UFA Ventures, Inc.

Date: 12/23/98

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Re: Final Report for Contract 215BA0016-3Y

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The following tasks were completed and future work outlined, including a draft test plan for FY1999.

PREPARATION FOR YMP BACKFILL ACTIVITIES

Yucca Mountain activities for FY1999 are anticipated to require specific information on the chemical and physical properties of the candidate getter materials and other backfill components necessary for defensible modelling of the source term, and possible controlling of the source term. There should be three tasks to this activity: At the end of this report is a draft test plan reflecting the present funding anticipated. the other tasks may be added as funding becomes available.

- 1) The immobilization capacity of the getter materials for specific radionuclides. This task will primarily include column sorption tests of getter materials with solutions spiked with radionuclides. The getter materials will include Apatite II, MgO (with NaPO_4 plus Ba, SrCO_3 , and soluble sulfate, with and without Apatite II), Gibbsite/Boehmite, and Hematite. Radionuclides will include Pu, U, Np, Am, Ra, Tc, and Th. Experiments will be performed under various anticipated repository conditions and with anticipated solution compositions. Occasional batch tests will be used to obtain specific K_d s and other thermodynamic data. Solid and liquid analyses will be needed for characterization of the effluent concentrations from the columns to assess performance and for use in geochemical modelling.
- 2) Intrinsic stability of the getter materials under repository conditions. The use of any candidate getter material will depend upon its anticipated lifetime in the backfill environment. Literature search for any existing data will be performed and augmented by solubility experiments on the getter materials. This especially important for the reactive materials such as MgO and the soluble sulfates and phosphates that may have a limited lifetime in the backfill. It is also necessary to decide how much getter material to emplace.

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3) Diffusion of radionuclides across a Richards Barrier. The Richards Barrier, if emplaced, will act as a hydraulic diversion barrier for the diversion of water around the waste package, and sand and gravel may be used beneath the packages for various reasons. It has been postulated that these materials will also act as diffusion barriers to radionuclide migration across them, especially under unsaturated conditions. Macroscale experiments in LANL's hot facility will be used to measure radionuclide migration across the interface of these barriers which will be constructed using crushed YM tuff and Overton Sand from Nevada. Tritium will be used as a conservative tracer.

These experiments will provide the data necessary to evaluate the retardation properties of the backfill materials and to determine whether precipitation or adsorption dominates in each material, and whether the repository environment is favorable for its performance. The scope of work may change as information develops from this activity and from other activities, as close interactions will occur between these activities.

In anticipation of these activities, we are performing several calculations and experiments. First, we are compiling information on the properties of the candidate backfill and invert materials for use in decision-making, for modelling purposes and for identifying data gaps. Table 1 provides the first draft of information on the possible backfill materials and Table 2 provides information on the possible invert materials.

Table 1. Summary of Properties for the Candidate Invert Materials

<u>Material</u>	<u>Saturated Hydraulic Conductivity</u>	<u>Saturated Volumetric Water Content</u>	<u>Residual Volumetric Water Content</u>
Concrete	10^{-12} to 10^{-10} cm/s	0.20	0.10
Grout	10^{-12} to 10^{-10} cm/s	0.25	0.15
Clay Loam	10^{-7} to 10^{-5} cm/s	0.40 to 0.50	0.10 to 0.20
Sand (fine to coarse)	10^{-2} to 1 cm/s	0.35 to 0.45	0.02 to 0.05
Gravelly Sand (function of grading)	10^{-1} to 10^{-2} cm/s	0.25 to 0.35	0.05 to 0.10
Gravel (tuff)	10 cm/s	0.56	0.07
Gravel (non-tuff)	10 cm/s	0.45	0.03

Of course, the properties depend upon the exact material chosen, e.g., whether the gravel has internal porosity like tuff gravel, or no internal porosity like basalt gravel, whether the sand is fine or coarse, or whether the clay is a swelling clay or not. If the concrete fractures, then the saturated conductivity increases dramatically up to 10^{-1} cm/s or more. The residual water content is in steady-state with the low infiltration rate expected in the drifts at 100% humidity, not air-dry as is often given for van Genuchten parameterizations. If the exact material is unknown, use the midpoint of the range given. Remember that these materials will be engineered and the aggregates well-sorted. If you need values of alpha and n, the ones in the original table are fine. The gravels, sands and apatite being evaluated are all very stable with respect to temperature, and their chemical and physical properties will not change during the thermal phase. However, the K_s s may change with temperature with respect to different radionuclides, and it is not predictable which direction it will go. Some data exists for this issue, but more experiments can be done quickly. General data exists for the properties of the getter materials listed below. Again, the exact properties will depend upon emplacement decisions, but the ones listed below are for anticipated choices. Those materials with a listing of *thermal instability* under the *Major Problems* category will irreversibly change properties during the thermal phase. Those materials with a listing of *chemical instability* under the *Major Problems* category will irreversibly change properties as a result of chemical interaction with infiltrating water and/or other aspects of the system such as concrete interaction with carbon dioxide. All others are relatively stable with respect to temperature and chemistry such that major changes in properties should not occur over the duration of the performance period (Klein, C. and C. S. Hurlbut, 1985. *Manual of Mineralogy*. John Wiley and Sons, New York; Carmichael, I. E., F. J. Turner, and J. Verhoogen, 1974. *Igneous Petrology*. McGraw Hill, New York). The aging of the getter materials with respect to sorption, e.g., reaction or corrosion products coating the surfaces, maturing of the concrete with carbon dioxide, raising of the pH, etc., is a complex issue that has separate effects for each material and for each condition and is beyond the scope of this initial Design Input. However, those materials without a listing of *chemical instability* under the *Major Problems* category should not be significantly affected by waste package corrosion, changes in surface reactivities, or other long term chemical effects. Of course, if every surface becomes coated with corrosion products, then the behavior of the entire drift would just devolve to goethite. However, this is unlikely given the slow transport of Fe under drift conditions anywhere but below the canisters.

Table 2. Summary of Properties for Candidate Getter Materials*

<u>Getter Materials</u>	<u>Dry Bulk Density*</u>	<u>Intended Function</u>	<u>Major Problems</u>
Smectite clays	1.2 g/cm ³	sorption, extremely low conductivity	thermal instability, unsaturated cracking
Depleted uranium	4 to 5	neutron absorber	expensive
Zeolites (or crushed zeolitic tuff)	1 to 1.2	specific sorption of radionuclides	thermal instabilities, slightly expensive
Calcite	1.4	sorption of radionuclides raise ionic strength, neutron absorber	uncertain lifetime, chemical instability
Lime	1.4 to 1.6	raise ionic strength/immobilize colloids sorb O ₂ and CO ₂	short lifetime, chemical instability
Concrete	2.2 to 2.5	raise ionic strength/immobilize colloids sorb O ₂ and CO ₂	uncertain lifetime, chemical instability
Apatite sand	1.5	immobilize U and Np	slightly expensive, production uncertain
Apatite II	1.4	better immobilization of U, Np and others	slightly expensive
Basalt gravel	1.5	reduction/immobilize Tc	
Pyroxene	1.7	reduction/immobilize Tc	expensive
Zero valent iron (or Fe ₃ O ₄)	4 to 5	reduction/immobilize Tc, sorb or co-precipitate other radionuclides	unknown corrosion issues, expensive chemical instability
Hematite (or Goethite) (or Fe ₂ O ₃)	2.6	sorb or co-precipitate other radionuclides	expensive
Borax	0.9	neutron absorber	uncertain lifetime, chemical instability
Periclase (MgO) with sodium orthophosphate or sulfate plus	1.4 to 1.6	very good at immobilizing radionuclides (Ba,Sr)CO ₃	slightly expensive, chemical instability
Boehmite (Al ₂ O ₃)	1.5	immobilize radionuclides	uncertain performance, expensive

*These materials are assumed to be emplaced with a grain-size equal to a silt or fine sand with a total porosity from 0.40 to 0.50 with a well-known unsaturated hydrologic properties. Some materials can be obtained in this form while others will have to be ground or engineered to this form. Dry bulk densities depend upon particle densities and porosities. Wet bulk densities depend upon the water content but may be assumed to be at the residual for a silt or about 0.25.

Calculation of the Amount of Getter Material Required to Immobilize Np

The amount of Getter material needed can be calculated from its K_d batch test behavior, the inventory of radionuclides to be sorbed, and the anticipated areal extent of the drifts. These K_d values are: 1) specific to the solution and concentrations used in the test, 2) do not reflect temporal effects and further sorption from later solutions, 3) do not necessarily translate to amounts of radionuclides immobilized in the field, and 4) are usually very conservative, i.e., more Np will probably sorb onto the getter than is reflected in the K_d value. This being said, using Np and apatite, with an inventory of 80,000 curies of Np (4.78×10^5 moles; 1.13×10^8 g), an average drift area of $1.83 \times 10^8 \text{ cm}^2$ with 84 drifts (assuming 57 kW/acre), a K_d for the apatite of 2,000 g/ml using 1g of apatite in 20 ml of 5×10^{-6} molesNp/liter, a dry bulk density for apatite of 1.5 g/cm^3 , then:

The amount of Np sorbed to 1 g of apatite = $(5 \times 10^{-6} \text{ molesNp/liter}) \times 0.02 \text{ liter} = 1 \times 10^{-7} \text{ molesNp}$

The amount of apatite needed to sorb 4.78×10^5 molesNp = $(4.78 \times 10^5) \div 10^{-7} = 4.78 \times 10^{12} \text{ g of apatite}$ (4.78 million metric tons)

The volume of apatite needed to sorb 4.78×10^5 molesNp = $4.78 \times 10^{12} \text{ g} \div 1.5 \text{ g/cm}^3 = 3.18 \times 10^{12} \text{ cm}^3$

The depth of apatite needed distributed over the cumulative drift area = $3.18 \times 10^{12} \text{ cm}^3 \div 1.83 \times 10^8 \text{ cm}^2 \div 84 = 207 \text{ cm} \approx 2 \text{ m}$

This calculation assumes even distribution of flow and sorption in the getter, which should occur if it is silt-sized.

A similar calculation for hematite which has about the same K_d as the apatite but twice the bulk density gives about a 1 meter fill.

It should be mentioned that at the time of the K_d work with apatite, the apatite used was North Carolina phosphate ore. This is presently not available in any significant amounts, and may not be available at the time needed by the YMP. We have searched for other sources, and found Apatite II which is about ten times more effective than North Carolina apatite and only twice as expensive, so for the same performance, a depth of fill for the Apatite II would be only 0.2 meters. Apatite II can be obtained in the required amounts for the YMP.

However, this gross calculation definitely overestimates the amount of apatite needed by at least an order of magnitude. 4.78 million metric tons of apatite would cost over \$2 billion! If Apatite II sorbs 5% of its weight in Np as is indicated by studies of other metals, then only $1.13 \times 10^8 \text{ g} \div 0.05 = 2.26 \times 10^9 \text{ g}$ of apatite are needed which is only 2,260 metric tons, two thousand times less than the above calculation, and costs only \$2 million, a huge cost savings. Simple column experiments using Np with Apatite II, hematite, and other materials should be run at LANL to determine the sorption efficiencies of these materials in the way that reflects the drift

environment. The gain in performance and cost savings together would be tremendous. Funds permitting, we will design and carry out these experiments during FY1999.

NEW SOURCES OF INVERT AND GETTER MATERIALS

Depending upon which invert and getter materials are finally chosen, commercial sources of these materials must be found that will be cost-effective for the YMP. Sand and gravel from the site present no problem, but other materials such as the Apatite II, hematite, zeolite, MgO and others will have to be obtained from commercial sources such as quarries or from industry in megaton amounts at reasonable costs. In fact, the ability to obtain megaton amounts at a reasonable cost will be one of the deciding factors in the final choice of a getter or invert material. We are locating commercial sources for these materials and expect to have a comprehensive list by the spring of 1999.

COMPACTION TESTS FOR APATITE II

Simple compaction tests were performed using a 35 cm³ sample of the medium-grained Apatite II to see the effect of overburden, e.g., the weight of the canister, on an invert of Apatite II. The sample was loaded into a titanium compression cell as it would be emplaced in the drift. A piston was used to compress the sample with a pressure of approximately 1 ton per square inch, followed by 2 tons per square inch. The 40 mm long sample (1.6 inches) compressed by 3.5 mm (0.14 inch) when subjected to 1 ton per square inch, a strain of 8.7%. When the pressure was removed, the sample rebounded 2 mm (.08 inch). The sample then compressed an additional 3.0 mm (0.12 inch) when subjected to 2 ton per square inch, a total strain of 16.2%. When the pressure was removed, the sample rebounded 1 mm (.04 inch). This strain behavior is much better than most other sorbent materials such as zeolite, clay or resin. Depending upon the final canister configuration, the Apatite II should have enough strength to perform well as an invert material. Further tests should be performed using ASTM compaction test methods.

PROPERTIES OF CANDIDATE BACKFILL SANDS

Two sands are being considered for backfill at Yucca Mountain. These are the nearby Sand Ramp-1 sand, a fine clastic sand with a fair amount of fines and lithic fragments, and the Overton Sand from the town of Overton about 30 miles away. In addition, the materials being investigated for the lower gravelly layer include the 8-20 sand and the 12-20 sand. The Overton Sand is an extremely well sorted fine-grained, clean quartz sand. From the properties measured, the Sand Ramp-1 sand is clearly better as a backfill and is immediately

adjacent to the site, making it much more cost-effective than the Overton Sand. Neither the 8-20 sand nor the 12-20 sand are appropriate for the lower layer. The properties measured as a function of the water content included electrical conductivity to provide the aqueous diffusion coefficient and the air permeability as a function of the water content. The results attached to this report.

X-RAY TOMOGRAPHY

We obtained time on a new high-resolution X-Ray Tomographic instrument that can produce 3-dimensional images of geologic materials at various degrees of saturation. We investigated the 8-20 sand and two fractured cores of tuff, the Topopah Spring tuff and the Prow Pass, that we have characterized previously. The results were obtained electronically configured into the movie for proper viewing of the cores, and were placed on the LANL YMP results page of our website at <http://www.ufaventures.com>

NATO PAPER AND WORKSHOP ON REMEDIATION OF RADIONUCLIDES AND HEAVY METALS IN SUPPORT OF NONPROLIFERATION

We attended the *NATO Advanced Research Workshop* from November 8 to the 14, in Krakow, Poland in support of LANL's initiative on global environmental management. Effort included preparation of a paper for the proceeding volume and a presentation at the workshop, entitled "PIMS: A Simple Technology For Clean-Up Of Heavy-Metals And Radionuclides Throughout The World." A copy of the paper is attached to this report.

SCFA DOE'S VADOSE ZONE BOOK

As part of the Department of Energy's Vadose Zone initiative, the Subsurface Contaminants Focus Area has called for researchers in the Vadose Zone to co-author a book on the Vadose Zone for use by DOE and subcontractors, especially LANL and the YMP. We are providing at least four papers to this volume outlining studies pertinent to the Vadose Zone and to LANL. The first four papers are attached to this report.

1999 DRAFT TEST PLAN FOR RPA20742 BACKFILL TRANSPORT PROPERTIES

Introduction

This plan describes the experimental work and investigations to determine the chemical performance of different materials that may be used as drift backfill in the proposed Yucca Mountain high-level nuclear waste repository. Whatever backfill material is chosen for either

engineering purposes, such as invert support of the package or protection against rockfall, or for hydrologic control such as drip shield or Richards barriers, the diffusion of radionuclides through the backfill is the most critical property of the backfill with regard to contaminant release and transport out of the drift. The hydrologic system underlying Yucca Mountain encourages fast path flow of infiltration through fractures and faults. The nominal infiltration rate for the repository horizon is between 1 and 10 mm per year. Even at these low rates, dripping will occur from the drift ceilings. Several designs have been proposed to reduce the impact of this dripping and subsequent leaching and transport of radionuclides from the drift, i.e., to lower the radionuclide release rates from the system to acceptable levels from a dose performance standpoint. Hydrologic barriers such as a drip shield or a Richards Barrier could divert this infiltration from the canisters and backfill, and lower release rates by changing the advective properties of the system. Chemical barriers can alter the solution chemistry and phase relationships within the backfill and lower release rates by changing the chemical properties of the system. A combination of barriers may be used to ensure robust performance in the face of indeterminate hydrologic conditions.

Whatever backfill materials are chosen, the diffusion coefficient will be the primary transport mechanism at very low water contents and must be determined for the range of conditions anticipated in the repository. It is expected that crushed tuff gravel will be used in some form, if only as an engineering material, e.g., invert or cover. Therefore, this task will focus on crushed tuff gravel diffusion.

Objective and Scope

This work will provide data necessary to evaluate the diffusion behavior of backfill. The scope of work may change as information develops from this activity and from other activities (Activities RPA30672 and 74), as close interactions will occur between these activities. Of critical importance is that these experiments reflect the backfill environment at the time when radionuclides diffuse through the backfill, after leaching from the waste forms and interaction with canister corrosion products, or at least bound the anticipated conditions as well as is known,

Relevance

Activities RPA30672 and 74 require specific information on the chemical and physical properties of the candidate backfill materials for defensible modeling of the source term and possible control of the source term. This work will determine the properties desired for optimal performance.

Experimental Approach

There is one task to this activity: Diffusion and transport across backfill materials, especially across the interfaces between possible barriers. This will be accomplished using a large-scale tracer diffusion test in a hot cell to measure the apparent diffusion coefficients of radionuclides, and smaller-scale effective diffusion coefficient tests. Any hydrologic diversion barriers, such as the Richards Barrier or a drip shield, if emplaced, will act as a hydraulic diversion barrier for the diversion of water around the waste package, and sand and gravel may be used beneath the packages for additional various reasons. These materials will act as diffusion barriers to radionuclide migration across them, especially under unsaturated conditions. To be an effective barrier, diffusion coefficients need to be well below 10^{-9} cm²/s. Macroscale tracer diffusion tests in a hot cell will be used to determine the apparent diffusion coefficient in the gravel, sand, or other backfill material decided upon by VMF. This task will also determine what the water contents will be in the repository from large scale experiments such as the ongoing Quarter-Scale Drift Test at Sandia. This task will also measure the effective diffusion coefficient as a function of water content in the candidate backfill materials using electrical conductivity and the Nernst-Einstein relationship (N-E) so that variations in whatever material is chosen can be taken into account in the performance assessments. Debye-Huckel corrections will be used to reflect high and low ionic strength conditions in the repository.

The choice of water chemistry is of critical importance, and must reflect repository conditions at the time when leached radionuclides will enter the getter materials. In order to leach radionuclides from the waste form, the water will have had to interact with caustic corrosion products, which can make the water very acidic. The first effort in this project will be to decide the major element chemistry of the water based upon past studies of aqueous chemistry in this environment. Because of the lack of knowledge and consensus on this issue, the water chemistry may be bounded by four compositions to reflect possible conditions: 1) high pH, low ionic strength, reflecting early interactions with concrete by water relatively unaltered by evaporation, 2) high pH, high ionic strength, reflecting later interactions with concrete by water that has significantly changed as a result of evaporation and resolubilized salts, 3) low pH, low ionic strength, reflecting later interactions with concrete by water relatively unaltered by evaporation, 4) low pH, high ionic strength, reflecting later interactions with concrete by water that has significantly changed as a result of evaporation and resolubilized salts. The radionuclide concentrations will also be decided based upon past experience and the solubility relationships between the chosen major element water chemistry and the solubility-limited relationships with the waste form. Tritium will be used as a tracer. To avoid artificially favorable

results from precipitation near the solubility limits of each radionuclide, the radionuclide concentrations will be at least an order of magnitude below the solubility limits, otherwise rapid precipitation could occur that is not related to the backfill.

Timeline

Experimental set-up can begin in March and experiments will occur between March and August. The tracer diffusion test can continue beyond the end of this task to observe longer-term effects.

Chart3 1&2 combo

Air Perm 98-0128a Overton Sand

Chart1

AIR PERM for 98-0128A Overton Sand

AIR PERM (1st pt) for 98-0128A Overton Sand

Chart2 1st pt

Air Perm 98-0128b Overton Sand

Chart2

AIR PERM (1st pt) for 98-0128B Overton Sand

Series1

Chart1

AIR PERM for 98-0128B Overton Sand

Chart2

AIR PERM (1st pt) for 98-0129B Ramp Sand

Chart3 1&2 combo

Air Perm 98-0129a Ramp Sand

Chart3 1&2 combo

Air Perm 98-0129b Ramp Sand

Chart1

AIR PERM for 98-0129B Ramp Sand

Chart1

AIR PERM for 98-0129 Ramp Sand

Chart2 1st pt

AIR PERM (1st pt) for 98-0129A Ramp Sand

Chart3 1&2 combo

Air Perm 98-0168D 8-20 SAND

Chart3 1&2 combo

Air Perm 98-0168c 8-20 SAND