

**Nevada Risk Assessment/Management Program – Phase 2 (NRAMP2)**

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**Quarterly Progress Report**

**July 1, 2007 through September 30, 2007**

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**Nevada Risk Assessment/Management Program (NRAMP) – Phase 2**  
**Quarterly Report (April 1, 2007 to June 30, 2007)**

**1.0 Radiological Source Characterization and Radiological Source Release Terms (PI: Ed J. Bentz, E.J. Bentz & Associates)**

**1.1 Progress – Summary**

Work conducted in this 4<sup>th</sup> quarter consisted of 3 major activities:

- Continue the receipt and reconciliation of Area 5 Radioactive Waste Management Site (RWMS) inventory data.
- Receive, review, install, calibrate, and run the Goldsim Area 5 Performance Assessment (PA) Model, and review the supporting parameters and assumptions in the 93-document reference set as a tool for regulatory compliance and closure assessment.
- Identify, review, and compare the interpretation of pertinent regulatory guidelines and orders by DOE sites in compliance for PA, Compliance Assessment (CA), and closure activities - as they may relate to the Nevada Test Site (NTS) Area 5 PA and closure activities (focus on exposure assumptions and parameters).

**1.2 Progress – Technical Work**

**1.2.1 Area 5 Source Inventory Data Acquisition and Reconciliation**

New data runs were received on 6/03/07 in Excel format for each Area 5 RWMS disposal cell. Upon examination and analysis, several inconsistencies were found:

- T07C: the volume data totals were greater than the engineered dimensions of the trench. This led to examination by the Nevada Site Office (NVO) and subsequent identification of a data mis-assignment of 139 shipments (160,403 cubic feet) from T08C into T07C.
- P04C: there were many entries that were very large (the dimensions of the individual physical package entries would exceed the dimensional constraints of the handling and transport equipment in existence at the DOE Complex Sites (the 15,593 volume entries representing individual shipments in the CURRENT database represented 1,673,805,098 cubic feet- which would exceed the entire size of the engineered dimensions of the Pit by a considerable margin). From previous communications with NVO staff, it was known that the total volume in P04C was 2, 481,825,219 cubic feet to 5/25/07. A computer mis-count at NVO is suspected. NVO examined the files sent, and discovered in the conversion from raw data to excel files at NVO, the field count had over-run for P04C, leading to the discrepancy.

A run was requested, received, and a corrected on August 7 of the CURRENT '93 data. Upon examination and analysis, multiple differences between the 6/07 data run and the new 8/07 run were found with respect to the number of shipments and to the volumes disposed (Cells P10C and T02C were identical; Cells P07U, P11U, T04C, T08C, T09C were almost identical – same number of shipments, very slight differences in volumes; all other Cells were different). A cell comparison of the differences, totaling 8371 shipments, was forwarded to NVO. Upon their

subsequent examination, they uncovered that the August 7 run used a different cut-off date of 12/31/05, instead of the working cut-off date of 5/25/07. Subsequently, NVO sent a corrected run (using the 5/25/07 cut-off) on 9/10/07. This new corrected run is in RAW text file format, and is undergoing conversion for use in ongoing analyses.

### **1.2.2 Model Receipt, Review, Run and Documentation in Support of Radiological Performance Assessment and Closure**

The model “Performance Assessment Model for the Area 5 Radioactive Waste Management Site on the Nevada Test Site, Version 4.002” and 93 model reference documents, including model user guide, abbreviated parameter set, and run log were received on August 2.

The model structure was reviewed and model set-up, installation, and calibration (initial run on Radon set parameters) were performed. The model was run in PA mode (1 of 7 computational modes) with latest assumption/input set (source term confined to RWMS cells: SLB; Pit 6 lower; Pit 13; GCD) for 10,000 year period (57 time period intervals) for 61 top radionuclides.

Overall documentation support for model, model inputs, and critical assumptions (93 references) over the main model components (inventory, source term representation, transport, exposure) were reviewed.

Specific assumptions and qualifications built into the model for the exposure sub-model (e.g. basis for numeric values used in PA IHI scenarios establishing weighted probabilities for scenario occurrence, institutional control period control erosion and consequent TEDE calculations) were reviewed. This is in preparation for comparison with regulatory driven guidelines and interpretations used by other sites.

Comparisons of exposure conditions, parameters, and assumptions among different DOE sites in meeting PA/ CA compliance requirements were initiated.

Specific inventory estimates established for comparison with above-cited raw inventory data were reviewed. Lack of historical records/incomplete records for some cells (inventories are grouped (and modeled) in the model by category - SLB, Pit 6 Lower, Pit 13, GCD - not by individual cell was noted. (The authors of the inventory model had to take pains to recreate missing records and provide estimation of omissions.)

### **1.2.3 Regulatory Basis and Guidance in Support of Radiological Performance Assessment and Closure**

The four key current regulatory documents providing guidance on PA / CA development, maintenance, and closure requirements as they relate to both the model assumptions above (DOE O 435.1; DOE M 435.1 IV P(2), P(3); DOE G 435.1 IV; DOE LLW PA & CA Format & Content Guide (B)) were reviewed.

The technical basis and development of the guidance were reviewed as it relates to PA/CA assumptions and interpretations used in the model assumptions (from AEA enabling authority

through the basic DOE Orders on overall radiological protection - DOE O 5400.4, to the waste management specific orders cited above).

The cited regulatory interpretation of the guidance by several DOE sites in their establishment and choice of alternative scenarios, IC time periods & probabilities, points of compliance to meet performance objectives, and source term containment assumptions in their approved PAs (Hanford; Savannah River; Fernald) were reviewed.

Review and comparison of above specific assumptions and supporting scenario-specific numeric parameters among DOE sites, NTS Area 5 PA model, and independent guidelines (e.g NRC; IAEA), starting with exposure compliance requirements were initiated.

### **1.3 Findings**

Overall: Model computations are sensitive to key parameter values and assumptions used, such as inventory estimation, exposure assumptions for compliance, and closure design.

Inventory estimation is difficult due to data omissions and conflicts in documentation. There is a need for reconciliation with historical documentation. In addition, the PA probabilistic approach utilizing probabilistic profiles for data inputs offers benefits over deterministic approaches, especially with regard to assessing the propagation of uncertainty. However, the use of the techniques is dependent on the provision of pdf profiles themselves. With regard to pre-'93 disposal inventory - and especially pre-1988 historical data paper records, there are issues of data quality, consistency, adequacy, and even existence.

Example: Historical Data Omissions in Data Base: Historical page records for T01U, T02U, T06U, T01C, T03C, T05C are not in the database. Also, there have been no records located for T06C.

Example: Reconciliation of disposal cell engineering "date openings" with disposal data filings (chronology) with WMD/LWIS/Historical Database records:

- Cell P03U: 1/87 (engineering data) vs. 11/12/85 (disposal data base).
- Cell P04U: 6/21/88 (engineering data) vs. 5/30/84 (disposal data base).

Closure design alternatives (in meeting Performance Objectives) rely mainly (in the model) on closure thickness (default set at 4 meters), utilizing development of 4 virtual cells (cross sectional geometries, and depth of disposal) to represent all the physical disposal cells. Note: Even with the attractive and beneficial assumption of reduced probabilities for occurrence of IHI scenarios (see discussion below), the Performance Objectives will not be met for an intruder agriculture scenario unless the cover thickness is at least 3 meters.

Parameters used for geometries need reconciliation with historical engineering documentation.

Example: Reconciliation of disposal cell engineering dimensional cell documentation with Goldsim volume reference parameters:

- Cell T04C: 3708 square meters (2002 Area 5 DSA RWMC – DSA 2151.100) vs. 1837 square meters from Goldsim reference “Area 5 RWMS parameter.doc” (2006).
- Cell T04C-1: 567.42 square meters (cited above DSA document) vs. 774.2 square meters (cited in above Goldsim parameter reference).

Compliance: Assignment of probabilities of occurrence for IHI scenarios plays a pivotal role in meeting RWMS Area 5 PA Performance Objectives. Other DOE waste management sites and closure sites (and other organizations such as NRC and IAEA) have not interpreted this approach within their regulatory guidance in meeting their Performance Objectives. This approach attempts to reflect the remoteness of the NTS site with regard to population centers.

Other DOE waste management sites have interpreted different points of compliance, and compliance time periods – as well as strict institutional control periods – in their approaches to meeting regulatory guidelines.

Source Term containment: Unlike the NTS PA, most DOE sites have utilized a “credit” for disposal package containment in their source terms. This has the impact of shifting longer term exposure peaks further out in time for long lived radionuclides, and reducing short-term exposure for short-lived radionuclides. For regulatory active IC time periods of 100 years, this facilitates compliance for short lived radionuclides.

Note: a reduced level-of-effort commensurate with current one-year budget authorization and the two-year base period of performance under the subcontract to UNLV is continuing.

## **2.0 Evaluation of Cap Subsidence due to Waste Package Degradation (PI: Moses Karakouzian, UNLV Department of Civil Engineering)**

### **2.1 Activities and Status**

This quarter the subsidence modeling approach was refined by focusing more on the quantitative aspects of uncertainty. This approach was applied to a mixed-waste site at Edwards Air Force Base (EAFB) in California. Figure 1 shows the result of 20 years of differential subsidence in the environmental site cover resulting in significant increases in hydraulic conductivity at the waste trench boundaries due to the large cracks created. These cracks significantly impact a number of mechanisms of subsidence because they permit an increased presence of water. Modeling the ten fundamental subsidence mechanisms at this particular waste site under several future scenarios yielded the differential settlement predictions shown in Tables 1 and 2. The scenarios involved (i) doing nothing, (ii) placement of a new 5-foot thick cover with proper long-term maintenance, and (iii) placement of a new cover without any maintenance allowing new cracks to open up.



*Figure 1. Differential settlement and tension cracks parallel to waste trenches.*

Note: Systematic differential settlement has resulted in tension cracks at the boundaries of the waste trenches. The top two photos show a large single crack along the long boundary and the environmental cover sloping laterally downward towards the center of the trench. The bottom right photo shows two cracks in the berm between two waste trenches. The berm is underlain by natural soils and rock and experiences little settlement. The bottom left photo shows sudden (in contrast to typically gradual) differential settlement at the trench boundary.

The literature review was augmented by looking more closely at probabilistic treatments of long-term landfill cover performance. Some more documents dealing with the landfill performance at the Nevada Test Site were also collected.

Next quarter work will focus on writing up a report summarizing the work to date and completing the GoldSim probabilistic subsidence model.

Table 1. Expected differential settlement predictions for EAFB study area.

<b>Mechanism</b>	<b>Scenario 1 2 years (feet)</b>	<b>Scenario 1 20 years (feet)</b>	<b>Scenario 2 2 years (feet)</b>	<b>Scenario 2 20 years (feet)</b>	<b>Scenario 3 20 years (feet)</b>
Immediate	0.0	0.0	0.1	0.1	0.1
Consolidation	0.0	0.1	0.1	0.3	0.4
Creep	0.0	0.1	0.1	0.3	0.3
Organic Decomposition	0.2	1.5	0.1	0.4	0.8
Inorganic Deterioration	0.0	0.0	0.0	0.0	0.0
Container Buckling	0.0	0.0	0.0	0.0	0.0
Structural Relaxation	0.1	0.3	0.2	0.4	0.5
Raveling	0.0	0.0	0.0	0.0	0.0
Subgrade Settlement	0.0	0.0	0.0	0.0	0.0
Cover Compression	0.0	0.0	0.2	0.2	0.2
<b>TOTAL SETTLEMENT:</b>	<b>0.3</b>	<b>2.0</b>	<b>0.8</b>	<b>1.7</b>	<b>2.3</b>

Table 2. 95 % Upper bound differential settlement predictions for EAFB study area.

<b>Mechanism</b>	<b>Scenario 1 2 years (feet)</b>	<b>Scenario 1 20 years (feet)</b>	<b>Scenario 2 2 years (feet)</b>	<b>Scenario 2 20 years (feet)</b>	<b>Scenario 3 20 years (feet)</b>
Immediate	0.0	0.0	0.1	0.1	0.1
Consolidation	0.0	0.2	0.3	0.5	0.7
Creep	0.0	0.2	0.2	0.5	0.5
Organic Decomposition	0.4	2.5	0.2	0.6	1.5
Inorganic Deterioration	0.0	0.0	0.0	0.0	0.0
Container Buckling	0.0	0.0	0.0	0.0	0.0
Structural Relaxation	0.2	0.5	0.3	0.6	0.8
Raveling	0.0	0.0	0.0	0.0	0.0
Subgrade Settlement	0.0	0.0	0.0	0.0	0.0
Cover Compression	0.0	0.0	0.3	0.3	0.3
<b>TOTAL SETTLEMENT:</b>	<b>0.6</b>	<b>3.4</b>	<b>1.4</b>	<b>2.6</b>	<b>3.9</b>

### **3.0 Fundamental Chemistry of Technetium and Actinides and Tank Waste Chemistry (PI: Ken Czerwinski, UNLV Department of Chemistry)**

#### **3.1 Project Abstract**

The research needs for DOE-EM center around remediation of contaminated sites and associated waste treatment. Broadly defined research is applicable to the following areas:

- Analysis and treatment of waste in the environment
- Treatment of waste currently stored on DOE sites (e.g., Tanks at SRS and Hanford)

While needs differ from site to site, commonalities exist that can support research capable of addressing crucial aspects of radionuclide chemistry germane to a range of EM issues. The different radionuclides at DOE sites are legion. However, a handful of isotopes are risk drivers due to their half-lives, environmental behavior, nuclear properties, and complicated chemistry. For these reasons the elements technetium, neptunium, plutonium, and americium are examined in this project, with emphasis placed on the role of Tc in EM needs. The studies contribute to solving issues related to environmental behavior, waste treatment associated with Tc and the actinides by examining fundamental Tc chemistry and tank waste chemistry.

#### **3.2 Technical Progress**

##### **3.2.1 Interaction of Technetium with Purolite Resin**

The removal of  $^{99}\text{TcO}_4^-$  from 200 Area groundwater is complicated due to the competition from the  $\text{NO}_3^-$  anion. The nitrate is at elevated concentration and has been found above drinking water standards (45 mg/L). In the 200 Area, a maximum nitrate concentration of 357 mg/L (5.76 mM) was observed in the east area while 1100 mg/L (17.7 mM) nitrate was measure in groundwater from 200 West Area (Newcomer et al., 1997). The chemical composition of uncontaminated Hanford Site groundwater (Table 3) shows the water to be basic with a pH of 8.4 (Mattigod et al., 2002). The elevate nitrate concentration observed at 200 Area can be over two orders of magnitude larger than ambient conditions. The natural groundwaters show sulfate, carbonate, calcium, and sodium to be the major natural ions in solution.

Anion exchange is a suitable method for the removal of pertechnetate from an aqueous solution. However, since the separation is based on anion exchange properties, competition from nitrate in 200 Area groundwaters necessitates the use of an exchanger with properties that enhance pertechnetate removal. Strong-base anion exchange resins, with two different types of exchange sites were developed for this task (Bonnesen et al., 2000). These resins function using a large trialkylammonium site for enhanced selectivity for large anions and a smaller trialkylammonium site for retention of good exchange kinetics and have been proposed for pertechnetate separation from anions found in groundwater.

For this study the sorption of Tc to Purolite A-530E (Table 4) was examined as a function of nitrate concentration as pH 8. The experiments were performed in batch method with 10 mL of solution phase and 100 mg of resin. The initial  $\text{TcO}_4^-$  concentration was  $1 \times 10^{-6}$  M. Samples of 100  $\mu\text{L}$  were periodically removed and the solution phase Tc concentration evaluated by

scintillation counting. The results show Purolite to be an effective resin for pertechnetate removal at all examined nitrate concentrations under the experimental conditions (Figure 2). This result indicates Purolite is a suitable resin for treatment of technetium containing groundwater at the Hanford site.

Table 3. Chemical composition of uncontaminated Hanford site groundwater (Mattigod et al., 2002). Concentrations are in mmol/L.

Analyte	Conc.	Analyte	Conc.	Analyte	Conc.
Cl <sup>-</sup>	0.677	Al <sup>3+</sup>	0.005	Mg <sup>2+</sup>	0.658
NO <sub>3</sub> <sup>-</sup>	0.027	B	0.005	Na <sup>+</sup>	1.305
SO <sub>4</sub> <sup>2-</sup>	1.135	Ba <sup>2+</sup>	0.001	Fe	0.003
C (org)	0.061	Ca <sup>2+</sup>	1.447	Si	0.577
CO <sub>3</sub> <sup>2-</sup>	2.623	K <sup>+</sup>	0.358	pH = 8.4	

Table 4. Purolite A-530E data.

Typical Chemical and Physical Characteristics	
Polymer Structure	Macroporous polystyrene- DVB
Appearance	Spherical beads
Functional Group	Quaternary Ammonium
Ionic Form - as shipped	Chloride – Cl <sup>-</sup>
Total Capacity (Cl <sup>-</sup> Form)	0.55 eq/l min
% Moisture (Cl <sup>-</sup> Form)	Approx. 50 %
Mean Diameter (microns)	Approx. 475
Uniformity Coefficient	1.2
Specific Gravity	1.04
Shipping Weight	620-670 kg/m <sup>3</sup> (38.5-42 lb/ft <sup>3</sup> )
Temp. Limit (Cl <sup>-</sup> Form)	100°C (212°F)
pH Limits	(Stability) 0-14 (Operating) 4.5-8.5

### 3.2.2 Technetium Homolog Studies

Research to date shows variations in suitable technetium homologs with oxidation state. Ion exchange experiments performed on Tc and Re separations and literature studies (Poineau et al., 2006) show high oxidation states of Re and Tc to be suitable homologs. For environmental conditions where the high oxidation pertechnetate is expected, perrhenate is a suitable homolog.

For lower oxidation states of technetium the results indicate rhenium is not a suitable homolog. Initial studies at the UNLV laboratory on the tetravalent oxidation state of Re and Tc in carbonate demonstrates stark chemical differences. The technetium species is soluble while the rhenium species precipitates. Further studies on this system are planned in the next quarter.

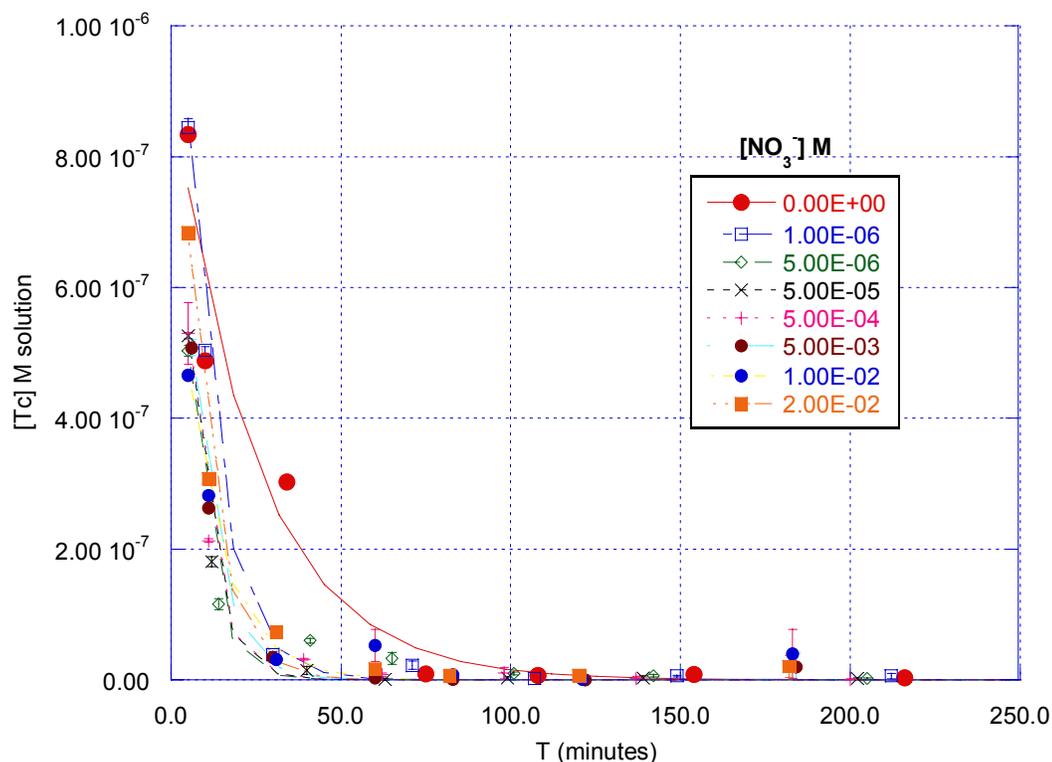


Figure 2. Sorption of pertechnetate to Purolite resin at pH 8 as a function of nitrate concentration.

Metallic Re and Tc also demonstrate differences in chemical behavior. In the formation of Zr alloys with the metals, differences are demonstrated between Re and Tc. The Zr-Re phase diagram shows the presence of a Zr-Re solid-solution up to 10 atomic percentage Re. When the amount of Re is above this level a number of Re-Zr intermetallics are formed.

In the UNLV laboratory, alloys of Zr and Tc were prepared (Table 5). The alloys were prepared by mixing powdered metals together, pressed into pellets, arc melted and sintered at 1400°C. The samples were examined by scanning electron microscopy, X-ray diffraction, and X-ray absorption fine structure.

Table 5. Composition of prepared Zr-Tc alloys.

Sample	Mass Tc in mg (mmole)	Mass Zr in mg (mmole)
A: Tc0.85 - Zr0.15	85.1 (0.859)	13.9 (0.152)
B: Tc0.68 - Zr0.32	70.4 (0.711)	30.8 (0.337)
C: Tc0.51 - Zr0.49	50.4 (0.509)	43.9 (0.481)
D: Tc0.15-Zr0.85	15.32 (0.155)	82.3 (0.902)

The high percentage Tc alloy (Sample A) produced a single phase intermetallic with a composition of  $Tc_6Zr$ . Rhenium does not make a similar compound. The composition in sample B produced two phases:  $Tc_2Zr$  and the  $Tc_6Zr$ . Sample C resulted in two phase:  $Tc_2Zr$  and a solid-solution of Zr and Tc in  $Zr_3O$ . The overall difference between the Re and Tc alloys is manifest in the larger Zr solid solution with the Tc alloy. The resulting phase diagram for Zr-Tc is presented for comparison to the Re-Zr data (Figures 3 and 4). Further experiments will investigate the Ru-Zr system as a homolog for Tc.

### 3.2.3 Tank Waste Studies

Efforts during this quarter were focused on preparation of samples and techniques for transmission electron microscopy (TEM) analyses of Hanford tank waste. Initial studies were performed on Bi-containing standards and the first analysis of Bi containing precipitates from Hanford tanks. The initial materials contained Cr, Al, and U. Further studies will examine the speciation of the material, particularly Cr, by electron energy loss spectroscopy (EELS).

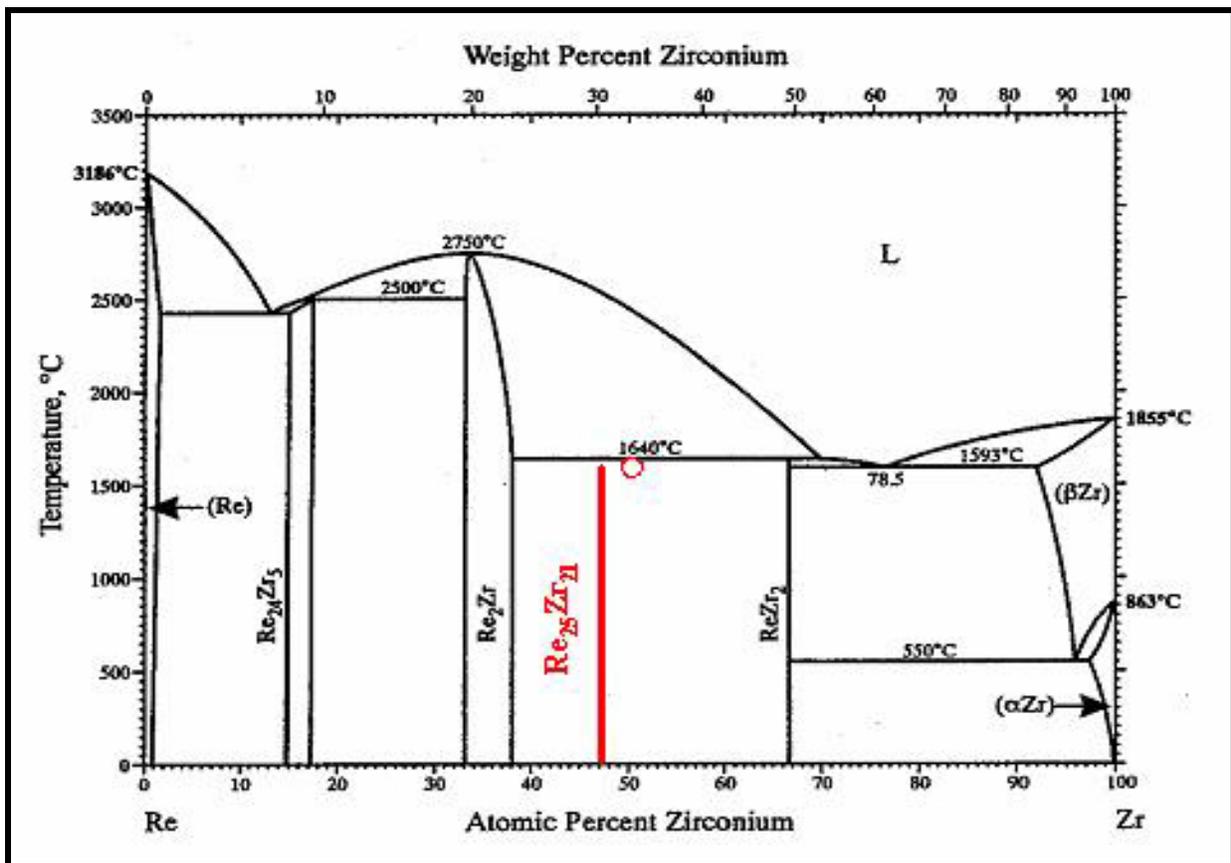


Figure 3. Zr-Re phase diagram.

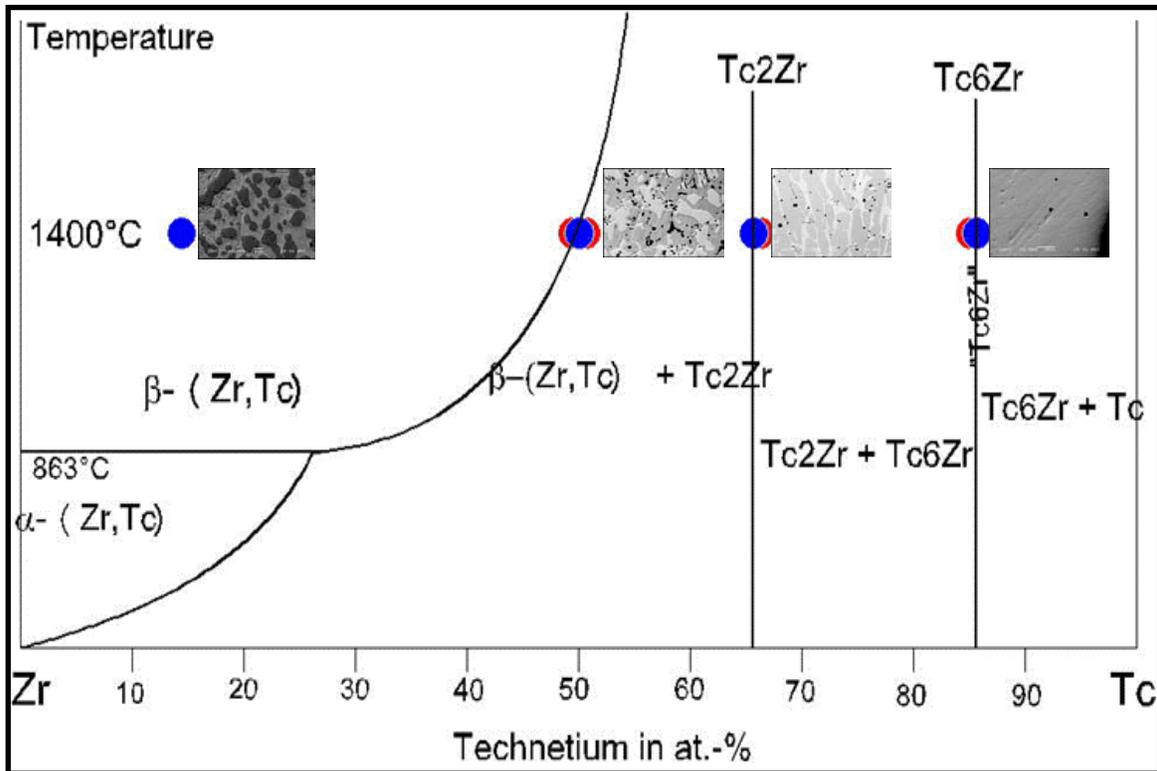


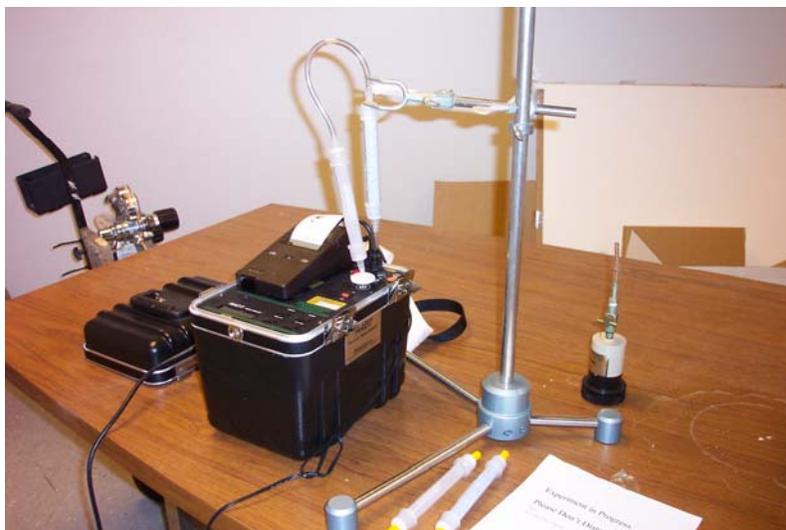
Figure 4. Experimental Tc-Zr phase diagram at 1400°C.

#### 4.0 Evaluation of Radon Release and Transport from Actinide-Bearing Waste Forms (PI: Gary Cerefice, UNLV Harry Reid Center)

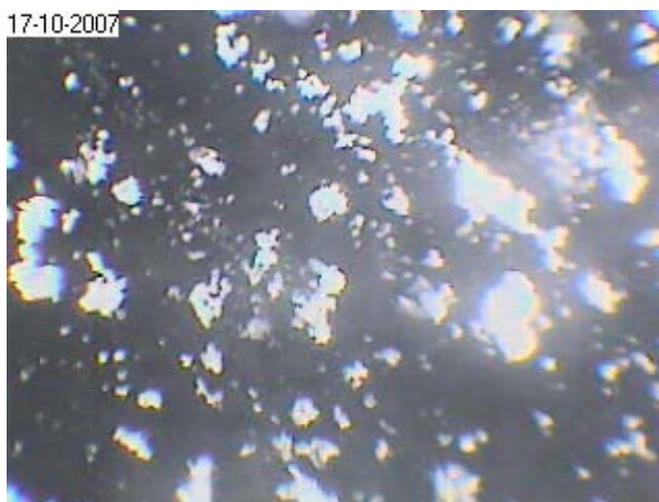
##### 4.1 Technical Summary

All equipment and materials have been procured to accomplish the determination of the emanation coefficients for the thorium nitrate salts under conditions of differing compaction of the material. The RAD 7 radon detector and apparatus to be used for evaluation of the emanation from thorium compounds is shown in Figure 5. The current experiments involve thorium nitrate. The tubes that are used as chambers for the emanations to collect in are glass drierite tubes that have been cleaned out and connected to allow a dry flow of the emanated gas into the detection chamber of the RAD 7.

More fine-particle thorium nitrate is being prepared as this will allow the greatest surface area for the emanation thoron to escape the material. A photograph of a microscope image of the particles that came through a 170 mesh screen is shown in Figure 6. The particles in this image are typically less than 3 microns in their largest dimension. There is some clumping of the particles.



*Figure 5. The RAD 7 radon detector and apparatus.*



*Figure 6. A microscope image of the particles that came through a 170 mesh screen.*

The preparation of approximately 100 grams of thorium nitrate powder will continue next quarter. Concurrently, with the preparation of this fine material, measurements will be taken to determine the characteristics of the thoron concentrations emitted from different packing of the thorium nitrate in the tubes.

The preparation of the fine material is completed with a set of sieves (45 mesh, 80 mesh, and 170 mesh). The output from each level is saved and particles from the 170 mesh sifting are passed through the ball mill again to attempt to get the smaller particles.

Evaluation of the surface area of the particles was attempted with each particle size. The initial results using the NOVA 1000 particle size analyzer were not encouraging as the thorium nitrate appeared to degrade as a result of the heating of the sample during the analysis. Recent results

(without heating) indicate measurements of the surface area are not conclusive but appear to yield a specific surface area of 0.1 m<sup>2</sup>/gram for the material that passed through the 80 mesh sieve. Approximately 20 grams of that material is stocked and about 100 grams will need to be prepared for the remainder of this part of the experiment.

#### 4.2 **Anticipated Next Steps**

- Complete preparation of the materials.
- Determine effective volume of RAD 7 setup.
- Continue surface area measurements.

#### 5.0 **Evaluation of Radionuclide Speciation and Release from Vitrified Waste Phases (PI: Tyler Sullens, UNLV Harry Reid Center)**

##### 5.1 **Highlights**

- Glass moldings, glass synthesis procedures, and molten glass pouring procedures were tested, modified, and established for glass fabrication.
- Test samples of undoped vitrified material were made using two separate formulations, from which one formulation was agreed upon for use throughout this project.
- Samples of vitrified material, doped with approximately 1, 5, and 10 w/w%, were made with no obvious heterogeneity or crystallinity.
- A PerkinElmer Elan DRC II ICP-MS, essential for characterization of material samples and dissolution tests, was installed in new laboratory space, with training attended by project personnel.

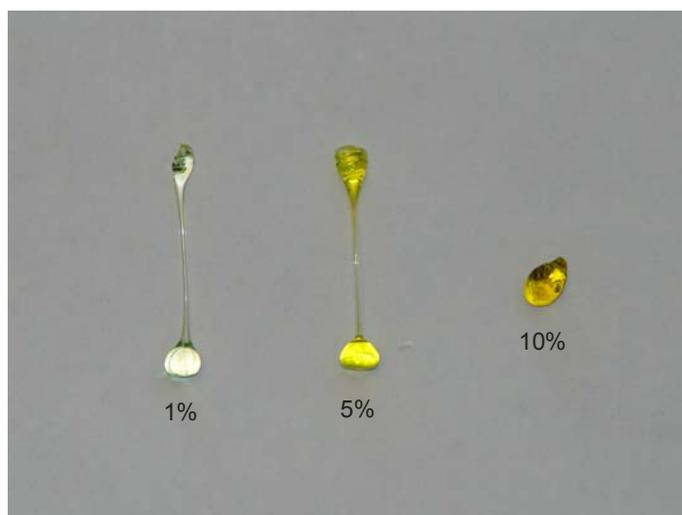
##### 5.2 **Technical Summary**

Progress during the third quarter of 2007 was made in both the synthesis of materials that will be evaluated for this project, as well as the installation of the equipment necessary for the analysis to be conducted. Research personnel tested two formulations of vitrified waste material that were undoped during the initial manufacturing and testing of the formulations. Based on the homogeneity and non-crystallinity that was observed after sampling cooling of Formulation 1, it was decided to use Formulation 1 for all samples prepared for this project for the duration of this project. The constituents of the formulations are given in Table 6.

*Table 6. Constituent weight percent of Formulations 1 and 2.*

Formulation 1 (w/w %)				
Na <sub>2</sub> O	Li <sub>2</sub> O	B <sub>2</sub> O <sub>3</sub>	ZnO	SiO <sub>2</sub>
15.448	7.506	5.945	N/A	71.100
Formulation 2 (w/w %)				
Na <sub>2</sub> O	Li <sub>2</sub> O	B <sub>2</sub> O <sub>3</sub>	ZnO	SiO <sub>2</sub>
6.989	7.432	13.435	2.936	69.172

For initial testing of the vitrified waste material with uranyl nitrate used as a dopant, several samples were made with varying weight percent doping (Figure 7). By varying the doping agent percentage (w/w%), it was discovered that heterogeneity becomes apparent with dopant concentration approaching 20%. Obvious darkening of the materials increases proportionally with dopant concentration. Further studies will determine the consequence of the nitrate anion of this dopant, with the possible future substitution of this nitrate with another inconsequential anion, such as oxide. Methods are under evaluation to develop multiple samples that are comparable in size, to obtain uniform samples for batch testing dissolution studies.

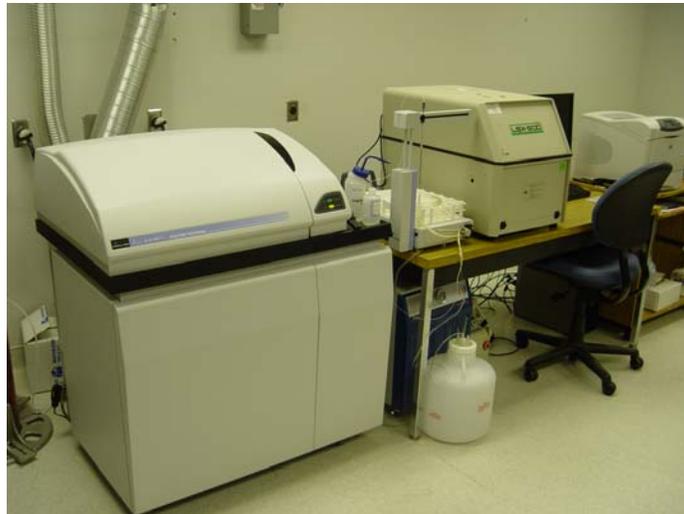


*Figure 7. Three samples of the vitrified waste material doped with approximately 1, 5, and 10 w/w% uranyl nitrate, respectively.*

Several pieces of equipment that were purchased and installed for this project. Several acid digestion bombs, along with four muffle furnaces, shown in Figure 8 were obtained in order to perform the dissolution studies for this project. A PerkinElmer Elan DRC II (Figure 9) was installed and will be essential for the characterization and concentration detection of the aqueous samples of the dissolution studies, as well as the solid vitrified waste material, both before and after dissolution studies. The laser ablation system, a Cetac LSX-500, which will be used for solid material sampling, was purchased and will be installed and coupled with the ICP-MS early next quarter.



*Figure 8. Two of the muffle furnaces that will be used for the dissolution studies of doped vitrified waste material, along with four acid digestion bombs, sealing bracket, and spanner wrench.*



*Figure 9. The PerkinElmer Elan DRC II and the Cetac LSX-500 laser ablation system.*

## **6.0 Evaluation of Synthetic Phosphate Minerals for Sr and U Remediation in Area 100 (PI: Tyler Sullens, UNLV Harry Reid Center).**

### **6.1 Highlights**

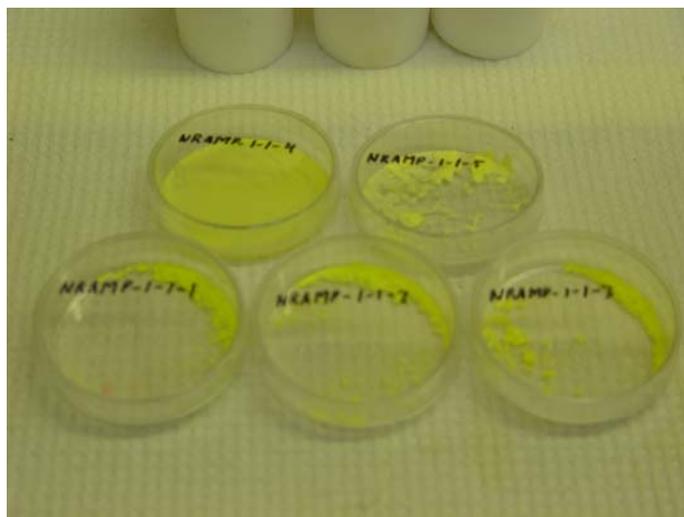
- The identification of task components, methodologies, and personnel was conducted.
- Initial reactions for the synthesis of synthetic phosphate minerals were conducted using hydrothermal methods.

- Muffle furnaces and acid digestion bombs, used for the synthesis of single crystals of synthetic phosphate minerals, were obtained.
- A Bruker APEX II single crystal X-ray diffractometer and a Bruker D8 Advance powder X-ray diffractometer, which will be essential for the identification of the synthesized materials, were installed in newly converted laboratory space.

## 6.2 Technical Summary

Task personnel were split into two teams: one team for the hydrothermal synthesis of single crystals of synthetic phosphate minerals and the second team for the precipitation of synthetic phosphate minerals. It was decided to begin synthesis reactions with the basic components (uranium, strontium, and phosphate sources only) being used initially, and continuing on to include other cation and anion sources that are relevant to the local environment of Area 100.

Initial reactions were carried out under hydrothermal conditions, with total solid reagent masses of 0.5000 g of material and 3.00 mL of DI water as a solvent (Figure 10). Reagents used for these reactions included  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{KH}_2\text{PO}_4$ , and  $\text{K}_2\text{HPO}_4$  at varying stoichiometries. The reagent materials were sealed in Parr 4749 23 mL acid digestion bombs and placed in muffle furnaces that were preheated to  $180^\circ\text{C}$ . The reactions were carried out for 3 days and then cooled at  $9^\circ\text{C}$  until at room temperature. Initial characterization of the synthesized materials will be conducted using single crystal X-ray diffraction. This will allow for the identification of the material, by comparison to known crystal structures or identification of novel crystal structures. SEM/EDAX will also be used for conformation of elemental composition.



*Figure 10. The products from the initial hydrothermal reactions with  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{KH}_2\text{PO}_4$ , and  $\text{K}_2\text{HPO}_4$  at varying stoichiometries. Samples NRAMP-1-1-1,2,3 produced crystalline products. Samples NRAMP-1-1-4,5 produced powder or microcrystalline products.*

Four muffle furnaces and several acid digestion bombs were obtained for the hydrothermal synthesis of the phosphate materials. Office spaces were converted into laboratory spaces for the installation of the newly obtained X-ray diffractometers (Figure 11). A Bruker APEX II single crystal X-ray diffractometer and a Bruker D8 Advance powder X-ray diffractometer also obtained and installed. These instruments will be essential for the characterization of the synthesized materials, more particularly single crystal for the hydrothermal products and powder for the precipitation products. Initial trainings on these instruments were conducted, with more detailed training to be held in the next quarter.



*Figure 11. The newly obtained and installed Bruker D8 Advance X-ray diffractometer (left) and Bruker APEX II single crystal X-ray diffractometer (right).*