72 of the International Commission on Radiological Protection (ICRP). Currently, more nuclear data is needed for the rare radionuclides produced from a mercury target.

The following technical work has been performed to date on the DCC project:

**Submitted the Data from this Work to National Journals**

Two papers have been submitted from this work. Both papers were submitted to the Health Physics Journal. Currently, both have been accepted with minor changes. The group is currently revising the articles as suggested. The papers discuss the developed methodology of calculating dose coefficients and present the values of these coefficients.

**Calculated Dose Coefficients for Radionuclides in Category 2**

Dose coefficients were calculated for 6 radionuclides in Category 2. All other radionuclides that were in Category 2 lacked sufficient data to perform the calculations.

**Presentation of Project at National and Local Meetings**

The scope of work of the UNLV DCC project was presented at the following national meeting:


The purpose of this task is to evaluate the tensile properties of three martensitic alloys namely, Alloys EP-823, HT-9 and 422, at temperatures relevant to the transmutation processes. Testing has been performed to evaluate the tensile properties of all three alloys at temperatures ranging from ambient to 600°C. The test materials were thermally-treated (quenched and tempered) prior to the evaluation of their tensile properties. The deformation characteristics of these tensile specimens, upon completion of testing, were evaluated by scanning electron microscopy (SEM).

An MTS machine was modified to accommodate ambient and high-temperature tensile testing of all three martensitic alloys in the presence of nitrogen. A high-temperature chamber, capable of testing tensile specimens in the temperature range of 100 to 1000°C, was added to this machine. A pair of custom-built water-cooled specimen grips, made of maraging steel (M250), was attached to the MTS machine. This water-cooled assembly was designed to prevent the grips from being heated from temperature inside the chamber by conduction. A laser extensometer, added to the MTS unit, measured the displacement of the test specimens in their gage sections due to plastic deformation at temperatures up to 400°C. An LVDT was used to measure extension of the test specimens at temperatures above 400°C. Temperature profiles were developed to determine the times needed to achieve the desired temperature as a part of the furnace calibration process.

Tests were conducted at ambient temperature, 100, 300, 400, 500 and 600°C using cylindrical specimens, machined in the longitudinal rolling direction. These specimens were fabricated from materials that were quenched in oil, and subsequently tempered for three different times prior to the machining operation. The evaluation of the tensile properties was performed according to the ASTM Designation E 8. The resultant data include the percentage elongation (%El), percentage reduction in area (%RA), yield strength (YS), ultimate tensile strength (UTS) and failure stress ($\sigma_f$) as functions of the testing temperature and tempering time. At least two specimens per material were tested under each of the three metallurgical conditions at the desired temperatures. The significant conclusions drawn from this task are given below.

- Fine-grained and fully-tempered microstructure, characteristics of quenched and tempered martensitic stainless steel, was observed by optical microscopy. No significant effect of tempering time on the metallurgical microstructure in terms of grain size was observed.
- The hardness of the test materials was significantly reduced due to tempering, showing more pronounced effect at longer tempering times.
- The magnitude of the YS, UTS and $\sigma_f$ for Alloy EP-823 was gradually reduced with increasing temperature. However, the extent of reduction of these parameters was more pronounced at temperatures beyond 400°C. A similar effect of temperature on these parameters was observed with Alloys HT-9 and 422.
- The magnitude of strain was gradually reduced to some extent with increasing temperature in the temperature regime of ambient to 300°C possibly due to dynamic strain ageing, as illustrated in Figure 21. However, the strain was significantly enhanced at temperatures beyond 400°C.
- No significant effect of tempering time was observed on YS, UTS, uniform elongation, %El and %RA irrespective of the testing temperature.
- The gradual enhancement in ductility at elevated temperatures was characterized by larger dimpled area (Figure 22), indicating increased plasticity.

UNLV researchers worked in LANL between July 1 and Sept. 15 to conduct experiments. Tests of the corrosion of different materials in LBE was performed. The influence of the process of gas introduction to the LBE was studied. Data analysis work was performed based on
accumulated data. Concurrently, progress was made on the simulation for transport in oxygen mixing.

In July, all work in LANL has to be suspended until the security risk level 3 is satisfied. This project’s experimental work will be able to start afterwards.

Data analysis for the previous experiments were carried out. The comparison of different electrode materials (Molybdenum and stainless steel) and a comparison of different quantitative values for the reference signal were investigated. Conclusions were that the corrosion for different materials is the same at lower temperatures (< 400°C).

Residual Gas Analysis (RGA) data analysis

The mass detection of the cover gas in the LBE container is obtained by RGA system. According to the ratio of partial pressure of H₂O and H₂ in the cover gas, the oxygen concentration in LBE can be obtained. Furthermore, the sensor signal can also be obtained theoretically.

The comparison of RGA data and sensor data shows good agreement. However, there are still some parameters that need to be verified and the measurement error of RGA needs to be compensated.

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) and the 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 using all four techniques. Future testing will be focused on the evaluation of residual stresses in irradiated materials, and welded specimens, with and without post-weld-thermal-treatment (PWTT). Transmission electron microscopic analyses will also be performed.

Test Results:

- Residual stress measurements by the RC method on cold-worked specimens showed tensile residual stresses in austenitic stainless steel. However, compressive residual stresses were observed in martensitic stainless steel. This difference may be attributed to
the difference in metallurgical phases and microstructures resulting from different thermal treatments imparted to them.

- Residual stress measurements by both ND and RC techniques on welded specimens showed similar patterns. Welded specimens consisting of similar material showed tensile residual stresses in the vicinity of the fusion line (FL). However, welded specimens consisting of dissimilar materials (austenitic and martensitic stainless steel on opposite side) showed a different pattern, in that residual stresses were compressive near the FL on the martensitic stainless steel side as opposed to tensile residual stresses on austenitic stainless steel side of the same specimen.

- The measurements of residual stresses by the PAS technique revealed a reduction in T-parameter with the increased plastic deformation for both austenitic and martensitic stainless steels. A reduced T-parameter indicates enhanced residual stresses in either Alloy.

**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.

(1) Materials test apparatus

Progress was made in the preparation of a laboratory at UNLV for the collocation of multiple experiments utilizing molten lead alloys. Review of the final plan for the space renovation is pending. Baseline environmental studies for lead activities at UNLV have started.

(2) Comparative gas phase studies

An Oxygen Control System from KALLA, Germany was accepted. Training of students occurred during the delivery and installation, and useful discussions were started with Drs. Mueller and Weisenburger of KALLA.

A tube furnace was set up for gas phase studies, and initial characterizations have started.

(3) Isotope labeling studies

Isotope labeling can be used to measure diffusion of materials under realistic conditions. Two methods are planned for the introduction of isotope labels into the steels systems under study.

For oxygen, chemical methods using O^{18} enriched reactants are possible. O^{18} enriched water has been purchased and steel samples will be electropolished to introduce a labeled oxide layer than then can be tracked using Secondary Ion Mass Spectroscopy (SIMS).

For iron and chromium, the ion beam/mass separator will be used. The apparatus has been brought back on line, and experiments (probably using the O^{18} water) will commence soon.
(4) Collaborative work

A major effort has been underway to aid efforts at LANL and INEEL.

Over 30 samples have been examined by SEM for LANL on a professional courtesy basis, and another 19 samples have been mounted for examination at UNLV. Those samples include some motivated by previous studies under the UNLV AFCI program.

Collaboration is ongoing with Dr. Loewen of INEEL in the investigation of the effects of silicon on the corrosion of steel by LBE. Four samples of iron have been obtained with varying amounts of silicon up to about 4% which have been exposed to oxygen controlled LBE in an isothermal test system at INEEL.

The silicon is found in three different forms in this system. These results are clearest in the X-ray Photoelectron Spectrometry (XPS) Sputter Depth Profiles (SDPs) shown in Figure 23.

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<td></td>
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<td>17 707  530</td>
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*Time of sputtering: 5,664 s ~ thickness 3.3984µm

*Oxide layer thickness (by WDS): hard to determine

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*Time of sputtering: 14,160 s ~ thickness 8.496µm

*Oxide layer thickness (by WDS): around 1.2µm

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*Time of sputtering: 11,532 s
### Sample %Fe %Si Binding Energy (eV)

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<tr>
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<td>533, 531</td>
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*Oxide layer thickness (by WDS): 1.5µm

### Sample %Fe %Si Binding Energy (eV)

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<th>Sample</th>
<th>%Fe</th>
<th>%Si</th>
<th>Binding Energy (eV)</th>
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<td>*Time of sputtering : 14,160 s</td>
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<tr>
<td>~ thickness 8.496µm</td>
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</table>

*Oxide layer thickness (by WDS): 1.5µm

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Figure 23. X-ray Photoelectron Spectrometry Sputter Depth Profiles.

In the oxide layer at the surface of the iron the silicon is in the form of a silicate – SiO₄⁻² (binding energy 102eV in XPS studies). At the bottom of the oxide layer/start of the metal layer the silicon is in the form of silica – SiO₂ (binding energy 103.5eV in XPS). In the metallic iron the silicon is in metallic form (binding energy of 99eV in XPS).
At the bottom of the oxide layer, both silica and carbide inclusions were found in the iron grain boundaries as shown in Figure 24. Iron and silica in the grain boundaries indicate significant mobility of silicon and oxygen under the test conditions. Further, both lead and lead oxide droplets were found at the bottom of the oxide layer, indicating failure of the oxide to protect the iron in localized areas.
Figure 24. WDS Maps of Fe-Si samples. All maps are 68 µm per side. Legend: Oxygen=red; Silicon=light blue; Bismuth=yellow; Iron=dark blue; Lead=green; Dark/Grey = (no signal)

Notes:
- Fe-44: Oxide layer has possibly been dissolved into LBE.
- Fe1-44 and Fe2-44: The oxide layer is at the surface of the bulk as a barrier to stop LBE intrusion into the bulk. However, the Si is not enough to make a full barrier. Hence, in this case LBE still can attack the bulk to some extent.
- Fe3-44: Si now is concentrated enough to make a nearly full barrier to protect the bulk from corrosion by LBE.
There are other interesting features of Fe2-44 and Fe3-44 WDS spectrum: Underneath of oxide layer the Si-depleted zone can clearly be seen. Especially, with Fe3-44, underneath of Si-depleted zone are Si-enriched zone and Si-depleted zone consequently.