Nuclear Waste Management Quarterly Progress Report October Through December 1980

**T. D. Chikalla
J. A. Powell**

March 1981

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NUCLEAR WASTE MANAGEMENT
QUARTERLY PROGRESS REPORT
OCTOBER THROUGH DECEMBER 1980

Compiled by
T. D. Chikalla and J. A. Powell
Nuclear Waste Technology Program

March 1981

Prepared for
the U.S. Department of Energy
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Pacific Northwest Laboratory
Richland, Washington 99352

FOREWORD

This document is one of a series of technical progress reports designed to report on radioactive waste management programs at Pacific Northwest Laboratory. These programs are funded by the Department of Energy's Office of Nuclear Waste Management. Only programs in the scope of this document that have significant, reportable results are included.

These reports are issued quarterly. The prior one in this series is Nuclear Waste Management Quarterly Progress Report July Through September 1980, PNL-3000-7.

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1. HIGH-LEVEL WASTE PROCESS DEVELOPMENT

D. E. Larson - Program Manager

The objective of the High-Level Process Development Program is twofold: 1) to process small volumes of nonradioactive and radioactive liquid wastes (commercial and defense) in laboratory-scale process equipment to define process effluent composition; to develop decontamination methods for the process effluents; and to evaluate the waste solidification processes and products; and 2) to analyze and document PNL-developed waste vitrification technology and the condition of the dismantled liquid-fed ceramic melter.

SUMMARY

Two radioactive runs have been completed to date with the laboratory-scale spray calciner/in-can melter (SC/ICM). The first run was with nonradioactive waste spiked with technetium-99 and iodine-131. The analytical results from this run are being analyzed. As anticipated, the ^{131}I volatilized extensively. Current run analysis indicates the greatest ^{131}I and ^{99}Tc removal from the process off-gas is in the venturi scrubber. The venturi scrubber is the first piece of process off-gas cleanup equipment in the off-gas system.

The second run (~9 hr) was with a Savannah River Laboratory (SRL) simulated defense-waste composition. The run was terminated when corrosive/erosive feeds apparently wore out the nozzle on the spray calciner. The nozzle had been in service over a 6-month period.

Investigation of the dismantled liquid-fed ceramic melter (LFCM) showed that the deteriorated condition of the melter drain wall was primarily due to thermal effects on the refractories. A stress analysis indicates that much of this effect on the wall may be avoided by appropriate melter design.

Results also show that the Monofrax K-3[®] corrosion mechanism in the dismantled LFCM is primarily caused by dissolution of the refractory by the glass and the formation of spinel layers on exposed refractory surfaces.

During this quarter, four reports were issued that document high-level waste vitrification process and waste-form development technology. One of these reports was the Spray Calciner/In-Can Melter High-Level Waste Solidification Technical Manual (PNL-3495), which completed on schedule a National High-Level Waste Program milestone.

LABORATORY-SCALE RADIOACTIVE SC/ICM AND EFFLUENTS

Results of the initial radioactive operation of the laboratory-scale SC/ICM have been completed and are being analyzed. The processed waste was a nonradioactive commercial acid-waste composition spiked with ^{131}I and ^{99}Tc . As expected, preliminary results indicate extensive volatilization of the ^{131}I . Some of the ^{131}I did remain in the calcine product. The highest concentrations of ^{131}I have been observed in the venturi

[®] Monofrax K-3 is a registered trademark of the Carborundum Company, Niagara Falls, New York.

scrub samples. Significant quantities were also observed in packed scrubber samples. Building effluent monitors detected ^{131}I during the week of the run, but these releases were well within safe limits.

During the second runs simulated radioactive SRL defense waste was processed through the laboratory-scale SC/ICM system for ~ 9 hr. The run was terminated earlier than expected during the planned 12-hr run when uncalcined feed was observed in the calciner cone. Apparently the corrosive/erosive SRL feed finally wore out the nozzle, preventing proper atomizing of the feed. This nozzle had been installed for a testing and service period of over 6 months. Since melter temperatures remained constant, the atomization problem was not noticed for ~ 2 hr because there was no indication that calcine was not entering the canister inside the melter. Analytical samples taken during this run are being analyzed.

A laboratory-scale nitrogen oxide destructor has been installed for nonradioactive tests to evaluate the catalytic destruction of nitrogen oxides with ammonia resulting from acidic high-level wastes. When the nonradioactive tests have been completed, radioactive tests will be initiated.

DISMANTLED LFCM EXAMINATION

The LFCM dismantled in FY 1980 is being critically examined. To date, the investigation has emphasized understanding 1) the effects of 3 years' exposure of simulated waste glass on the glass-contact refractory and 2) the nature of the extensive cracking of this refractory.

Core samples were obtained from the glass-contact refractory made of Monofrax K-3 to examine chemical effects on the brick. These

samples were investigated by optical and electron microscope techniques. Examinations have shown that the refractory is a porous solid solution of two phases, one with relatively high aluminum content and the other rich in chromium. Glass was present in the pores of each glass-contact refractory sample to a depth of ~ 3 cm. A layer of spinel crystals was found on the vertical refractory surfaces exposed to molten glass. The spinel layer varied in thickness up to 0.32 cm. A chromium gradient (the highest chrome content nearest the surface of the refractory) is present in the spinel layer exposed to the circulating glass. However, the spinel that formed in areas of stagnant pools of glass, such as in refractory internal pores, did not contain this variation in chromium content. This suggests that the waste-glass compositions processed were saturated with chromium and that improved refractory service life may be obtained by increasing the chromium content of the glass-forming materials.

An investigation of the thermal stresses to the melter is under way to reconcile the differences in cracking between the melter wall containing the glass drain and the refractory on the opposite wall. The K-3 refractory forming each of these walls was extensively cracked. Although the wall opposite the drain was intact, fist-size chunks of refractory had fallen from the drain wall to the melter floor. This study has shown that the orientation of the isotherms present in the refractory relative to the glass-contact face are very important to the integrity of the walls. In ceramic materials, cracks propagate in the direction of the principal stresses. These stresses are parallel and normal to the isotherms in the refractory. In the wall opposite the drain the isotherms are parallel to the

glass-contact face. The isotherms in the drain wall are not oriented parallel to the surface but are inclined $\sim 45^\circ$ from the surface. This effect creates a situation whereby the cracked portions of the drain wall slough off and fall to the melter floor, exposing new refractory wall material to attack by the molten glass. Redesign of the melter drain area to control thermal stresses can substantially improve refractory performance in this region.

VITRIFICATION TECHNOLOGY ANALYSIS AND DOCUMENTATION

Several documents were issued that analyze and summarize waste vitrification process and waste-form development:

- Chick, L. A. and C. Q. Buckwalter. 1980. Low Leach Rate Glasses for Immobilization of Nuclear Wastes. PNL-3522, Pacific Northwest Laboratory, Richland, Washington.
- Brouns, R. A., G. B. Mellinger, T. A. Nelson, and K. H. Oma. 1980. Immobilization of High-Level Defense Waste in a Slurry-Fed Electric Glass Melter. PNL-3372, Pacific Northwest Laboratory, Richland, Washington.
- Larson, D. E. 1980. Spray Calciner/In-Can Melter High-Level Waste Solidification Technical Manual. PNL-3495, Pacific Northwest Laboratory, Richland, Washington.
- Chick, L. A., G. L. McVay, G. B. Mellinger, and F. P. Roberts. 1980. Annual Report on the Development and Characterization of Solidified Forms for Nuclear Waste, 1979. PNL-3465, Pacific Northwest Laboratory, Richland, Washington.

Satisfactory progress is being made in issuing other documents on glass development and the SC/ICM process.

2.0 ALTERNATIVE WASTE FORMS

J. M. Rusin - Project Manager

The mission of the Alternative Waste Forms Program is to develop and evaluate selected processes and waste forms as alternatives to the reference borosilicate glass process for immobilizing high-level radioactive liquid wastes. Specific waste-form technologies being developed are glass ceramics, coatings, and matrices that are included in the multibarrier concept.

The program is a part of the overall National High-Level Waste Long-Term Management Program under the direction of the lead Savannah River Office and contributes to the 1.3 Fixation area of that program. This function contains two work elements, and the program is structured accordingly:

Work Element 1.3.1 Waste Form Development and Characterization

Work Element 1.3.2 Process and Equipment Development.

SUMMARY

Investigations of 76-68 glass incorporated in a 100% lead matrix indicated that samples annealed under vacuum do not show the same reaction zones observed under air anneals. Data suggest that the presence of oxygen or metal oxide may increase glass-metal reactions. Leach testing also indicated that metal-encapsulated 76-68 cross sections leach at a lower rate than a similar glass-only cross section.

Microstructural examination of glass matrix-encapsulated simulated waste marbles indicated little discernible reaction between the two materials after preparation. Titanium matrix-encapsulated flint glass marbles, prepared at 800°C, produced three reaction layers ~4 µm thick in total. Simulated waste glass marbles encapsulated in a titanium matrix tended to disperse in the matrix under the preparation conditions used.

Leach tests have been completed on eight carbonaceous materials in the range 200 to 300°C using deionized water in an air atmosphere. Powdered graphite has the lowest

leach rate, but none of the materials leaches at a rate more than about 10 times greater than the graphite.

The nickel sulfate-bonded graphite matrix samples received from NUKEM in West Germany were leach tested in 90°C deionized water up to a period of 28 days. Nickel is detected in the leachant, and the nickel concentration is nearly linear with (time)^{1/2}. The results correspond to a dissolution of ~10 µm of NiS in a year under these conditions.

Leach tests have been conducted on low-temperature pyrolytic carbon (PyC)-coated quartz substrates and TDS-211 glass marbles. The release of silicon was increased for the PyC-coated quartz particles. An increase in sodium, silicon, aluminum and boron dissolution was observed for the coated TDS-211 samples. The increased leaching may be attributed to surface reactions during the coating process.

Several cesium-containing materials have been neutron-irradiated to convert a portion of the cesium to ¹³⁴Cs, which then transmutes to barium with a 2-yr half-life. The materials were annealed after irradiation to

remove the neutron damage. Measurements of density, leach rate, microstructure and x-ray diffraction parameters are being made periodically to determine any effects due to the transmutations. About 4% of the cesium had transmuted to barium at the time of the most recent measurements, and essentially no changes in the above properties were found.

A hot-pressing system for remote fabrication of crystalline waste forms in air, inert gas, or reducing atmospheres, and designed for use in 324 Building hot cell (D-cell), was successfully demonstrated with "hands-on" operation in the laboratory. Five hot-pressing experiments using nonradioactive SPC-4P supercalcline powders were completed. Densities of samples hot-pressed in air at 1100°C averaged 6% greater than that of cold-pressed samples sintered in air at 1200°C.

About 100 kg of calcine were produced from simulated Savannah River Plant sludge by spray calcination for use in producing pelletized substrates. Several additives were tested to develop a formulation for pellets suitable for PyC chemical vapor deposition (CVD) coating. Mixtures of glass frits and phosphates resulted in the best-appearing pellets. Cornstarch at a 5% level was found to enhance pellet properties.

Glass marbles have been produced at a rate of 10 kg/hr on a new marble process. The process uses a 60-cm aluminum wheel that has a series of hemispherical molds around the circumference. In a separate process, glass coatings have been applied on glass marbles produced on the vibratory marble machine at a rate of 35 kg/hr. The process consists of applying a glass frit to the marble as it is being formed and then fusing the surface of the frit coating.

The quality of low-temperature CVD PyC coating is improved by lowering the concentrations of nickel tetracarbonyl. The best

coating prepared in a fluidized bed was applied at ~500°C from a reactant mixture containing 2.84 mol% acetylene, 0.002 mol% nickel tetracarbonyl, and the balance hydrogen. The coating rate was 5.5 $\mu\text{m/hr}$. The coating rate in the screw-agitated coater (SAC) under similar conditions was 1 to 2 $\mu\text{m/hr}$.

Aluminum coatings, 1 to 1.5 mm thick, have been applied to ~1 ℓ of TDS-211 glass marbles using a commercial wire gun system. The marbles were produced on the vibratory marble machine, allowed to cool for about 5 min, and then were coated in a vibrated bed for ~10 min. The aluminum-to-glass bond appears to be extremely good.

Three papers were presented, one paper was accepted for publication, and one report was issued during the quarter.

WASTE FORM DEVELOPMENT AND CHARACTERIZATION

Metal Matrix Interaction Studies - J. W. Wald

Investigations of the mechanics, kinetics, and chemical stability of metal matrix-encapsulated glass and ceramic simulated nuclear waste forms are continuing as a technical exchange with the Hahn-Meitner Institute in Berlin, Germany. The most current investigations have dealt with the encapsulation and heat treatment of PNL glass 76-68 and HMI glass MOD-102 in 100% lead and 90% lead-10% tin matrices. Initial microscopy examination of encapsulated and air-annealed specimens indicated the presence of glass-metal reaction zones as large as ~250 μm after 550°C at 140 hr. Subsequent annealing of identical samples, under the same conditions of time and temperature, with the exception of vacuum encapsulation of the test specimen, has shown no reaction zone. This result seems to imply that the

presence of oxygen or metal oxide at the glass-metal interface increases the reaction of glass and metal matrix. Similar results have been duplicated for both glasses under study.

Individual materials and unreacted 76-68 glass encapsulated in 90% lead-10% tin have been initially leach-tested following the MCC-1 type of conditions (Strachan et al. 1980). For a scoping type of leach evaluation, polished cross sections have been leached at 90°C for 14 days in deionized water at a surface area-to-solution volume ratio of 1 to 10. The intent was to examine leached surfaces by microscopy as well as solution analysis by induction-coupled plasma spectroscopy (ICP). Corrosion products formed readily on the lead and lead-tin alloys when leached under the above conditions. In both cases, the lead was found to go into solutions and crystallize on the metal surface as an apparent lead-oxide/hydroxide. The presence of 10% tin somewhat reduced the observed corrosion; however, similar behavior was observed between the two metals. Glass 76-68, when leached without matrix, exhibits a crazed, mud-flat type of surface morphology. When the glass was leached in the presence of the metal matrix (encapsulated), a similar surface morphology was observed. ICP analysis of the leachate, however, indicated a reduction of 25 to 50% in leached ion concentration such as was observed in the glass-only sample. Additional scanning electron microscope (SEM) examination of the leached surface of the encapsulated glass sample showed a high level of lead. This "plating" of lead ions on the glass surface might have been responsible for the lower leach rate.

Titanium/Glass Matrix Development - W. E. Gurwell

Metallographic work and scanning electron microscopy-x-ray energy dispersive analysis have been completed on the titanium and glass matrix samples that were fabricated and reported on last quarter. There was little discernible reaction between the simulated waste marbles and the glass matrix (Code 7570--Corning Glass Works, Corning, New York).

Reactions were observed for the titanium matrix samples. Between the titanium and the flint glass marble were three diffusion layers totaling about 4 μm in thickness. The flint glass marble was sufficiently viscous even at the 800°C fabrication temperature to infiltrate the titanium powder matrix only to a depth of 0.3 mm (about two titanium powder particles deep).

The waste glass marbles, being much more fluid, infiltrated the titanium powder matrix almost completely. However, the titanium envelope was essentially intact, having been infiltrated only slightly by the waste glass. The waste glass dissolved the titanium particle surfaces. The titanium content of the glass increased with the length of flow through the titanium metal particles. The waste glass developed a microstructure of two different precipitates in a "matrix." These waste glass precipitates were not present in the glass samples matrix.

Carbon Leaching - W. J. Gray

Leach tests have been completed on the eight materials listed in Table 2.1 using deionized water in an air atmosphere. The

TABLE 2.1. Materials Used in Leach Tests

Material	BET Surface Area, m ² /g	Form
Graphite	12	Graphite powder
GC-1000	53	Glassy carbon powder
GC-2600	37	Glassy carbon powder
PyC-SPC-2	0.097	Supercalcine beads coated with PyC
PyC-1	0.036	Beads with outer coating of PyC
PyC-2	0.019	Beads with outer coating of PyC
SiC-1	0.012	Beads with outer coating of SiC
SiC-2	0.012	Beads with outer coating of SiC

first three materials are powders; the last five are particles $\sim 500 \mu\text{m}$ in diameter. The two materials with outer coatings of silicon carbide also have inner coatings of pyrolytic carbon. A decision was made to use BET (Brunauer-Emmett-Teller) surface areas to calculate the reaction rates (leach rates) plotted in Figures 2.1 and 2.2 rather than the iodine surface areas that were used in some cases in the previous quarterly report. This was done because it was learned that iodine surface areas, when done properly, are intended to agree with the BET surface areas, and BET surface areas are more easily measured.

Results are shown in Figures 2.1 and 2.2; they are divided into two figures merely to improve the readability. Graphite exhibits the lowest leach rate, but none of the materials leaches at a rate more than about 10 times greater than the graphite. Furthermore, these rates are far lower than for many other types of materials, including alumina and vitreous silica (Gray 1980).

It was shown previously (Gray 1980) that the reaction being measured is with air rather than with the water. Therefore,

efforts are still being made to measure reaction rates in an oxygen-free system.

Graphite Matrix Materials - L. R. Bunnell

Two graphitic materials are currently being examined as candidate matrices. One of these is made from natural graphite flake bonded with NiS and is made by NUKEM in West Germany. The other is similar to the matrix used by General Atomic Company (GAC) to make HTGR fuel and is graphite flour bonded by either petroleum pitch (thermoplastic) or an artificial resin (thermosetting). Samples of NiS-bonded graphite, with and without supercalcine, have been provided by NUKEM, and GAC has produced samples of supercalcine-containing matrix.

As impermeability to water is a prime requirement for a graphitic matrix, a sensitive instrument has been assembled to demonstrate watertightness of the various candidates. The GAC-produced materials have been provided both as formed and after partial or full carbonization of the binder. The as-formed material is probably the least permeable, but its utility depends in turn

FIGURE 2.1. Reaction Rates of Carbonaceous Materials in Deionized Water in an Air Atmosphere

FIGURE 2.2. Reaction Rates of Carbonaceous Materials in Deionized Water in an Air Atmosphere

on the binder's resistance to γ -radiation. Samples were inserted into a cobalt facility for irradiation to $\sim 10^{10}$ rads, after which they will be compared with unirradiated counterparts. Watertightness and freedom from noticeable degradation will imply good performance as a matrix.

The NiS-bonded graphite containing ~ 40 vol% supercalcine is presently being leach-tested. The material containing no calcine is leached (in 90°C distilled water) at a rate that would correspond to a dissolution of the NiS binder to a depth of $\sim 3 \mu\text{m}$ in 28 days. The data are nearly linear when plotted against $(\text{time})^{1/2}$, which would correspond to a dissolution of $\sim 10 \mu\text{m}$ of the NiS in a year under these conditions. The

residue after dissolution of all binder would be graphite flakes at 65% TD, which would still constitute a matrix, if permeable to water.

Coated Particle Leach Tests -

C. Q. Buckwalter

Coated particle samples have been leached according to the guidelines provided by the Materials Characterization Center procedure MCC-1 Static Leach Test in deionized water (Strachan et al. 1980). The more durable samples, such as ZrO_2 , are being leached hydrothermally at 150°C .

Quartz substrates and TDS-211 glass marbles CVD-coated with low-temperature PyC have

been leach-tested. The carbon coating in both cases increased the levels of silicon dissolution. Dissolution was about doubled for sodium, aluminum, silicon and boron from the TDS-211 glass marbles as shown in Table 2.2. The increase may be attributed to surface interactions during the coating process.

Zirconium-oxide substrates were PyC-coated by GAC. Due to the extreme durability of ZrO_2 , the coated particles were hydrothermally leached at 150°C. After 14 days, no zirconium has been detected in solution.

Transmutations - W. J. Gray

The second round of post-irradiation examinations has been essentially completed on samples irradiated in the HFIR^(a) for 3 months beginning in January 1979. Final measurements of the ^{134}Cs activity in the samples show that only 10 to 12% of the cesium was converted to ^{134}Cs rather than the 16 to 21% expected. It appears, however, that some of the glasses must have lost some cesium during preparation. Therefore,

(a) The high-flux isotope reactor at Oak Ridge National Laboratory.

archive samples of all the materials are being chemically analyzed to determine the actual amount of cesium present. This will probably increase the calculated percentage of cesium that was converted to ^{134}Cs somewhat, but not up to the expected 16 to 21%. It will also slightly change the leach results given here in Table 2.3.

Results of density measurements were reported in the January-March 1980 quarterly report (Platt and Powell 1980). Little if any change in density was observed. Optical and scanning electron microscopy work has been completed. All samples appear unchanged from the microscopy results obtained in May 1979. X-ray diffraction results have been totally unsatisfactory. Perhaps more meaningful results can be obtained when the new shielded x-ray diffraction unit at PNL is completed about April 1981.

Results of the leach tests are shown in Table 2.3. After the leach solutions were analyzed for cesium, they were passed through ion-exchange columns to remove the cesium, thereby reducing the radioactivity sufficiently for the solutions to be analyzed further by ICP. The ion-exchange treatment interferes with the analysis of alkaline and alkaline-earth elements. Aside from these,

TABLE 2.2. Leach Results for PyC-Coated TDS-211 Glass Marbles^(a)

Sample	Element Leached, $\mu g/cm^2$			
	Si	Na	B	Al
Uncoated ^(b)	4.4 $\pm$ 0.4	3.3 $\pm$ 0.3	0.71 $\pm$ 0.07	0.34 $\pm$ 0.03
PyC-coated ^(c)	9.0	5.0	1.3	0.58
PyC-coated ^(d)	9.0	6.5	1.4	0.60

(a) 90°C 28 days deionized water, SA/SV = 1:10.

(b) 3-sample replication

(c) Screw-agitated coater

(d) Fluidized-bed coater

TABLE 2.3. Percentage Loss of Elements During Leach Tests of HFIR Samples^(a)

Material	B		Al		Si		Mo		Cs	
	6/28/79	6/5/80	6/28/79	6/5/80	6/28/79	6/5/80	6/28/79	6/5/80	6/28/79	6/5/80
1 Simulated Waste Glass	ND ^(c)	0.78	-- ^(d)	--	0.92	0.88	0.15	ND	0.39	0.64
	ND	1.08	--	--	0.35	1.05	0.09	ND	0.46	0.62
	ND	0.94	--	--	0.43	1.07	0.09	ND	0.41	0.74
2 High Cs Glass with Cm	10.6	20.3	--	--	4.8	6.9	5.8	12.8	16.1	17.7
	19.9	15.9	--	--	7.9	6.9	11.8	9.0	25.4	14.3
	40.4	8.9	--	--	10.6	3.4	31.9	6.7	27.5	9.2
3 High Cs Glass	28.9	14.2	--	--	7.3	6.7	19.0	7.9	25.7	14.9
	26.3	12.3	--	--	6.6	4.8	18.1	7.9	24.4	13.6
	92.0	17.1	--	--	20.8	8.1	62.3	10.7	31.4	18.3
4 High Si Glass	ND	0.34	ND	ND	0.13	0.12	--	--	0.38	0.33
		0.39		ND		0.15		--	0.33	0.35
	ND	0.66	ND	ND	0.13	0.17	--	--	0.26	0.29
5 High Al Glass	ND	0.64	0.16	ND	0.22	0.79	--	--	0.32	0.28
	ND	0.14	0.27	ND	0.49	0.47	--	--	0.35	0.35
	ND	0.14	1.2	ND	0.58	0.57	--	--	0.70	0.41
7 Pollucite	--	--	0.21	ND	0.53	1.2	--	--	1.25	2.25
	--	--	0.17	ND	0.57	1.15	--	--	1.66	1.50
	--	--	0.26	ND	1.0	1.1	--	--	1.52	2.04
8 Supercal- cine ^(b)	--	--	0.97	0.80	3.2	2.2	0.76	0.08	2.91	0.85
	--	--		1.20	2.8	2.2	0.60		3.16	0.42
	--	--	0.84	0.70	3.3	2.3	0.77	0.10	2.95	0.49

(a) Leach tests were conducted for 7 days at 90°C in deionized water.

(b) Powder samples.

(c) ND element not detected in leach solution.

(d) Element not present in sample.

the only elements detected in the leach solutions are those listed in Table 2.3.

Clearly there is considerable scatter in the data. Despite the scatter, however, it is clear that transmutations are not greatly affecting the leach rates. The relatively large apparent reduction in the leach rates of molybdenum and cesium for material No. 8 must be viewed with skepticism unless results from the third round of leach tests (to be conducted about June 1981) confirm the trend.

Hot-Cell Fabrication of Crystalline Waste Forms - D. W. Brite

A hot-pressing system for remote fabrication of crystalline ceramic waste forms in air, inert gas, or reducing atmospheres has been successfully demonstrated with "hands-on" operation in the laboratory. The system was designed for use with the hydraulic laboratory press that will also be used for cold-pressing pellets of the same material. Following the initial series of demonstration runs, in which five hot-pressing experiments using nonradioactive SPC-4P supercal-cine powders were completed, the equipment was transferred to 324 Building for additional out-of-cell testing and modification before installation in the hot cell (D-cell, 324 Building).

Three of the samples were hot-pressed in air in an alumina die. Prepressed pellets were surrounded with granular-fused ZrO_2 in the die. A diamond core drill was used to cut through the ZrO_2 annular layer and remove the pellet after hot-pressing was completed. A layer of ZrO_2 particles remaining imbedded in the pellet surface was removed using a belt sander prior to determination of density by immersion in isopropyl alcohol. The alumina die was suitable for reuse upon removal of the loosely adhering ZrO_2 .

The remaining two hot-pressed samples were fabricated using a graphite die in an argon atmosphere. The argon atmosphere was provided by purging the furnace with a flow of 5 to 7 cfh argon. Some inleakage of air occurred, as evidenced by a reduction of ~ 0.005 in. in the exposed portion of the initially 0.5-in.-dia lower punch. However, no oxidation was detected on the internal surface of the die or on the portion of both punches contained within the die.

The experimental conditions used in these hot-pressing experiments, the density measurements, and the microstructural observations are shown in Table 2.4. For comparison, samples cold-pressed from this same SPC-4P powder and air-sintered at $1200^\circ C$ for 2 hr had an average density of 3.99 g/cm^3 . X-ray diffraction analysis of the first four samples indicated that all samples appeared to be crystallized to about the same extent, which was less than 50% of what is generally seen in samples cold-pressed and air-sintered at $\sim 1200^\circ C$ for 4 hr. Apatite and fluorite phases are well developed. Scheelite is possibly present, while the presence of monazite and pollucite is questionable. Higher temperatures and/or longer processing times are indicated in order to obtain all the desired supercal-cine crystalline phases.

Hot-Cell Demonstration - L. L. Petkus

Efforts are under way to fabricate pellets of the supercal-cine waste form from high-level waste. The fabrication will be performed in D-cell of the 324 Building radiochemical cell. In this reporting period, the cell has been cleaned out and prepared to receive the fabrication equipment. Drafts of the Run Book and Run Plan are being reviewed for cold checkout, and the equipment is being tested for operability.

TABLE 2.4. Hot-Pressing Conditions, SPC-4P Supercalcine

Sample No.	Die Material	Atmosphere	Outgassing		Hot Pressing			Pressure During Cooling	Hot Pressed Density, g/cm ³	Microstructural Appearance
			Temp., °C	Time, hr	Temp., °C	Pressure, psi	Time, hr			
HPA-1	Al ₂ O ₃	Air	--	--	1130°C	5000	1/2	no	4.23	Slight porosity in central area near one end only. Lenticular shaped low-porosity zones in this area.
HPI-1	Graphite	Argon	--	--	1100°C	5000	1	no	4.11	Thin, low-porosity-shell laminar cracks, possibly due to swelling upon release of pressure at temperature.
HPA-2	Al ₂ O ₃	Air	800-850	1	1100°C	5000	1 1/2	yes	4.26	Slight porosity in central area. Lenticular shaped low-porosity zones in this central area.
HPI-2	Graphite	Argon	810	1	1100°C	5000	1 1/2	yes	4.27	Low-porosity shell. Very slight porosity in central area.
HPA-3 ^(a)	Al ₂ O ₃	Air	800-850	1	1100°C	5000	1 1/2	yes	4.21	Not available to date.

(a) Heated in air at 800°C for 2 hr before loading into hot-pressing die.

and remotability. An informal safety assessment was performed which concluded that the installation was not a significant change from present activities and presented no unresolved safety questions.

PROCESS AND EQUIPMENT DEVELOPMENT

SRL Pellet Development - H. T. Blair and R. L. Treat

The objective of this work is to develop spherical ceramic substrates containing Savannah River defense wastes that are suitable for the application of low-temperature PyC coatings. These pellets must meet the following criteria: be produced using a disc pelletizer; be 1/4 in. or larger in diameter; be sufficiently tough to preclude attrition during coating; be dense; contain 70% or more waste; and be sintered at a sufficiently low temperature to minimize the volatility of cesium.

About 104 kg of calcine were produced from simulated Savannah River Plant sludge by spray calcination for use in producing the pelleted substrates. This calcine includes prescribed quantities of cesium, strontium, cerium and neodymium that will serve as tracer elements in comparative leach studies. These studies will be conducted by Savannah River Laboratory to aid in the selection of promising waste forms for further development.

An extensive developmental effort was undertaken to produce pellets having the desired properties. The following conclusions were reached:

- A low-softening-point glass frit was found to be the necessary base additive in providing suitable pellet properties. Glass frits tested included SRL Frits 211 and 131, barium metaphosphate, aluminum meta-
- phosphate, and an 84% lead oxide frit. About 25 to 30% frit on a total weight basis was required. Pellet densities range between 2.5 and 3.5 g/cc, with the denser pellets produced using the lead frit.
- Certain soluble glass formers--sodium orthophosphate, sodium silicate, and borax--were found to reduce the required sintering temperature when 5 wt% was added. Pellet bloating was observed, however, when sodium silicate and borax were used; no bloating was apparent with sodium orthophosphate.
- Cornstarch admixed with the other dry additives was found to improve pellet formation properties and the homogeneity of the final pellet product. At least 5% cornstarch was required to produce suitably strong green pellets. The use of cornstarch allows the use of water alone as the liquid addition during pelletizing. Other liquids tested, such as phosphoric acid, nitric acid, sodium hydroxide, and various salt solutions, seemed to have a higher surface tension than water as they did not wet the dry mix as well. Uneven wetting caused areas of variable density and toughness to be formed within individual pellets.
- Heat-treating the calcine to remove volatile constituents prior to pelletizing did not improve pellet quality.
- Milling of the calcine and additives mixture was found necessary in producing dense and homogeneous pellets.
- Sintering temperatures above 900°C were necessary to produce high-quality pellets. The highest quality pellets were produced between 1000 and 1200°C, depending on the additives used. Recipes have been adjusted to permit good-quality pellets to be produced at ~1000°C, regardless of the

low-softening-point frit used. Good-quality pellets can generally be produced over a 30°C range.

- Dense alumina balls were found to provide the best base on which to sinter green pellets. Sintering temperatures are limited by the tendency of the pellets to stick together and to the alumina balls.

Process and Equipment Development -

S. C. Slate and M. A. McLean

The objective of this work is to investigate new marble making methods and new coating systems. Tests were conducted this month to show the feasibility of producing marbles with a gobbing wheel and of coating waste marbles with an inert glass frit.

The new marble process uses an aluminum wheel that is about 60 cm in diameter. The wheel is vertical and has a series of hemispherical molds around the outside edge. These molds break up a continuous stream of molten glass and form the glass into marbles 1 cm in diameter. The marbles remain in the wheel until they cool enough for handling. Marbles were produced at 10 kg/hr. Further tests of the wheel are planned to obtain more data on its operation. This concept can be easily scaled up for higher pouring rates by increasing the wheel diameter and using additional cooling.

The new coating process applies an inert glass coating to a waste marble. The process consists of applying a glass frit to the marble as it is being formed and then fusing the surface of the frit coating. Marbles were produced and coated at a rate of 35 kg/hr. The coatings were about 1 mm thick and had some porosity. Additional work is planned to improve methods for applying the frit, to improve the fusing operation, and to characterize the coating.

Low-Temperature PyC Coatings -

M. F. Browning, R. W. Kidd and B. L. Janco (BCL)

Progress was made in the effort to increase the PyC coating rate and at the same time keep the coating quality at acceptable standards or above. The coating rate was studied as a function of acetylene concentration, different catalysts, nickel carbonyl concentration, retention time and hydrogen/argon ratio. In general, coating rates were found to increase with acetylene, nickel carbonyl, and hydrogen concentration. It has been determined, however, that lower concentrations of nickel tetracarbonyl than used in earlier tests could be used to improve coating quality and still maintain a relatively good coating rate. The best coating prepared in a fluidized bed was applied at ~500°C from a reactant mixture consisting of ~2.84 mol% acetylene, 0.002 mol% nickel carbonyl, and the balance hydrogen. The coating rate was 5.5 µm/hr. These coating conditions were adapted for use in the SAC with significant improvement in coating quality over that obtained in earlier work. The coating rate, however, was only 1 to 2 µm/hr.

SPC-4E was sintered and classified to produce a substrate suitable for several types of coatings. The coatings will be characterized at PNL as to leach resistance, with the objective of providing comparative coating data to Savannah River Laboratory in April.

Wire Gun Demonstration -

K. H. Oma and L. E. Peterson

A wire gun was set up and operated for the purpose of laying down metallic coatings on glass and ceramic waste forms. Coatings applied by this technique could serve to

separate waste particles during matrix encapsulation and to prevent an increased waste form leach rate due to wicking.

The wire gun operates by feeding the coating material in a wire form concentrically through an oxyacetylene flame. Air is blown with the flame to atomize the wire as it melts and to propel the molten material to a substrate.

A coating of high-purity aluminum 1.0 to 1.5 mm thick was applied to a 1 liter batch of TDS-211 glass marbles. The marbles were produced on a marble machine, allowed to cool about 5 min, and then were coated in a vibrating bed for ~10 min. Several coated marbles were broken using both a hammer and a hydraulic press. The aluminum-to-glass

bond was extremely good and did not appear to separate at any point even though the glass had been severely broken and fragmented.

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3. NUCLEAR WASTE MATERIALS CHARACTERIZATION CENTER

R. D. Nelson - Program Manager

The objective of the Materials Characterization Center (MCC) is to ensure that qualified materials data are available on waste materials. This objective is to be met by 1) developing standard test methods, 2) testing waste materials by the standard methods, and 3) publishing the test methods and data, after review and approval by the Materials Review Board (MRB), in a Nuclear Waste Materials Handbook.

SUMMARY

The MCC-1 Static Leach Test was resubmitted to the Materials Review Board and has been expanded to include detailed instructions for preparing specimens for each of four waste-form categories and to define five specific test matrices. A round robin using one of these matrices is under way. The MCC-6 Alpha-Decay Effects in Radioactive Waste Forms Test has also been submitted to the MRB for approval. The purpose of this test is to accelerate property changes so that they can be measured in experimentally practicable times. In addition, the MCC-11 Tensile-Strength Test for use with brittle waste forms was submitted to the MRB.

The Workshop on Compositional and Microstructural Analysis of Nuclear Waste Materials held in November was attended by 41 participants from 18 laboratories. As a result of this workshop, an analytical round-robin test of reference specimens is under way to identify any significant discrepancies in procedures and to provide data on the relative precision, detection limits, and data bias of analytical methods currently used by participating laboratories.

PROGRAM MANAGEMENT - R. D. Nelson, W. A. Ross, and J. E. Mendel

Presentations concerning the MCC and its development of test methods were made to the Materials Research Society, the American Geophysical Union, and the Conference on the Leachability of Radioactive Solids. In addition, the status and plans for MCC test methods and property measurements were discussed at meetings with high-level-waste contractors and the Alternative Waste Form Peer Review Panel.

WASTE-FORM MATERIALS CHARACTERIZATION - J. E. Mendel, J. L. Daniel, M. D. Merz, and D. M. Strachan

The MCC-1 Static Leach Test was revised and resubmitted to the MRB for approval. This revision incorporates changes that reflect comments received during the initial review of MCC-1 by the MRB Procedures Panel. In particular, existing waste forms were divided into four categories based on their differing specimen preparation requirements (Table 3.1).

TABLE 3.1. Waste-Form Categories

Category	Specific Examples
Inorganic monoliths	Glasses, cements, cermets, crystalline ceramics
Coated pellets	Coated glass marbles, crystalline beads
Pellets in matrices	Glass marbles or crystalline beads in metals, graphite, ceramic matrices
Organic forms	Bitumen, hardened resins

In addition, five specific test matrices were defined to meet objectives ranging from rapid evaluation to more comprehensive understanding of long-term behavior. These matrices were as follows:

- Matrix A - 7 days, 90°C
- Matrix B - 28 days, 90°C
- Matrix C - 28 days, 40, 70, and 90°C
- Matrix D - Long term, 90°C
- Matrix E - Long term, 40, 70, and 90°C

A round-robin test of MCC-1 using Matrix B is under way to provide data for a statistical analysis of the results from different laboratories relative to specimen preparation, leachants, test procedures, and analytical techniques. Sample materials include National Bureau of Standards (NBS) borosilicate glass, PNL 76-68 waste glass, and basalt.

A draft of MCC-6 Alpha-Decay Effects in Radioactive Waste Forms Test was submitted to the MRB. This test method is used to prepare waste-form specimens in which the effect of alpha-emitting radionuclides is accelerated so that changes in density and leach rate induced by the alpha decay can be measured in experimentally practicable times. Specimens prepared using MCC-6 are also suitable for the measurement of alpha-decay-induced changes in such properties as microstructure, tensile strength, and stored energy. Specimens of simulated radioactive waste forms are doped with short-lived alpha-

emitting actinides. Generally, ^{238}Pu ($t_{1/2} = 87.7$ yr) is used for transuranic and defense high-level waste (HLW) forms and ^{244}Cm ($t_{1/2} = 18.1$ yr) is used for commercial HLW forms. Specimens are prepared in which either 1) the accumulated dose is 5×10^{18} alpha decays/cm³ or 2) the accumulated dose is equivalent to that the waste form will receive in 1×10^6 yr.

The MCC-11 Tensile-Strength Test, which is used to measure the static tensile strength of brittle nuclear waste solids, was submitted to the MRB for approval. In this test, a right-circular cylinder of the waste solid is loaded between two hardened, parallel bearing blocks, one of which is moving at a constant speed relative to the other. The load is applied diametrically, with the flat surfaces of the specimen being parallel to the applied load (Figure 3.1). As the moving bearing block applies an increasing load, the resultant stress eventually increases to the fracture strength of the material and the specimen splits along the vertical diameter, usually with subsidiary fracture at other locations. The fracture tensile strength is calculated from the measured maximum load by Equation (1).

$$T = 2P/\pi dt \quad (1)$$

where P = applied force at initiation of fracture

d = specimen diameter

t = specimen thickness.

FIGURE 3.1. Diametral Test Specimen and Apparatus

The data obtained using MCC-11 will be useful for ensuring that waste forms can withstand stresses anticipated during handling, stresses caused by thermal gradients, and stresses that exist in the waste repository.

The MCC conducted the Workshop on Compositional and Microstructural Analysis of Nuclear Waste Materials November 11 and 12 to evaluate the various analytical methods being used by the different laboratories to study the performance of nuclear waste forms. The 41 participants representing 18 laboratories in the United States and Canada identified the analytical methods used in the different laboratories, discussed areas of concern, listed specific standards and reference materials currently in use, and recommended ways to verify interlaboratory comparability of data.

The major conclusion of the workshop was that analytical round-robin tests of reference specimens should be conducted either prior to or concurrently with the MCC-1 round robin. Such an analytical round robin

is now under way. The laboratories will use their respective analytical procedures on three kinds of reference materials. These are 1) three synthetic solutions containing different proportions of elements commonly found in leach test solutions, 2) a leachate resulting from an accelerated test applied to PNL 76-68 glass, and 3) a simulated waste-glass solid. Results are expected to reveal any significant discrepancies in procedures and provide information regarding the relative precision, detection limits, and data bias for methods currently used by participating laboratories.

Other conclusions of the workshop were as follows:

- Most laboratories are not sufficiently evaluating the statistical significance of analytical data.
- The analytical methods to be used in MCC test procedures should not be specified; this will permit each laboratory to use its preferred methods. However, similar results from analysis of appropriate reference materials must be demonstrated.
- Since there are currently no certified materials entirely suitable for use as references to verify analytical procedures for nuclear waste materials, other generally available NBS standards should be used to check basic methods until specific reference materials are available.
- Surface analysis methods are of increasing importance in predicting long-term behavior of highly stable waste forms.
- Analytical data submitted to the MCC should always include a current analysis of the best available reference material or standard and a statement of the analytical precision for each element reported.

In other activities, initial testing of a shielded x-ray diffractometer (SXRD) was completed. Results showed good resolution of spectrum data (Figure 3.2) and a sensitivity comparable to that of a nonshielded commercial XRD.

A report from Effects Technology, an MCC subcontractor, emphasized the need to use a drop tower in a dynamic-strength test for brittle waste forms. Such a drop tower is being installed and will be used in the development of the MCC-10 Impact Test.

FIGURE 3.2. Performance Test of Shielded X-ray Diffractometer. The pattern of the SXRD compares very closely with those of the unshielded XRD and the "ideal" spectrum.

4. TRU WASTE IMMOBILIZATION

C. R. Palmer - Project Manager

W. A. Ross - Associate Project Manager

The objective of this project is to conduct a comparative assessment of alternative immobilization systems for selected transuranic wastes and to recommend the most promising technology for development and demonstration.

SUMMARY

This quarter's activities have focused on the details of the comparative assessment, including the assessment model, the experimental methods to conduct leach tests and their interpretation, and preparation for the cost estimates. Tests to determine the feasibility of producing crystalline forms were started, and an assessment of the role of cracks in leaching was completed.

CRYSTALLINE TRU WASTE FORM FEASIBILITY -

R. P. May, R. O. Lokken, J. L. Ryan,
L. A. Chick, and G. H. Bryan

A scoping study has been outlined and testing implemented to determine the feasibility of forming desirable actinide-containing phases in typical TRU waste. Samples of reference blended transuranic sludge and ash (TBW-R) (Platt and Powell 1980) have been mixed with rare earths and alumina, phosphate, and/or titanate additions and spiked with 0.1 wt% ThO₂. The melted and slow-cooled samples are now undergoing phase characterization. The presence of monozite or other stable phases containing significant thorium will be an indication of the potential ability of producing a crystalline TRU waste form.

A study has been completed on sintering pure waste. Cold-pressed pellets of pure

TBW-R waste were sintered for 2 hr at temperatures from 900 to 1100°C for times ranging from 5 min to 24 hr. The maximum observed crystallinity was about 40 wt%. The principal crystalline phase observed above 950°C was hematite (Fe₂O₃); this is not surprising since Fe₂O₃ comprises 20 wt% of the waste. At 1000°C, hematite reaches half its maximum content at 45 min and approaches an equilibrium level at about 3 hr. Pseudobrookite (Fe₂TiO₅) is also formed above 950°C and is generally present at about one-half the concentration of hematite. At 1000°C, pseudobrookite reaches half its maximum observed concentration at 2 hr and reaches its maximum observed concentration at 24 hr (the longest time tested). There appear to be two more crystalline phases, which are not yet identified, formed in these samples. Above 950°C, they contribute <10% of the total crystallinity, but become the major phases at 900°C.

COMPARATIVE ASSESSMENT MODEL - D. W. Fraley, R. L. Engel, and C. R. Palmer

The utility theory approach and assessment model developed during FY 1980 were critically reviewed to ensure that they remain consistent with project objectives and to identify any modifications needed to complete the assessment within time and budget constraints. A decision was made to

expand the model's ability to accept more attributes, allowing the assessment to be performed with natural rather than proxy attributes (for example, "actinide leach rate" and "matrix leach rate" instead of "radio-nuclide confinement"). This expanded capability was accomplished during the quarter. We decided to perform an initial assessment using a decision panel of PNL staff members. This assessment will serve to test the methodology using comparative waste form and process data obtained this fiscal year, and it will be followed by an assessment with a panel of external experts next year if results warrant. A work plan to perform the initial assessment was developed.

COMPARATIVE STUDY - W. A. Ross, C. R. Palmer, G. H. Bryan, L. A. Chick, and R. O. Lokken

The leach-testing matrix for the six reference waste forms has been designed, and agreement has been reached with the Materials Characterization Center (MCC) on their performing the 90°C MCC-1 leach tests on the samples. Since the MCC-1 leach test has not been approved by the Materials Review Board, the current draft of the test method will be used to allow completion of the tests this fiscal year. This project will complete the 40°C MCC-1 leach testing. About 35 samples of each form will be tested with testing times out to 6 months.

In preparation for the leach tests, the TRU project is participating in the MCC-1 round robin. This will provide a reference between various parties doing leach testing. The tests are under way and will be completed in January and results reported to the MCC.

Additional characterization tests for mechanical and thermal behavior have been

selected, and testing of these properties will begin next quarter along with basic chemical and microstructural characterization of the samples.

STATIC LEACHING OF PLUTONIUM-BEARING WASTE FORMS - G. H. Bryan, C. R. Palmer, and R. E. Thornhill

Specimens of hydraulic cement and borosilicate glass (two of our six comparative-study waste forms) containing plutonium-bearing sludge and ash (TBW-R obtained from Rocky Flats) have been leached up to 28 days in deionized water at 90°C, using the draft MCC-1 procedure. Cement (portland II) samples were prepared with 35 wt% waste as-received, as well as with waste that had previously been calcined at 800°C to create a fired plutonium oxide. Borosilicate glass, designated 80-207 (Chikalla and Powell 1980), was prepared at a 50 wt% loading.

Normalized losses based on plutonium were compared for the two sets of cement samples to observe whether any advantage was gained through calcination. No significant differences between the sets were observed for any leach period; it was noted, however, that the plutonium solution concentration for periods greater than 3 days remained constant at about 8×10^{-11} moles/l, which might indicate that the solubility limit had been reached.

Our earliest leaching of TRU glass had also suggested a solubility constraint. Rai and Strickert (1980) reported that leaching of plutonium from doped glass beads proceeds as though the controlling solid phase is PuO_2 . Extrapolation of crystalline PuO_2 solubility data (Rai et al. 1980) to the pH

region of interest for our glasses (~ 9.5) yields a predicted maximum concentration of about 1×10^{-10} moles/l, which is the concentration we had observed in the earlier tests, within analytical error.

To test the PuO_2 solubility hypothesis, we conducted a series of short-term static leach tests with glass 80-207. These tests were based on the MCC-1 procedure: static deionized water at 90°C , leachant volume to sample surface area (V/SA) ratio of 0.1 m, and time periods from 1 to 28 days. At the completion of each test the leachate was acidified and analyzed for plutonium and americium using the extraction/scintillation counting method discussed below. Figure 4.1 illustrates the acidified-leachate plutonium concentration versus time (americium results are not yet available). Note that in all tests the pH was between 9.1 and 9.5. It is also important to note that the leachates were not filtered before acidification and

analysis, so that the quantity present includes any polymeric or insoluble species that formed after being released from the glass. Nevertheless, the data suggest that a maximum concentration is limiting the release, and the concentration may indeed be the solubility limit of PuO_2 . To better understand these data, attempts will be made to measure the PuO_2 solubility limit in the higher pH region, and radioanalyses will be performed on filtered unacidified leachates.

ANALYSIS OF ACTINIDES IN TRU WASTE FORM LEACHATES - C. O. Harvey, F. P. Roberts, G. H. Bryan, and R. E. Thornhill

Analysis of our initial leachates for determination of plutonium and americium had been accomplished by alpha-energy analysis of 0.5-ml samples dried on stainless steel planchettes. While qualitative results were

FIGURE 4.1. Plutonium Concentration in Unfiltered Acidified Leachates from Leaching of Glass 80-207 in Static Deionized Water at 90°C (V/SA = 0.1 m)

obtained, it became apparent that concentrations were too low for analysis with acceptable statistical confidence. Alternative analytical methods were reviewed with respect to certain criteria. Some of the more important considerations were the precise independent determination of americium and plutonium at concentrations as low as 10^{-11} moles/l, the ability to perform such analysis in leachates of high ionic strength (e.g., salt brine), and the ability to analyze a large number of leachates (e.g., 400 per year) quickly and inexpensively.

We have tentatively selected a simple extraction/scintillation approach originally developed for analyzing samples of animal origin (Keough and Powers 1970). The method utilizes direct extraction of plutonium from the acidified leachate into a toluene solution of di(2-ethylhexyl) phosphoric acid and scintillators. Liquid scintillation counting is performed with both phases present in the vial. Americium is determined separately by counting the extraction raffinate for the 60 keV gamma. Uranium (if desired) will be determined by fluorimetry.

Five short experiments were initiated during the quarter to verify the suitability of this analytical method for our leachates. Questions to be resolved by these experiments include the precision of the extraction/scintillation procedure for low plutonium concentrations, the effectiveness of leachate acidification and rinsing techniques in removal of actinide plate-out, and the extraction efficiencies for the several plutonium species which may be present. Regarding the latter uncertainty, it may be necessary to adjust the plutonium oxidation state prior to extraction. These experiments will be completed early in the second quarter.

LEACHING OF CRACKED MONOLITHS - J. M. Perez and J. H. Westsik, Jr.

One concern regarding the comparison of monolithic and pelletized waste forms has been the effect of cracking in monoliths (due to thermal shock or mechanical stress) on their leaching behavior. A common conservative evaluation of the effects has been to assume the total surface area available for leaching equals the sum of the exterior monolithic area plus all cracked surfaces. A preliminary series of static leaching experiments were conducted on borosilicate glass pellets arranged so that the effects of crack width and the ratio of cracked surface area to total area could be examined. The details of the study were reported at a recent leaching conference and will be described in the proceedings (Perez and Westsik 1980). In general, it was found that leaching from cracks is less significant than that from outer surfaces due to mass transport constraints, and that leaching from very tight (near-zero width) cracks is effectively nil. It is, however, still possible that cracks of critical dimensions may accelerate leaching due to localized pH effects.

PROCESS EVALUATION - C. L. Timmerman and R. L. Treat

A cost and engineering evaluation is being undertaken to evaluate the selected TRU waste form processes. A description of the reference processes based on the Rocky Flats combined ash and sludge wastes in the amount of 190,800 kg/yr was published (Timmerman 1980). As a part of the description, an evaluation of the TRU waste loading within a container, the container volume per

day, and the number of containers per day were estimated and are shown in Table 4.1. This information and the facility process equipment layouts will be given to Kaiser Engineers for development of a cost estimate for each process, which will be a significant part of the process and product evaluation being conducted this year.

A criticality analysis was performed on the borosilicate glass and cement waste forms processes. No criticality problems exist with these or with any of the waste forms processes in light of the plutonium concentrations present in the TRU wastes.

TABLE 4.1. TRU Waste Loadings and Process Rates

Process	Waste Loading in Waste Form, wt%	Waste Loading in Container, wt%	Container Processing Rate, ℓ /day	Containers/ day ^(a)
In-can melting	50	38.3	460	0.6
Joule-heated melting	50	48.0	530	2.7
Glass marble	50	46.2	1060	5.3
Cast cement	25	23.6	2280 ^(b)	11.4 ^(b)
Pressed cement	35	31.8	3260 ^(b)	16.3 ^(b)
Cold-pressed sintered ceramic	33	30.4	1920	9.6

(a) All processes use a 55-gal drum container except the in-can melting process, which uses a canister 0.6 m dia x 3 m tall.

(b) Process rates based on 215 days/yr versus 300 days/yr for other processes.

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5. TRU WASTE DECONTAMINATION

R. P. Allen - Project Manager

The objective of this program is to develop electropolishing and related metal cleaning and finishing techniques into an integrated large-scale decontamination system capable of decontaminating large volumes of TRU- and other surface-contaminated solid waste.

SUMMARY

The process demonstration work continued with the sectioning and decontamination of a TRU-contaminated glove box. This represented the first combined use of the plasma arc torch and double-cut hydraulic shear to section the metallic material from a glove box. A pilot-scale demonstration of the vibratory finishing decontamination of more than 32,000 lb of uranium-contaminated molybdenum was completed. Significant progress on installing the glove box line for use with the vibratory finishing decontamination system has been made since the labor-management dispute was resolved at Hanford. Monte Carlo neutronic calculations were completed for the evaporator holding tanks and 55-gal drums of solid neutralized electrolyte, and calibration curves were prepared for the ^3He neutron detector. The manual acquisition of criticality safety control data was demonstrated using this ^3He neutron detector. Transfer of advanced decontamination technology to the Federal Republic of Germany was initiated.

PROCESS DEMONSTRATION

Substantial progress was made in the process demonstration work during this reporting period. Routine integrated operation of

the disassembly, sectioning, and decontamination systems continued with the processing of another TRU-contaminated glove box. A pilot-scale demonstration of the vibratory finishing decontamination of more than 32,000 lb of uranium contaminated molybdenum was completed. Significant progress has also been made on installation of the glove box line that will be used with the vibratory finishing decontamination system.

A TRU-contaminated glove box with 128 ft² of contaminated surface area was disassembled; sectioned using circular and reciprocating saws, a plasma arc torch, and a hydraulic shear; and decontaminated to non-TRU levels using the vibratory finisher. The decontaminated material and components included Plexiglas® from the glove box panels, the plastic glove ports, the Hypalon® gloves, and the stainless steel from the frame. The only major component of the glove box not decontaminated was the high-efficiency particulate air (HEPA) filter. The glove box was ~48 in. high, 48 in. deep, and 72 in. long. It was constructed of a stainless steel frame with a stainless steel back, floor, and sides, and a Plexiglas front panel.

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The metallic portions of the glove box were sectioned into strips ~6 in. wide using a hand-held plasma arc torch. These strips were then sectioned into 6-in. squares using the double-cut shear, which had been installed in the sectioning/pretreatment facility earlier (PNL-3000-4). This represents the first integrated operation of the plasma arc torch and shear for the sectioning of metallic glove box material.

Two significant problems were encountered during the processing of this glove box. The first was the fixing of loose contamination inside the box to minimize airborne contamination while the box was being disassembled and sectioned. The hand-held spray bottles used to apply the fixative to the contaminated surfaces of the glove box proved inadequate because this glove box was larger and more contaminated than those processed previously. A new system for applying fixatives to the inside of glove boxes was designed to remedy this. The system consists of an air compressor and pressurized reservoir that are located outside the glove box and a spray wand that is used inside by means of one of the gloves. The contamination control problem was increased by the HEPA filter, which had been left installed in the glove box and continued to release contamination until it was finally removed and bagged out of the glove box. This indicated that the HEPA filter should be removed or at least sealed early in the processing of a glove box.

The other problem encountered with this glove box was that it was coated with a tough, abrasion-resistant film, probably a clear epoxy, which was not removed by standard vibratory finishing techniques. The film was finally removed by pretreating with methyl chloride, which softened the film enough to permit removal by the vibratory

finisher. This was a very successful solution for the metallic material from the glove box but less so for Plexiglas. Although the methyl chloride removed the film and surface contamination from the Plexiglas it may have melted it somewhat and possibly caused entrainment of contamination into the surface. Because of this, additional pretreatment methods will be evaluated for removing epoxy coatings from Plexiglas.

A pilot-scale demonstration of the decontamination of 32,000 lb of small pieces of uranium-contaminated molybdenum (Figure 5.1) by vibratory finishing was completed. More than 600 lb of molybdenum could be decontaminated in a single 1-hr load with contamination levels typically reduced from 40,000 dis/min to <1000 dis/min. The decontamination was performed in a 12-ft³ annular vibratory finisher using 0.25-in., cone-shaped steel media and a 10% sodium hydroxide solution for the compound. Prior studies (PNL-3000-6) had indicated that vibratory finishing with ceramic media is an effective method for decontaminating large amounts of molybdenum broken into small pieces. This latest demonstration showed that vibratory finishing with steel media is also an effective method for decontaminating molybdenum. The use of steel media is preferred over ceramic media for decontamination because the steel media produce no secondary waste from media wear, whereas ceramic media produce relatively large amounts of wet sludge. Additionally, valuable materials balance data were obtained from the demonstration.

The solution-handling system for the vibratory finisher was redesigned to allow either flow-through or recirculation of the liquid compound (Figure 5.2). Fresh 10% sodium hydroxide solution was introduced into the system using the normal flow-through compound system provided with the vibratory

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FIGURE 5.1. Typical Small Pieces of U-Contaminated Molybdenum Decontaminated by Vibratory Finishing

FIGURE 5.2. Diagram of Compound-Handling Systems for Vibratory Finishing

finisher by the manufacturer. A compound recirculating system was designed and added to the vibratory finisher by project staff. The combined use of the two compound systems allowed us to easily switch from one system to another, thereby permitting direct comparison of the effect of fresh compound or of recirculating contaminated compound. Previously, decontamination to low levels, as was desired in this demonstration, had been achieved using only fresh compound. If low-level decontamination could be obtained also by using recirculated compound, then liquid secondary waste production could be significantly reduced.

It was found that a higher than normal flow rate is needed when recirculated compound is used. A normal flow rate during vibratory finishing is ~ 2 gal/hr/ft³ of machine capacity. The vibratory finisher used during this demonstration has a working capacity (the volume of the process tub minus required free board) of 10 ft³. Hence a flow rate of ~ 20 gal/hr is considered normal and is effective for decontamination with the flow-through compound system because the compound is clean and uncontaminated. This demonstration indicated, however, that with the compound recirculating system a flow rate four times normal, ~ 80 gal/hr, was needed to achieve as effective decontamination as with fresh compound. Since the recirculating system increases decontamination effectiveness without producing additional secondary waste, the higher compound flow rate is not a disadvantage.

The debris from the vibratory finishing process was removed by filtering the recirculated compound through a single 25- μ m filter element 2.5 in. in diameter and 10 in. long. The high flow rates for the recirculated compound were necessary to effectively remove the particulate debris from

the compound. At the normal flow rate, sludge formed in the bottom of the compound reservoir, causing uneven filter loading and thus tending to reduce filter efficiency and life. Moreover, this formation of sludge required that the compound reservoir be emptied and the sludge manually removed before effective decontamination could resume. At the higher flow rate, 80 gal/hr, the recirculating compound remained relatively clear, sludge formation in the compound reservoir was eliminated, and good decontamination was achieved.

The materials balance for the demonstration is shown in Table 5.1. It is apparent that increasing the flow rate has reduced the amount of secondary waste produced by the decontamination. Caution must be used in assigning absolute values to the information presented in the table as the amount of debris associated with the contaminated molybdenum varied throughout the demonstration. The differences, however, are sufficiently large that at least a general trend can be assumed.

Vibratory Finishing Decontamination System

The installation of the glove box line that will be used with the vibratory finisher decontamination system is again proceeding after a 5-month delay due to a labor-management dispute at Hanford. Figure 5.3 shows

TABLE 5.1. Summary of Materials Balance Data from Vibratory-Finishing Decontamination of 32,000 lb of molybdenum

	Compound Flow Rate, gal/hr	
	20	80
Amount of material decontaminated, lb	17,000	15,000
Liquid waste, gal	90	35
Number of filter cartridges used	31	9

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FIGURE 5.3. Floor Plan of High-Production Vibratory Finishing Decontamination System Showing Location of Newly Installed Glove Box Line

the floor plan, depicting the positioning of the glove box line and the high-production annular vibratory finisher. The glove box line has been connected to the sectioning/pretreatment facility. It consists of a general-purpose glove box and a two-level preparation glove box that will house the double-cut shear, which is currently in the sectioning/pretreatment facility. The glove box line will be connected to the vibratory finisher by a transition piece and flexible bellows.

Progress prior to the work stoppage was limited to placing the glove boxes in the room and aligning them. Since work has resumed, the windows and gloves have been installed in the glove box line, the glove boxes sealed to each other and to the sectioning/pretreatment facility, and the hole

cut in the sectioning/pretreatment facility, allowing access to the glove box line from the sectioning/pretreatment facility (Figure 5.4).

The transition piece has been installed between the glove box line and the high-production vibratory finisher. It remains isolated, however, from the glove box line by a diaphragm because of problems encountered with the containment lid on the vibratory finisher. The original plans called for part of the transition piece to be securely bolted to the containment lid of the vibratory finisher and to be isolated from the rest of the transition piece by a flexible bellows as shown in Figure 5.5. However, this added weight on the containment lid caused too much stress when the finisher was vibrating and resulted in the

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FIGURE 5.4. View of the Interior of Glove Box Line Connecting Sectioning/Pretreatment Facility with High-Production Vibratory Finisher, as Seen from Sectioning/Pretreatment Facility

TRANSITION PIECE

FLEXIBLE BELLOWS

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FIGURE 5.5. Transition Piece Connecting High-Production Vibratory Finisher to Newly Installed Glove Box Line

failure of the bolts that held the transition piece to the containment lid and the lid to the finisher. Furthermore, cracks appeared in the section of the transition piece that was bolted to the containment lid.

To resolve this problem, the transition piece will be redesigned to reduce the stress on the bolts, and longer bolts with spacers will be used to mount the containment lid to the vibratory finisher. The longer bolts should better withstand the vibratory stress and thus last longer. Spacers are currently being fabricated so that testing of the longer bolts can begin.

Technology Transfer

During November 1980, R. P. Allen and M. W. McCoy of PNL, E. A. Bracken of DOE Richland Operations, and A. Taboas of DOE Albuquerque Operations visited the Karlsruhe Nuclear Research Center (KfK), located in the Federal Republic of Germany (FRG). This trip was in response to the strong interest expressed by KfK in the advanced decontamination technology developed under TRU Waste Program sponsorship at PNL. The visit established contacts at KfK and Battelle-Institut e.V. (BI) and allowed the DOE and PNL personnel to become familiar with the KfK facilities and decontamination needs. Information was obtained also on activities in progress at the KfK in decontamination and other fields that will benefit U.S. alpha waste management activities. Access to the U.S. technology has been requested as part of the USDOE/FRG waste treatment exchange agreement. These technology transfer activities would involve representatives from PNL, where the technology was devel-

oped, and also from BI, who have been asked by KfK to act as consultants to KfK in this area.

Criticality Safety Studies

Monte Carlo neutronic calculations have been completed by Los Alamos Scientific Laboratory personnel for the evaporator holding tanks and for 55-gal drums of solid neutralized electrolyte. Based on these calculations, calibration curves have been prepared and the ^3He neutron detector system (PNL-3000-7) has been used for the manual acquisition of criticality safety control data for these decontamination system components. The calibration curves were prepared for both weapons-grade plutonium metal and for weapons-grade plutonium oxide at source-to-detector distances of 0 in. and 12 in. Additionally, calibration curves for the dual evaporator, used to process aqueous waste, are being prepared to permit acquisition of criticality control data for this system.

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6. KRYPTON SOLIDIFICATION

G. L. Tingey - Project Manager

The objective of this program is to develop techniques for storing radioactive krypton in a solid matrix. Two techniques being investigated are 1) dissolution of krypton in low-density glass followed by densification at high temperature and 2) ion implantation of krypton in sputter-deposited metal matrices.

SUMMARY

Crystalline sputtered metals were further examined using a continuous substrate bias of -1000 V. The results of these tests using a titanium target indicate that the krypton trapping rate is still inferior to that with amorphous iron-yttrium alloys by a factor of about 3.4. Systems studies have yielded a comparison of various sputtering-chamber sizes. The results suggest that, using the optimum size, six sputtering chambers would be required to implant all the krypton from a 2000-t/yr reprocessing plant.

Further studies of dissolution of krypton in glass show the importance of loading time on the krypton concentration, especially at temperatures of 900°C or above. The release of krypton from the loaded glass is accompanied by devitrification, comminution, and softening at temperatures above 600°C. The lower loading pressures (about 40 MPa) appear to yield a more favorable product from the point of view of krypton release than do the high pressures.

ION IMPLANTATION OF KRYPTON DURING SPUTTER DEPOSITION - E. D. McClanahan, G. L. Tingey, J. F. Neshitt, R. W. Moss, and E. N. Greenwell

Entrapment of Krypton in Sputtered Titanium

Previous work in our laboratory and elsewhere has shown the feasibility of ion implantation of krypton in a growing metal film as it is being sputter-deposited (Tingey et al. 1979; Whitmell et al. 1980; Schmidt et al. 1980). These studies have concentrated on two techniques for the deposition as follows:

1. Implanting krypton in sputtered crystalline metals using a negative substrate voltage comparable to that of the target. This system requires that the substrate be pulsed to yield a net deposition rate on the substrate surface.
2. Implanting krypton in a metal alloy selected to yield an amorphous sputtered metal deposit. For this system, the krypton can be trapped with a negative voltage about one-tenth that of the target; therefore, the substrate voltage can be maintained continuously.

Recent results (Schmidt et al. 1980) from the KfK Laboratory in West Germany suggested the use of a combination of these two techniques; that is, deposition of a crystalline deposit using a continuous substrate bias of about -1000 V. This technique permitted the elimination of the high-current switching apparatus while using a simpler one-component metal target. They reported krypton concentrations in sputtered titanium approaching that observed in amorphous metals.

To further test this approach in our system using a thermionic-supported plasma, we have sputtered titanium with krypton ions accelerated to a target at -2500 V with a substrate bias of -1000 V. During the sputtering, the krypton uptake was about 25 cm^3 of Kr(STP)/g of sputtered deposit (5.7 atom%). The product was smooth, well bonded, krypton-containing titanium film. Gas release measurements from a small portion of this film were performed and show a total krypton content of 25.5 cm^3 of Kr(STP)/g of deposit. The release of krypton was negligible at temperatures below 750°C but occurred within 2 hr as the temperature increased from 750 to 1100°C .

Although this approach to trapping is certainly feasible, it does not appear to have advantages over the amorphous alloys

(i.e., $\text{Fe}_{0.79}\text{Y}_{0.12}\text{Kr}_{0.09}$). The total krypton concentration is somewhat lower in the titanium deposit, but, more importantly, the net sputtering rate is significantly reduced, partially due to reverse sputtering from the highly charged substrate. Table 6.1 shows a comparison of the important parameters for sputtering from both the amorphous iron-yttrium and the crystalline titanium target. The net gas trapping rate in the titanium film is reduced by about a factor of 3.4 from that of the amorphous alloy. This reduction would produce a corresponding increase in the number or size of the sputtering chambers and also in power consumption. Since there appears to be an economic incentive to reduce the number or size of the sputtering chambers, iron-yttrium is still preferred over the crystalline titanium target.

Systems Evaluation

In an earlier quarterly report (PNL-3000-6), we described a preliminary design for a ^{85}Kr ion-implantation facility to handle the krypton output from a 2000-t/yr nuclear fuel reprocessing plant. One of the criteria for this design was to use a system that was a relatively small scale-up from the currently

TABLE 6.1. Comparison of Sputtering from Iron-Yttrium and Titanium Targets

Target/ Chamber Size	Sputtering Rate, g/A-hr	Krypton Content		Density, g/cm ³	Geometrical Efficiency, %	Target Current, A	Entrapment Rate, cm ³ /min(a)
		cm ³ /g	cm ³ /cm ³				
Fe-Y/1X	5.3	32	192	6.0	80	4.6	610
Ti/1X	2.5	25	112	4.5	63.3	4.5	178
Fe-Y/2X	5.3	32	192	6.0	92	9.0	1400
Ti/2X	2.5	25	112	4.5	72.8 ^(b)	9.0	410

(a) Gas volumes in cm³ of gas at standard temperature, pressure.

(b) Estimated from 1X data.

tested system. In an attempt to optimize the economy of the facility, we evaluated the potential and costs of several sputtering-chamber sizes. The results of this cost analysis are shown in Table 6.2, where the sputtering units identified range from the current laboratory apparatus to one six times longer and with diameter increased from 14 to 19 cm. Although accurate cost estimates cannot be made until detailed design specifications are developed, the table's order of magnitude costs serve adequately for comparison.

Results seem to indicate some cost savings by increasing the size of the unit so that only six sputtering chambers are required. Further increases appear to yield no significant cost savings. Furthermore, the cost savings from the larger systems would not appear worthwhile if a significant decrease in reliability or operating efficiency were expected. A 2X scale (31 cm long by 14 cm ID) sputtering chamber is cur-

rently being investigated and certain components tested. A higher capacity substrate current limiter has been constructed, and tests are now under way. Furthermore, the geometric efficiency (ratio of the substrate weight gain to weight of target metal sputtered) has shown a significant increase in going to the larger units. The geometric efficiency of the 2X system was determined to be 92% for amorphous metals compared to 80% for a 1X system. Further increases are expected in geometric efficiency for even larger chambers.

DISSOLUTION OF KRYPTON IN LOW-DENSITY

VITREOUS SILICA - G. L. Tingey, J. M. Lytle, and K. R. Wheeler

Another approach to storage of ^{85}Kr is to load the krypton in a porous glass matrix at high pressure and then sinter the matrix while maintaining the pressure. This yields a product that has a very low krypton release

TABLE 6.2. Preliminary Cost(a) Comparison for Krypton Ion Implantation Facility (2000 MTHM) Using Various Sizes of Sputtering Chambers

	Chamber Size, Length x Dia, cm				
	15.5 x 14	31 x 14	56 x 14	93 x 14	93 x 19
Chambers required	32	16	10	6	4
Capital costs, \$1000					
Facility	7,800	5,300	4,500	3,700	3,700
Equipment	8,000	4,800	4,000	4,400	4,800
Installation	<u>5,500</u>	<u>2,700</u>	<u>1,600</u>	<u>900</u>	<u>600</u>
Total	21,300	12,800	10,100	9,000	9,100
Operating costs, \$1000/yr					
Labor	2,480	1,800	1,460	1,280	1,200
Materials	1,280	1,044	917	827	778
Power	<u>200</u>	<u>220</u>	<u>245</u>	<u>270</u>	<u>300</u>
Total	3,960	3,064	2,622	2,377	2,278

(a) Includes no contingency, escalation or interest costs.

rate. The krypton loading concentrations, shown in the most recent quarterly report (PNL-3000-7), are a function of loading pressure and may exceed 15 cm^3 of Kr(STP)/g of glass at a pressure of 140 MPa.

Recent experiments have been conducted in an effort to determine the optimum time for loading the krypton into the glass. Figure 6.1 shows the krypton loading achieved as a function of time at temperature following a 4-hr heat-up period. At 900°C , the maximum loading was achieved when the sample was maintained for about 5 hr but decreased thereafter. With only limited data available at 850°C , it appears that in ex-

FIGURE 6.1. Volume of Trapped Krypton Versus Time at Indicated Temperature and 34.9 to 37.3 MPa Pressure for Thirsty Vycor® Glass

®Registered trademark of Corning Glass Works, Houghton Park, Corning, New York.

cess of 5 hr may be required to obtain the maximum loading, with no evidence of a decrease up to 24 hr.

During heating, the glass sinters with an initial decrease in pore volume as shown in Figure 6.2. The initial sintering appears to be essentially the same at 850 and 900°C , both yielding a minimum pore volume of about $0.06 \text{ cm}^3/\text{g}$ of glass. At 900°C , the glass samples shrink to a minimum volume and then expand. The expansion, which occurs after about 5 hr, may be caused by high internal pressures acting on the partially softened glass. The internal pressures result if the pores contract further after closing off if other gases such as H_2O , CO , CO_2 or H_2 are desorbed. At 850°C , no expansion is observed, probably because of the higher viscosity of the glass.

During the sintering process, the glass surface area also decreases markedly, indicating the reduction or closing of the porosity. BET (Brunauer-Emmett-Teller) surface area measurements using N_2 sorption on sintered samples yielded a surface area of $0.5 \text{ m}^2/\text{g}$ as compared to $100 \text{ m}^2/\text{g}$

FIGURE 6.2. Pore Volume Versus Time for Thirsty Vycor Glass Sintered in the Presence of Krypton at 33 to 38 MPa. Temperature is increased to 850 or 900°C in 4 hr and held for the remainder of time.

obtained before krypton loading and sintering. This marked decrease in surface area clearly shows that the open pores are effectively closed.

The previous quarterly report (PNL-3000-7) also described the results of relatively long-term release measurements. However, some very interesting observations were made using temperature-programmed release studies. The results are shown in Figure 6.3. In this figure, the log of the release rate, in units

FIGURE 6.3. Rate of Krypton Release Versus Release Temperature for Two Samples of Thirsty Vycor Glass, Each Loaded and Sintered at 900°C for 1.5 hr and the Indicated Pressure of Krypton. The release temperature was increased from 400 to 1290°C at 100°C/hr.

of percent of the original loading, is plotted as a function of temperature. Two separate experiments are plotted for comparison. Both samples were loaded with krypton at 900°C and held at this temperature for 90 min. One, however, was loaded with a krypton pressure of 33 MPa while the other was loaded at 141 MPa. As depicted in the figure, the release curves are erratic. Apparently several processes are occurring during the heating that tend to affect the release rates. At least three different temperature ranges are apparent, 400 to 700, 700 to 1000, and 1000 to 1300°C. At present, experimental data are insufficient for a clear understanding of the mechanism of release. However, we have made several observations and postulates worthy of mention.

In the region below 600°C, release rates vary greatly with time during the early stages of release, indicating the presence of very small, but measurable, quantities of krypton that are sorbed or trapped very near the surface and thus released very early in the programmed-temperature experiments. More meaningful data in this temperature region are attained by long-term measurements.

From 700 to 1000°C, the release appears to be a much more typical diffusion mechanism. An Arrhenius plot of the diffusion coefficient for this region has yielded an activation energy of about 20 kcal/mole for a sample loaded at 34 MPa. Of greater concern is the increased krypton release rate of the sample loaded at 141 MPa. Other samples loaded at pressures of ~140 MPa invariably show a rate of krypton release one or two orders of magnitude greater than samples loaded at lower pressures. At present, the reason for these high rates has not been investigated.

In the transition temperature between this and the next region there is a marked increase in rate for the sample loaded at 33 MPa. We have interpreted this rate increase to be associated with a self-comminution process that is always observed. In some cases the sample is stressed to the point where it breaks into a powder. In other instances the sample holds together, but massive cracking is observed. We have postulated that this comminution decreases the diffusion path markedly and, thus, the release rate increases.

In the higher temperature region (1000 to 1300°C), the release rates become very rapid. The Arrhenius plot of this region yields a

somewhat higher activation energy (~ 40 kcal/mole), which is postulated to be due to diffusion from partially devitrified SiO_2 . Above ~ 1150 to 1200°C , glass softening occurs, producing major expansion or foaming of the sample. These data suggest that the retention of krypton in samples loaded at ~ 40 MPa may be superior to that for samples loaded at ~ 140 MPa. Furthermore, krypton loadings of about 7 cm^3 of $\text{Kr}(\text{STP})/\text{g}$ appear to be adequate. In light of this observation, further work should be done to evaluate the optimum loading pressure considering release behavior as well as krypton concentration.

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7. THERMAL OUTGASSING

L. L. Burger - Project Manager

The objectives of the Thermal Outgassing Program are to:

- 1. develop a method for the safe and effective removal of volatile fission products from irradiated fuels*
- 2. evaluate the use of thermal outgassing using various sweep gases or vacuum outgassing for the removal of ^{14}C , ^{129}I , and ^{85}Kr*
- 3. apply the information obtained from both experiment and theory to spent fuel reprocessing, interim and long-term storage, and to reactor safety.*

SUMMARY

Results from the 6-hr sweep-gas test on Shippingport UO_2 fuel were very encouraging. The first tests showed that with a small amount of hydrogen present in the purge gas (helium), more than 99% of the tritium was removed from the fuel sample in 4 hr. With helium only, the rate of release was slower, roughly 50% in 4 to 5 hr at 1500°C . Sweep-gas equipment has been modified to obtain krypton, xenon, and tritium results simultaneously. Vacuum outgassing equipment is being assembled in the 327 Building hot-cells on schedule.

THERMAL OUTGASSING - L. A. Bray

Experiments were completed in FY 1980 using helium or $\text{He} + \text{H}_2$ as the sweep-gas. The release of xenon, krypton, and tritium was observed during the 6-hr heating cycle. Analysis of the treated fuel showed that 18% of the tritium remained in the Shippingport UO_2 fuel after heating at 1500°C using helium as the sweep-gas and that no detectable tritium was found in the fuel using 6%

$\text{H}_2 + \text{He}$. Less than 10% of the xenon and of the krypton remained in the fuel after heating at 1500°C using helium as the sweep-gas; >84% of the xenon and 52% of the krypton were found in the fuel after using 6% $\text{H}_2 + \text{He}$. The results are shown in Figure 7.1.

The design of a new flow-scheme for the sweep-gas system has been completed. The old scheme separately collected and analyzed the fission gases, xenon and krypton, in one run and measured tritium in a second run. This required two full days and separate fuel pieces. The new scheme allows simultaneous collection of the fission gases and tritium in one run, with subsequent measurement of each. This was accomplished by redesigning the tritium trap and placing it between the purification columns. With this design, the tritium is removed from the carrier gas for measurement before the fission gases are collected on the cryogenic charcoal trap. In addition, an electronic mass flow-meter system capable of more accurately measuring several different gas flows has been ordered.

FIGURE 7.1. Tritium, Xenon and Krypton Release from Shippingport UO_2 Fuel as a Function of Sweep-Gas Composition

Vacuum outgassing equipment is being assembled in the 327 Building hot-cells on schedule. All the electrical leads to the in-cell equipment are being converted to quick disconnects for ease of installation. All additional equipment required has been received.

The technical program plan has been revised to support the enhanced budget.

This change will allow a topical report, based on the literature search, to be prepared in draft form by September 1981. The suggested contents of the topical report, Gas Release on Thermal Treatment of Irradiated Fuels, have been outlined and submitted. Sweep-gas and vacuum outgassing tests have been prioritized and scheduled for completion during FY 1981.

8. IODINE-129 FIXATION

L. L. Burger - Project Manager

The objective of this program is to develop technologies that will provide safe and effective removal and packaging of iodine-129 for initial treatment, for interim storage and equipment, and for permanent isolation. The technologies must be related to all phases of the nuclear fuel cycle.

SUMMARY

Static leach tests of iodine compounds from cement indicate that most of the leaching occurs during the first 5 to 10 hr. The iodine concentration from most samples goes through a maximum at considerably less than the saturation value for the compound, indicating that precipitation is occurring in a different form.

Attempts to produce an iodine sodalite without going through the hot-press step resulted in the release of most of the iodine. Modifications of the synthesis step are being examined.

WASTE FORM CHARACTERIZATION

Static leaching studies continued for barium iodate, mercuric iodate, iodine-loaded silver mordenite, each in cement at a concentration of 0.8 mmol I/g dry cement, and for a new iodine sodalite hot-pressed at 1000°C and 2000 psi. Figures 8.1, 8.2, and 8.3 show the normalized fraction leached from the barium iodate, mercuric iodate, and iodine-loaded silver mordenite containing cement samples, respectively. Distilled water was the leachate. The normalized fraction was calculated by multiplying the fraction leached, calculated from the leach-

ate concentrations, by the geometric volume-to-surface ratio. This ratio was typically 0.5 cm. After 180 days, the normalized fraction leached was 2×10^{-3} cm for the barium iodate sample, and 3×10^{-3} cm for the mercuric iodate sample. The leach results with Columbia River water and seawater were nearly the same. However, at an earlier time, the amount of barium iodate leached by seawater was an order of magnitude higher than for the other samples. After 55 days, the normalized fraction leached was $\sim 1 \times 10^{-3}$ cm for the iodine-loaded mordenite sample and after 14 days 7×10^{-5} cm for the iodine sodalite.

At 150 days the barium iodate leachates were filtered using ultrafine glass filters and the solids dissolved with 2M HNO_3 . The beakers were then rinsed with 2M HNO_3 and the combined wash solutions analyzed. Three to eight percent of the leached iodine was found in the wash. This amount of iodine does not account for the full decrease in the iodine concentration in the leachate seen after 40 days (Figure 8.1). This indicates that some iodine reprecipitates onto the cement matrix. Similar behavior is seen for the mercuric iodate sample after 90 days.

In each case most of the leaching occurs during the first 5 to 10 days. However, the plateau reached is well below the saturation limit for the iodine compound. Minor

FIGURE 8.1. Static Leaching of 0.4 mmol BaIO₃(2)/g Dry Cement

FIGURE 8.2. Static Leaching of 0.4 mmol HgIO₃(2)/g Dry Cement

fluctuations, and in some cases a significant drop in iodine concentration in the leachate, indicate more complex reactions. Analysis of leachate samples for other cations is being completed. This should aid in the interpretation.

Other work in progress includes methyl iodide sorption, effect of NO₂ on iodine-loaded zeolites, and the effect of water on the iodine retention of silver zeolites.

SODALITE STUDIES - W. I. Winters and R. G. Johnston (RHO)

Previous studies have shown that iodine can be incorporated into synthetic sodalite to form a durable material suitable for the storage or disposal of ¹²⁹I. After synthesis in an aqueous system, the solids were hot-pressed at 3000 to 7000 psi at about 1000°C.

FIGURE 8.3. Static Leaching of AgZI in Cement, 0.8 mmol I/g Dry Cement

Present efforts have been aimed at 1) investigating possible iodine loss during the hot-press cycle and 2) the possibility of avoiding this step by employing a simple heat treatment.

Sodalite feed material (remaining from FY 1980 work) was prepared using kaolin clay, NaOH, and NaI, as described in our FY 1980 final report. One-gram portions of this material, containing 15 wt% iodine, were cold-pressed into 1/2-in. pellets. The pellets were placed in a small quartz boat and inserted into a quartz-lined tube furnace with a 1 l/min air-flow through the tube. Temperatures in the tube furnace were mapped using a platinum-rhodium thermocouple. The temperature was raised slowly to 100°C, and the gases were trapped in two bubblers containing 250 ml of 1M NaOH. During the heat-up, purple iodine vapors were observed coming off at about 400°C. Large amounts of iodine sublimed on the tygon tubing leading to the traps, indicating that to accurately measure iodine losses will require an experimental modification. An attempt to introduce the pellets directly into the furnace at 1100°C still showed signs of large iodine losses. Assay of the pellets following sin-

tering indicated that greater than 99% of the iodine had been volatilized.

The effects of modification of feed preparation processes will be determined. Sintering experiments will have to be delayed because laboratory renovations will require moving the experimental apparatus.

Accurate assay of analysis of iodine in the feeds and products offers another means of determining iodine losses. The titration of iodine using standard AgNO_3 and a specific ion electrode for end-point detection was investigated for determining iodine in sodalite. AgNO_3 was standardized against sodium chloride using chromate as an end-point indicator. Dry potassium iodide was dissolved in H_2O , in 0.1M HNO_3 , and in 0.01M H_2SO_4 , and titrated with the standardized AgNO_3 to determine the effect of acids on the titration and the specific ion electrode. Several samples of feed material and a sample of hot-pressed product were prepared by placing 1 g of the material in 20 ml of 1M acid (H_2SO_4 or HNO_3) and allowing it to stand for 10 to 20 min before diluting to 100 ml with deionized water and titrating with AgNO_3 . The results of these tests are tabulated in Table 8.1. The method gave a

TABLE 8.1. Titrimetric Analysis of Iodine

Sample	Weight, g	Matrix	I Weighed, mM or wt%	I Titrated, mM or wt%
KI	0.2077	H ₂ O	1.251 mM	1.226 mM
KI	0.1722	0.1M HNO ₃	1.037 mM	1.030 mM
KI	0.1782	0.1M H ₂ SO ₄	1.073 mM	1.065 mM
Sodalite feed	1.0293	0.2M HNO ₃	14.2% ^(a)	15.10%
Sodalite feed	0.9525	0.2M H ₂ SO ₄	14.2% ^(a)	15.21%
Sodalite feed	1.0592	0.2M H ₂ SO ₄	14.2% ^(a)	15.20%
Sodalite feed	0.9840	0.2M H ₂ SO ₄	14.2% ^(a)	15.30%
Sodalite product	0.7148	0.2M H ₂ SO ₄	20.9% ^(a)	21.01%

(a) X-ray emission analysis.

result of 15.20 ± 0.08 wt% iodine for the feed compared to 14.2 wt% as determined by x-ray emission last year. The difference may be explained by the water content of the samples. The hot-pressed sample was a high-temperature product that had been finely ground. This sample gave a result of 21.0 wt% compared to 20.9 wt% by x-ray. The titration method is probably more precise than x-ray analysis, easy to carry out, and

directly referable to a primary standard. Either HNO₃ or H₂SO₄ can be used to leach iodine from the sodalite; however, H₂SO₄ is probably preferred since NO_x could oxidize I⁻ to I₂, giving low results. The iodine-specific ion electrode gives a large, sharp end-point detection. Electrode response is rapid except near the end-point. Titrations of sodalite in H₂O only were not possible because of an unstable end-point.

9. MONITORING AND PHYSICAL CHARACTERIZATION OF UNSATURATED ZONE TRANSPORT

T. L. Jones - Project Manager

The objective of this project is to develop monitoring instrumentation systems and burial media-waste characterization methods to evaluate the migration of contaminants from disposal sites for low-level solid wastes.

SUMMARY

Tritium profiles were measured in the test caisson at the Burial Waste Test Facility (BWTF). These profiles show accelerated movement in the irrigated caisson relative to the ambient caisson. This is to be expected because the irrigated caisson is receiving three times the ambient level of precipitation. A new method of measuring tritium concentrations in soil samples was tested. This method involves combustion of the soil sample and condensation of the tritium as opposed to the leach and extraction technique used previously. The results indicate that comparable results can be obtained in less time using the sample oxidizer.

FIELD MEASUREMENTS - A. C. Campbell and K. O. Schwarzmiller

The movement of tritium placed in a test caisson at the Burial Waste Test Facility in May of 1979 is still being closely monitored. A fourth sampling of the soil in the caisson was conducted in September 1980, and the analytical results are shown here. The tritium contained in the soil samples was extracted and analyzed using liquid scintillation techniques.

Figure 9.1 shows the tritium profile for the caisson receiving only ambient precipitation. Figure 9.2 shows the tritium profile for the irrigated caisson, which receives three times the ambient precipitation at about the same distribution. It is quite clear that the tritium is being redistributed in the irrigated caisson much faster than in the ambient caisson. This is to be expected, of course. The tritium does appear to be leaving the profile through the top of the caisson by evaporation; however, no detectable levels of tritium have been obtained in surface samples. This phase of the field tritium experiment is drawing to a close, and the next effort will be to analyze these results quantitatively in a modeling effort.

LABORATORY ANALYSIS - A. C. Campbell and T. L. Jones

Tritium concentrations in the BWTF soil samples have previously been determined using liquid scintillation counting techniques. The samples were prepared by adding distilled water to the sample, which was then shaken and centrifuged. A small aliquot of the liquid was injected directly into a toluene-based liquid scintillation cocktail and counted. Sample activity was calculated by dividing the net counts per

FIGURE 9.1. Field Tritium Concentrations in Ambient Caisson

FIGURE 9.2. Field Tritium Concentrations in Irrigated Caisson

minute by the counting efficiency of that particular sample. This quarter a new sample preparation method, oxidation, was tried in order to reduce the quenching and to produce more uniform samples. Oxidation involves the combustion of a solid or a liquid sample at 900 C. The tritium is collected as tritiated water in a xylene-based scintillation cocktail.

Determination of Quench Correction Curve

Counting efficiency is influenced by sample geometry, absorption, and scintillation cocktail efficiency. Chemical and optical interferences and even slight differences in sample configuration decrease or "quench" the signal detected by the counter, which corresponds to a decrease in counting efficiency. A series of quenched samples with known amounts of tritium is used to produce an efficiency curve; from this curve the efficiency of a sample with unknown quenching and activity can be determined.

Our BWTF tritium soil samples contain both chemical and optical quenching factors. The water in the samples and that added to extract the tritium is a quenching agent. Color also quenches a sample. Water-quenched standards, prepared using the oxidizer's scintillation cocktail, were counted under

conditions similar to those of the samples. The quench-corrected efficiency curve for tritium is given in Figure 9.3.

Comparison of Sample Oxidation and Direct Counting

A test was done to compare the oxidation of a liquid sample to the direct injection of that sample into the oxidizer scintillation solution. Samples from the last BWTF sampling were used. The values for both the oxidized and directly counted samples (given in Table 9.1) averaged 1% lower than the original values. This is well within the range allowable due to deviations in the counting procedure and standard activity calculations. The directly counted samples were not expected to have higher counting efficiencies. They were, however, 10% higher than those of the oxidized samples. Apparently the oxidation process quenched our samples more than their color did. Soils counted directly in scintillation cocktail have lower efficiencies than oxidized soil samples (37% versus 42%). Analytical time will be reduced in the future by oxidation of the soil samples instead of adding water to the samples to extract the tritium.

FIGURE 9.3. Quench Correction Curve for Tritium

TABLE 9.1. Comparison of Oxidized Solution with Directly Counted Solution

Caisson	Depth, m	Activity, pCi/g		Efficiency	
		Oxidized	Direct	Oxidized	Direct
Irrigated	3.81	1375	1214	0.404	0.453
	5.03	2814	2697	0.402	0.451
	6.25	883	787	0.405	0.459
	7.16	4340	4391	0.400	0.439
Ambient	0.76	282	282	0.410	0.451
	1.07	422	408	0.395	0.448
	1.37	1205	1346	0.413	0.455
	1.68	1996	2094	0.418	0.453
	1.98	3727	3938	0.397	0.454
	2.59	9104	9464	0.412	0.453
	3.81	9826	9898	0.416	0.459
	5.03	4667	4730	0.413	0.457
	6.25	340	346	0.413	0.460
	7.16	1186	1208	0.418	0.463

10. WELL-LOGGING INSTRUMENTATION DEVELOPMENT

R. L. Brodzinski - Project Manager

The objective of this research program is to develop appropriate well-logging equipment capable of determining ^{90}Sr , ^3H , and transuranics at sensitivity levels that will provide useful information for the proper operation of a shallow-land burial site.

SUMMARY

A computer program that produces integrated peak areas from germanium diode gamma-ray spectra will be modified to provide integrated values for the ^{90}Sr bremsstrahlung radiation in the spectra. A calibration technique has been designed that will provide the necessary parametric data for this program.

Wiring of the control panel and assembly of the gas proportional counter for the tritium logger have been completed.

Laboratory experiments on the application and sensitivity of x-ray fluorescence spectroscopy to the well-logging analysis of actinides have been initiated.

DEVELOPMENT OF LOGGING SYSTEMS CAPABLE OF MEASURING ^{90}Sr - R. L. Brodzinski

The computer program SLAVE currently produces integrated peak areas from germanium diode gamma-ray spectra. This, or a similar program, will be modified to produce an integrated value for the ^{90}Sr bremsstrahlung radiation in the spectra. A calibration technique has been designed that will provide the necessary parametric data for inclusion in the computer program used for

field data reduction. The calibration technique will yield concentration conversion values for a variety of matrices, well diameters, and casing materials. The technique will also provide conversion data for ^{90}Sr surface analyses.

DEVELOPMENT OF LOGGING SYSTEMS CAPABLE OF MEASURING TRITIUM - C. Menninga and R. L. Brodzinski

Wiring of the control panel for the tritium logger has been completed. Fabrication and assembly of the gas proportional counter for the tritium analyzer have also been completed.

DEVELOPMENT OF LOGGING SYSTEMS CAPABLE OF MEASURING ACTINIDES - J. H. Reeves and R. L. Brodzinski

Laboratory experiments on the application and sensitivity of x-ray fluorescence spectroscopy to the well-logging analysis of actinides have been initiated. A 50 mCi ^{57}Co isotopic excitation source has been obtained, and the physical configuration of the source/sample/detector system is being optimized. Use of ^{141}Ce as a second activation source is being considered.

The 145.45 keV photon from this isotope could provide the ability to excite americium and curium isotopes in the matrix as well as provide a second energy (in addition to the

122 keV photon from ^{57}Co) for determining the location of plutonium contaminations in the matrix.

11. MOBILITY OF ORGANIC COMPLEXES OF RADIONUCLIDES IN SOILS

J. L. Swanson - Project Manager

The objective of this project is to develop and employ standard procedures for evaluating the migration of organic complexes of low-level waste radionuclides in soils.

SUMMARY

The effect of EDTA on the sorption of Eu(III) by Hanford soil was measured. An effect was observed at EDTA concentrations above about 10^{-7} M; the magnitude of the effect varied nearly proportionally to the first power of the EDTA concentration.

EUROPIUM(III) MOBILITY STUDY - J. L. Swanson

Data illustrating the effect of EDTA on the sorption of Eu(III) by Hanford soil are

presented in Table 11.1. An EDTA concentration as low as about 10^{-7} M gives a measurable decrease in the sorption coefficient. The sorption coefficient then decreases with increasing EDTA concentration, approximately proportionally to the first power of the EDTA concentration. The sorption coefficient value is about 100 at 5×10^{-5} M EDTA.

The fact that comparable sorption coefficient values were obtained when equilibrium was approached from both directions provides good evidence that an equilibrium condition was indeed achieved in these experiments.

TABLE 11.1. Effect of EDTA on Eu(III) Sorption

<u>[Na₂ EDTA], M</u>	<u>[Eu], (c) M</u>	<u>Apparent K_d (a,b)</u>	
		<u>Desorption Direction (d)</u>	<u>Sorption Direction (e)</u>
0	2.7×10^{-7}	-	$\sim 1 \times 10^5$
4.5×10^{-7}	8.6×10^{-8}	-	2.1×10^4
4.5×10^{-6}	2.7×10^{-7}	1.2×10^3	1.4×10^3
4.5×10^{-6}	2.7×10^{-7}	1.3×10^3	1.5×10^3
4.5×10^{-5}	2.7×10^{-9}	1.1×10^2	-
4.5×10^{-5}	8.6×10^{-8}	-	9.2×10^1

(a) $K_d = (\text{counts/min} \cdot \text{g soil}) / (\text{counts/min} \cdot \text{ml solution})$.

(b) Measured after 3 to 4 wk of vigorous agitation at $\sim 22^\circ\text{C}$.
Solution pH = 8.0 ± 0.1 . Solution:soil ratio = 30 ml/g.
Hanford soil ($< 500 \mu\text{m}$). Solutions filtered through 2-nm filter before analysis.

(c) If all Eu were in solution.

(d) Eu solution contacted with soil for 4 days before EDTA added.

(e) EDTA present when Eu solution contacted soil.

No precise measurements were made of the time required to achieve equilibrium, but it was found that the degree of agitation was definitely important and that, even with vigorous agitation, two weeks was not sufficient time in some cases. Preliminary evidence indicates that the time required to achieve equilibrium may be greater at higher solution:soil ratios.

The fact that comparable sorption coefficient values were obtained with different europium concentrations (at a given EDTA concentration) indicates that a sorption process, rather than a solubility process, is indeed controlling the concentration of europium in solution.

These sorption coefficient values were measured after passing the solutions through filters having a 2-nm pore size. Roughly comparable values were often (but not

always) obtained when centrifugation or filtration through filters having a 450-nm pore size were used to clarify the EDTA-containing solutions. It thus appears that sorption of soluble europium by the filtration medium was not a problem in this work, at least in the presence of the indicated amounts of EDTA.

TECHNETIUM MOBILITY STUDIES - L. Y. Martin and J. A. Franz

A paper, "Effect of Organic Ligands on the Soil Behavior of Technetium-99," was presented in November at the International Conference of the American and European Nuclear Societies in Washington, D.C.

A draft report summarizing the technetium mobility studies is being reviewed and revised.

12. WASTE MANAGEMENT SYSTEM STUDIES

J. V. Robinson - Project Manager

The objectives of this program are to evaluate alternative systems for treatment and disposal of radioactive wastes and to develop information required to ensure effective communication with the public.

SUMMARY

The Human Affairs Research Center (HARC) began work on several of the seven tasks they will perform this fiscal year. Considerable effort was expended on the task to provide technical services in public participation planning in connection with the National Plan for Radioactive Waste Management.

An effort to provide standardized sections and methodologies for use in Hanford waste management EISs continued this quarter. Two reports from this task were cleared for publication.

Work began on a task to provide assistance to other DOE field office contractors in the preparation of waste management environmental impact statements.

A report prepared to assist the lay public in understanding the technical aspects of nuclear waste management was reviewed by DOE Richland Operations (RL) and DOE Headquarters (HQ) personnel and by some outside consultants.

A report on dilution disposal of nuclear waste was being prepared for submission to DOE-RL for clearance.

A workshop entitled "Waste Management Health Physics" was conducted for HQ staff at HQ.

Experiments were conducted on a core taken from the Mid-Pacific gyre to establish the feasibility of an approach to the measurement of the migration rate of certain radionuclides and certain other parameters of interest.

SOCIAL PERCEPTIONS, CONFLICT, AND INSTITUTIONAL ISSUES RELATED TO NUCLEAR WASTE MANAGEMENT - S. M. Nealey (HARC)

Efforts on this program proceeded at a minimal level, pending resolution of FY 1981 tasks to be pursued. Such resolution was achieved in December. As a result, seven tasks as described below were approved.

- Task 1 Revision and issuance of final topical reports of work completed in draft form at the end of FY 1980.
- Task 2 Technical services in public participation planning and implementation in connection with the National Plan for Radioactive Waste Management.
- Task 3 Analysis of data and completion of reports of survey findings on public perceptions of radioactive waste and other hazards.
- Task 4 Comparative analysis of existing survey data on public concerns and attitudes toward radioactive waste management.

Task 5 Analysis of the conduct and outcomes of hearings related to radioactive waste management.

Task 6 Analysis of regional issues in nuclear waste management.

Task 7 Analysis of decision incentives.

During the first quarter of 1981, work on Task 1, revision and completion of topical reports, was begun. A meeting was held regarding the social science research planning tasks, and plans were made for finalizing the report. The other two topical reports--on conflict mediation and on the transfer of information about a waste repository site--are awaiting feedback from the sponsor, which is anticipated to come in January.

During the first quarter, a considerable amount of work was done on Task 2. A complete rewrite of Chapter 11, Volume 2, of the National Plan was done in October and revised in November. In addition, HARC scientists spent time working with DOE and MITRE to determine how best to conduct workshops for special interest groups and to determine whether public participation plans were adequate for the various waste management program areas.

Work on Task 3 was also carried out during the first quarter. Data from the two surveys were collected by the end of September, keypunched in October, and analyzed in November and December. Write-ups of the data were begun in November and continued through December. First drafts of these reports are due in January.

ENVIRONMENTAL IMPACT STATEMENT (EIS) STANDARDIZATION ANALYSIS^(a) - M. A. Mueller

Two reports, entitled Standardized Input for Hanford Environmental Impact Statements

(PNL-3509) and HADOC - A Computer Code for Calculation of External and Inhalation Doses from Acute Radionuclide Releases (PNL-3503), received clearance for publication. Comments have been received from those people at PNL, Rockwell Hanford Operations, Westinghouse Hanford, and United Nuclear Corporation involved in or responsible for environmental impact statements for their company's Hanford operations. Some changes in the documents will be required to respond to the comments. We plan to publish the reports early next quarter.

ENVIRONMENTAL IMPACT STATEMENT (EIS) SUPPORT TO DOE-HQ - M. A. Mueller

This project is to enable the Assistant for Environmental Activities (AEA) to exercise early (and continuous) involvement in Office of Nuclear Waste Management (ONWM) Environmental Impact Statement (EIS) preparation carried out by DOE contractors. Direct participation by PNL personnel in EIS development, from inception through completion, and timely monitoring and reporting of such participation to the AEA through DOE-RL, will be accomplished. The basic objective is to enhance the consistency of EISs with the new Council on Environmental Quality (CEQ) regulations for compliance with the National Environmental Policy Act (NEPA). This will be accomplished by providing guidance and support to the contractors so there is continuity and consistency with NEPA in EISs. The results of this project will be cost-effective preparation and review and EISs that are more useful to DOE decision makers. This project is also a mechanism for the ONWM, through the PNL task force, to get more and earlier involvement in the preparation of EISs so that they more

(a) For background information see PNL-3000-6, an earlier report in this series.

accurately reflect consistent program policy and objectives.

Randal Scott, ONWM's Assistant for Environmental Activities, visited the Hanford Site in November and met with the principal investigators on the project. The meeting was used as a forum to discuss Mr. Scott's expectations for the project and some of the mechanics for handling the task. A February 11, 1981, meeting has been planned to discuss in detail the approach to be taken. Mr. Scott and all team members from PNL and HARC are expected to attend.

It has been decided that the first EIS for this task will be on a Uranium Mill Tailings Remedial Action (UMTRA) site; Salt Lake City, Durango, and Shiprock are being considered. The team to provide this support is being formed. In anticipation of support on an UMTRA program EIS, task members are in the process of reviewing the draft NEPA Implementation Plan for the Uranium Mill Tailings Remedial Action (UMTRA) Program.

WASTE MANAGEMENT INFORMATION FOR THE LAY PUBLIC^(a) - R. L. Murray (North Carolina State University)

A draft report entitled Understanding Nuclear Waste Management, PNL-3570, was reviewed by DOE-RL Program Office and Public Affairs personnel. The report is being developed for publication. DOE-RL sent the report to DOE-HQ requesting comments, and the report is also being reviewed by PNL staff and some selected outside consultants. PNL continued to analyze various means for disseminating the information contained in PNL-3570 to the public.

(a) For background information see PNL-3000-6, an earlier report in this series.

A speech by Dr. R. L. Murray entitled "Development of Educationally Useful Information on Complex Technical Projects: Nuclear Waste Management as a Case Study" was cleared by RL. It is based on the work he did on PNL-3570 and will be given at the annual meeting of the National Science Teachers Association in New York City in April 1981.

DILUTION DISPOSAL OF RADIOACTIVE WASTES^(a) - G. L. Benson

Final revisions were being made to a draft report entitled Near Surface Geologic Disposal of Radioactive Waste - An Initial Assessment, PNL-3580. We plan now to submit it to DOE-RL for clearance next quarter.

WASTE MANAGEMENT HEALTH PHYSICS WORKSHOP^(b) - C. M. Unruh

A handbook entitled Waste Management Health Physics was approved and cleared by DOE-RL. It was used during the first workshop held at DOE-HQ the week of November 17, 1980. A second workshop is tentatively planned around March-April 1981.

NUCLIDE TRANSPORT EXPERIMENTS - J. C. Lau

Work done by PNL's Physical Sciences Department on the spectrum of radionuclides present in the natural uranium and thorium decay chains, together with the long-lived spontaneous fission products, has demonstrated that these should be extremely useful in studies of the integrity of potential repositories and the possible movement of

(b) For background information see PNL-3000-7, the report for the fourth quarter of 1980.

nuclear wastes from potential repositories. The two subjects that could be successfully addressed by use of these natural radionuclides are

- time scale for any past migration as evidenced by disequilibrium of the uranium/thorium chains
- aqueous transport of radionuclides in candidate repositories or similar geologic environments.

To use naturally occurring radionuclides for investigations of the above areas, it is essential that sufficiently sensitive analytical techniques be available for their measurement. PNL has the rare capability to achieve the sensitivities required for measuring the radionuclides of interest. These types of geochemical studies, along with more conventional chemical investigations, should aid in establishing the integrity of potential high-level waste repositories. This approach, applicable both to continental (rock) repositories such as basalt, granite and salt dome and to deep sea sediments, should allow the following important observations to be made on the candidate repositories:

1. establishment of any past movement of natural radionuclides or spontaneous fission products over time scales ranging from 1000 to 10 million yr
2. establishment of the adsorption/desorption rate of the various natural radionuclides from natural waters to the associated strata.

This information is useful to the selection of candidate repositories for the isolation of high-level radioactive wastes.

Toward the end of FY 1980 PNL's Physical Sciences Department began to conduct such experiments related to the seabed sediment. Arrangements were made for PNL to receive samples from a 25-m sediment core sample taken from the Mid-Pacific gyre. This particular core has been the subject of a very intensive series of examinations conducted by the Sub-seabed Program scientific team.

The results obtained in FY 1980 from this core indicated that the method should yield important results not achievable by other known means. Consequently, effort was expended this quarter to complete the experiments, analyze the data, and write a draft report.

A draft report summarizing the work to date, entitled Radionuclide Transport Studies for Confirming the Integrity of Potential Nuclear Waste Repositories, PNL-3698, was nearly completed at the end of this reporting period. We plan to submit it to the Sub-seabed Program Office for comment and to DOE-RL for clearance next quarter.

13. WASTE MANAGEMENT SAFETY STUDIES

P. J. Pelto - Project Manager

The objectives of this program are to aid in ensuring that waste management and its inherent safety function are given proper emphasis during nuclear fuel cycle evaluations; develop assessment methods; and identify portions of waste management systems that could benefit by safety design emphasis.

FY 1981 work in this program is divided into methods development and safety assessment. Work was begun in both of these areas this reporting period.

An outline of a report summarizing the results of the FY 1980 state-of-the-art safety methods survey was prepared, and work was started on this report. Work also continued on the development of safety indices

to aid in setting waste management safety R&D priorities.

A preliminary safety assessment of a reference away-from-reactor spent fuel storage facility is being performed to demonstrate and refine the methods development work. Work began on preparation of a systems description that will form the basis for the preliminary safety analysis.

14. ASSESSMENT OF EFFECTIVENESS OF GEOLOGIC ISOLATION SYSTEMS

F. H. Dove - Project Manager

The objectives of the Assessment of Effectiveness of Geologic Isolation Systems (AEGIS) Program are to:

- 1. develop the capabilities needed to assess the post-closure safety of geologic repositories*
- 2. demonstrate the assessment capabilities by performing analyses of reference sites*
- 3. apply the assessment methodology to assist the National Waste Terminal Storage Program in site selection, and waste package and repository design*
- 4. perform repository site analyses responsive to the time schedule and to the level of sophistication required to meet the licensing needs of the National Waste Terminal Storage Program.*

SUMMARY

Work directed recently at an integral form of the hydraulic conductivity inverse problem is expected to give results that are smoother with respect to input velocity fields than previous methods have been. Last month a candidate numerical procedure for this problem was formulated. This procedure follows from a variational principle that is related to the result presented by Arnold (1980).

Work continued on obtaining exact solutions for two fractures of different size and intersecting at angles other than 90° . Such results are needed to better understand the flow division at intersections and to verify that the approximation is representative of intersecting cracks. Exact solutions are being obtained for intersection angles that can be represented as the quotient of two integers. Under such conditions the required integrals can be evaluated exactly.

A method has been found that permits use of all terms in both the mean concentration

and its variance calculation for contaminant transport under uncertainty. This is particularly important since the problems of approximating the reciprocal powers of matrices, solution updating, etc. are no longer present. An additional benefit is a simplification of the computations. The simplification has been carried out only for the one-dimensional case, but the extension to the two-dimensional case is not seen as a problem. The simplification occurs because of the simple matrix form for the finite-difference approximations. It is not clear whether the matrix for the finite element approximation will permit this type of simplification.

The analytical basis for selecting optimal repository design parameters using geohydrologic response functions to minimize environmental contamination was completed for the first-phase problem of dry deposition of contaminants. The design parameters are repository locations, orientation, and shape. In the first-phase problem, the deposition of contaminants was assumed not to change the ambient ground-water flow field.

The Geologic Simulation Model (GSM) for basalt was essentially completed, and results of several hundred Monte Carlo-mode simulations were used for logic checkout and debugging. The manual (PNL-3542) describing the structure and operation of this model was cleared and is now being revised. Adaptation of the GSM to analysis of salt anticlines of the Paradox Basin was begun, as were studies of fault-plane permeability and crustal stress-strain. These studies will increase the flexibility of the GSM and improve its internal submodels.

Working papers intended for inclusion in the basalt Reference Site Initial Assessment (RSIA) draft report were: Basalt RSIA Release Scenario, revised following Office of Nuclear Waste Isolation (ONWI) and Rockwell review; Aquifer Recharge Calculations for Basalt RSIA, submitted to ONWI and Rockwell for review; and The Potential for Human Intrusion in Basalts of the Pasco Basin and a working paper on numerical hydrologic modeling of the Columbia Plateau and the Pasco Basin, prepared for internal review.

Potential radiation doses at one million years after disposal of spent reactor fuel in a salt dome were calculated for a revised list of radionuclide content, with no significant differences noted in comparison with previous calculations. The DITTY1 code for calculation of population doses integrated over 10,000 years was completed and debugged. Dose analyses continued for evaluation of the Environmental Protection Agency (EPA) Draft High-Level Waste (HLW) Criteria.

PROJECT MANAGEMENT - F. H. Dove

The Technology Program Plan (TPP) for FY 1981 was prepared and reviewed internally. It will be revised and submitted to the DOE,

the ONWI, and the Nuclear Waste Technology Programs Office (NWPTO) for approval in January 1981.

In FY 1981, the AEGIS Program is again divided into two functional branches--one for research and development of performance assessment methodology and the other for application of the existing methodology to reference site initial assessments, site selection, and various ONWI support activities. Maintenance of the methodology development work separately from the application work allows continual research and development without interference by immediate demands of site assessments. Additionally, maintenance of an applications group helps to focus the preparation of site assessments and other applications of methodology. The Methodology Development branch of AEGIS will consist of the following tasks:

- Flow Methodology Development
- Transport Methodology Development.

The other major branch of AEGIS, Site Applications, will be divided into the following four tasks:

- Scenario Analysis
- Hydrogeologic Analysis
- Transport Analysis
- Dose Analysis.

The scope of AEGIS in the past has been limited to post-closure, far-field, long-term analysis. It excluded the consideration of processes that are induced by the presence of the wastes that may affect the repository integrity, and it excluded the consideration of nuclear waste disposal options other than geologic isolation. The scope of AEGIS will be gradually expanded to incorporate near-field, short-term aspects of geologic isolation into a comprehensive performance assessment methodology. In FY 1981, AEGIS will continue its research and development efforts for assessment capability

including the assimilation of near-field models assembled by INTERA and also use existing methodology to perform reference site initial assessments, site selections, and other ONWI and DOE support activities.

The AEGIS Quality Assurance Plan, PGM-2 (Revision 1), was approved and issued on November 17, 1980. The revised plan incorporates changes suggested during the internal Battelle audit of the AEGIS program in May 1980. All corrective actions as a result of audit findings have been completed. Because the use of expert consultants is an integral part of the AEGIS Geologic Simulation Model, a new quality assurance procedure (AEGIS-3) for the selection and use of expert consultants and documentation of their contributions has been drafted. After review and comment, the procedure will be revised and implemented during the methodology demonstration of adapting the Geologic Simulation Model to the Paradox Basin.

The AEGIS program will support ONWI licensing activities in FY 1981 by contributing to the preparation of a licensing topical report entitled "Performance Modeling for Site Selection" which will be used to help define the DOE position and to obtain Nuclear Regulatory Commission (NRC) approval of the role, value and limitations of performance modeling in the site-selection process. The report will identify the nature of performance modeling to be used in various phases of site characterization, qualification and selection. The report will not discuss the details of models, model development or model verification except to the extent that such background information is necessary to formulate a DOE position. Although formal authorization of a change in scope to project funding has not been received, work has begun to provide written contribution by mid-January.

Special requests during this quarter included a review for DOE-RL of the technical documentation for 10CFR60 and a review of Volume D of the Arthur D. Little, Inc. report for the EPA entitled Technical Support of Standards for High-Level Radioactive Waste Management (EPA-520/4-79-007D). The AEGIS response compared EPA results with those published in the DOE document entitled Management of Commercially Generated Radioactive Waste (DOE/EIS-0046F), compared EPA and DOE analytical methods (AEGIS), and identified report omissions, errors, and other specific findings. Because of the variability of geologic systems, such studies must be done on a site-specific and not a generic basis.

Reviews of ONWI-9 (draft), entitled NWTS Waste Package Program Plan, and the Basalt Waste Isolation Project Site Characterization Plan (RHO-BWI-CD-51 Rev 2) were also completed as special requests with written comments forwarded to NWTPO.

AEGIS and Waste/Rock Interaction Technology (WRIT) personnel attended an ONWI coordination meeting for the Waste Isolation Performance Assessment Program (WIPAP) contractors on October 30-31, 1980. The coordination meeting was successful in improving communication and interactive cooperation within WIPAP.

AEGIS staff are scheduled to present seven papers at the Symposium on Uncertainties Associated with the Regulation of the Geologic Disposal of High-Level Radioactive Waste in Gatlinburg, Tennessee, on March 9-13, 1981. The papers will be organized as a series discussing various aspects of uncertainty encountered during applications of AEGIS methodology. C. R. Cole and M. G. Foley attended the NWTS Information meeting in Columbus, Ohio, December 9-11,

and gave presentations on Paradox Basin Sensitivity Analysis and the Geologic Simulation Model, respectively

METHODOLOGY DEVELOPMENT - R. W. Nelson

Flow Methodology Development - C. T. Kincaid

In the past quarter, work on the hydraulic conductivity inverse subtask has been directed at an integral form of the inverse problem that probably gives results that are smoother with respect to input velocity fields than do previous methods. A candidate numerical procedure for this problem was formulated that follows from a variational principle that is related to the result presented in PNL-SA-8768. Based upon these results, we expect that the numerical procedure should be an improvement over present techniques. It is not expected that this procedure will, however, alleviate all ill-posedness problems.

Developmental work on fluid flow under uncertainty was started with initial consideration centering on the application of the mathematical tools developed by A. G. Gibbs (FY 1980). The outcome of this in-depth scrutiny of flow under uncertainty is an overall recognition of the problem's being somewhat more complicated than that of uncertainty in transport. Specifically, the storage or time derivative term of the flow equation contains stochastic information in the form of an imprecisely known storativity. Use of the finite element technique gives rise to a matrix multiplying the vector of known potentials. These two related events lead to more complex matrices; consequently, their products and triple products are also complicated.

The continuing work toward describing flow in a fractured permeable medium pro-

vided significant results during the quarter. Dr. Strack, under contract to PNL, obtained an exact analytical solution for the flow field associated with two fractures intersecting at right angles. The two fractures in the porous material had different fracture widths and lengths, which resulted in an unequal flux redistribution at the intersection.

An approximate analytic solution for two intersecting fractures meeting at any angle was also derived. This result requires representation of the intersecting fractures by more segments than if a completely closed form expression were applied. Comparison with the 90° exact solution, however, gives excellent agreement when using more segments in the approximation. Exact solutions were also obtained for intersection angles that can be represented as the quotient to two integers. Under such conditions, the required integrals can be evaluated exactly.

Detailed development is under way to provide rapid and direct solution capability for very complicated combinations of intersecting and nonintersecting fractures. The input and output routines are completed which allow interactive construction of complex fracture patterns and output of the resulting flow system potentials and streamlines. An important part of this capability is providing ways to handle fractures that intersect flow boundaries. Encouraging progress has been made in handling such intersections with rectangular flow boundaries.

Transport Methodology Development - E. M. Arnold

Significant progress has been made in the application of geostatistics to determine the hydraulic conductivity and ground-water potential data covariance structure. This

structure is necessary to provide the required pore velocity input uncertainties for the new stochastic convective transport equations. Specifically, the work included the geostatistical modeling of field data from the Hanford Reservation. The drift and covariance structure of hydraulic conductivity and ground-water potential data are currently being characterized for use as input to the initial stochastic convective contaminant transport code.

Determination of a way to overcome computational problems in the uncertainty transport development work was an important accomplishment during the quarter. The computational problem arises from the more involved numerical solution requirements for stochastic as compared to deterministic transport equations. In classical deterministic numerical solution methods for time-dependent problems, only results at two consecutive times are involved in the step-wise solution process. By contrast, the numerical solutions of the uncertainty transport equations are found to involve results from all preceding times in the solution sequence. The very involved time-coupling of the numerical solution methods under uncertainty requires forming powers of large matrices, each arising from a triple vector of matrix products.

Work on this problem previously centered on finding an appropriate approximation for the large matrices to reduce computations to a reasonable level. One approximation tried was the use of an identity matrix where only the main diagonal elements from the large matrices were raised to powers. Difficulty had also been found in numerically calculating the variance with sufficient accuracy. There was really no way to determine whether the resulting lack of accuracy was related to the large matrices approximation or to

the poorly estimated variance by numerical means.

A method was found by C. A. Oster that permits the use of all terms under some conditions in both the mean concentration and its variance calculation in the time sequence. This is particularly important since the problems of approximating the reciprocal powers of matrices, solution updating, etc., are no longer present. An additional benefit is a simplification of the computations.

The simplification has been carried out only for the one-dimensional case, but the extension to the two-dimensional case is not a problem. The simplification occurs because of the simple form the matrix takes for the finite difference approximations. It is not clear, however, whether the matrix for the finite element approximation will permit this type of simplification. In the finite-difference case, the troublesome summation is replaced with a linear combination of matrices that are computed recursively from a two-term relation. In the one-dimensional case there are two such matrices; in the two-dimensional case there are five.

With the one-dimensional code and Gibbs' analytical solutions, one can test the use of approximations such as replacing the reciprocal powers by diagonal matrices. Such comparisons for the expectation and the variance have been and are being made in some detail. Results thus far indicate it is entirely feasible to solve the one-dimensional problem for both the mean concentration and its variance without making any approximations. A similar statement can be made about the two-dimensional case, but it will have a higher cost associated with a solution. However, unless the resulting matrix is simple, some approximations will

probably be used. In the case of the finite-element formulation with a highly irregular boundary, the matrix would contain too many nonzero elements to consider the approach developed to the present. If the boundary is simple, the resulting matrix might permit one to avoid these approximations.

Because the geohydrologic response functions are really overall contaminant inflow-outflow relationships for a particular subsurface repository and associated geohydrologic system, they effectively summarize all the pertinent happenings between the source of contaminant and its exit to the biosphere. Some secondary or side benefits have been realized in their use beyond the direct use as system evaluators that significantly aid in the effective communication of technical results. They are useful in demonstrating or comparing the significance or sensitivity of system parameters or effects on overall repository performance. If a large change in the graph of the response function results from a parameter change, it is immediately apparent. Further, the simplicity in either directly evaluating the magnitude of system change due to a parameter change is very helpful. In each case, it is easy to visualize or see expected effects on the overall system performance as caused by the sensitivity change.

Response functions are also useful in setting up distributed process control approaches to provide more usable repository site selection and utilization procedures. The initial problem is being set up and handled as an adjunct formulation to provide minimal effects to the biosphere by optimal repository placement in a deep regional ground-water flow system.

SITE APPLICATIONS - M. G. Foley

The second revision of PNL-2955, entitled Reference Site Initial Assessment for a Salt Dome Repository, has been completed. Revision included consideration of all comments received from individual peer reviewers, an ONWI task force, and staff within the Nuclear Regulatory Commission (NRC). These comments have been summarized and many have been addressed in detail in a new chapter added to the first volume of the report. Criticisms of the AEGIS analysis ranged from over-conservatism to nonconservatism. Other changes to the report included the following:

- strengthening of conclusions in the Executive Summary and dose chapters
- preparation of an abstract
- improvement of the Assumptions section
- inclusion of new dose calculations for intrusion events far into the future (up to one million years after closure)
- inclusion of new dose calculations for doses to the solution mine operators
- consideration of an alternative scenario of reduced scope for solution mining but resulting in identical consequences to the general population and to individuals consuming the resultant table salt.

The second revision of PNL-2955 will be submitted to clearance in the next quarter.

Preparation of the basalt RSIA draft report is still in progress. Hydrologic and transport calculations have not been completed; consequently, the draft report will not be available for review by ONWI and Rockwell before the end of January 1981.

Scenario Analysis - M. G. Foley

The input-output and statistical packages of the Geologic Simulation Model, formerly called the Release Scenario Analysis Model, were completed, and several hundred Monte Carlo simulations were run. Data from these runs were used for logic checkout and debugging. Test input data were replaced with input data from expert consultants as these were received. The consultants found more difficulties than expected in providing high-quality, auditable input data, and their contributions were not completed by the end of the quarter. Despite the lack of a complete set of operational input data, the GSM in the Monte Carlo mode was useful in characterizing the effects of uncertainties in knowledge of present ground-water characteristics of the Pasco Basin on the initial modeled ground-water flow system. Peer review of the GSM was facilitated by clearance of the user's manual (PNL-3542), by transfer of the model and documentation to Arthur D. Little, Cambridge, and by final preparation for publication of the GSM conceptualization report (PNL-2892).

Revision of the working paper Basalt RSIA Release Scenario was completed. This working paper and one entitled The Potential for Human Intrusion in Basalts of the Pasco Basin, still in review, will be incorporated in the basalt RSIA draft report.

Adaptation of the GSM to salt anticlines of the Paradox Basin was started. This is intended to be a technology demonstration effort rather than a fully developed RSIA, and it is expected that the GSM for the Paradox Basin will be less detailed than that for the Columbia Plateau. Efforts during this quarter were limited to a field reconnaissance of the Paradox Basin, led by

Dr. R. J. Hite of the U.S. Geological Survey, and to reviews of the literature.

Work on the fault-zone permeability and crustal stress-strain studies was also begun. As in the case of the Paradox Basin modeling, work during this quarter was limited to a review of the literature.

Hydrogeologic and Transport Analysis - C. R. Cole

Two working papers were prepared for inclusion in the basalt RSIA draft report. One entitled Aquifer Recharge Calculations for Basalt RSIA was transmitted to ONWI and Rockwell in early November for review and comment. This working paper was unscheduled initially; however, the importance of documentation during the analysis was revealed by the lack of quantitative data on the regional transmissive properties of the deeper basalts and by the extensive efforts associated with the regional recharge calculations. It should be noted that both the BWIP hydrologic needs for the Pasco Basin and the AEGIS regional and local modeling needs for the basalt RSIA were successfully fulfilled through an equal Battelle-Rockwell funding of the supporting technical investigation. A working paper on numerical hydrogeologic modeling of the Columbia Plateau and Pasco Basin was also in review.

All hydrologic and transport data were stored in appropriate computer files, but preliminary analyses with the Pasco Basin FE3DGM flow model were delayed by problems with the hydrologic data. Disparities between structure, potentiometric surface, and transmissivity maps were apparently the result of inconsistent choices of map boundaries during digitizing. These problems and ones resulting from under-estimating the complexity of the modeling task (especially

in connection with interfaces between regional and local hydrologic models) delayed completion of the hydrologic and transport modeling for the basalt RSIA by almost 2 months. Completion is not expected before the end of January.

Dose Analysis - J. K. Soldat

Potential radiation doses at one million years after disposal of spent reactor fuel in a salt dome were recalculated using a revised list of radionuclide contents. No significant differences were noted between the latest results and the doses calculated previously. Discussion between AEGIS and ONWI personnel led to an agreement on work to be performed to generate a preliminary estimate of radionuclide release standards for comparison with those of EPA. ONWI authorized completion of the dose code DITTY1 required for calculation of population doses integrated over a 10,000-yr period, and performance of the necessary dose calculations. Encoding of the computer program DITTY1 was completed. The program is fairly complex and quite comprehensive with regard to possible scenarios and exposure pathways. The code is operational on the UNIVAC 1100/44 and has been debugged. Spot comparison, however, with the PABLM code occasionally yields different answers. The two codes are currently being reviewed to find an explanation for these differences.

Preliminary calculations of the potential health effects from release of the quantities of radionuclides listed in the EPA Draft HLW Criteria were repeated with two

different scenarios during December. The EPA release criteria were designed to result in not more than 10 health effects over 10,000 years for a generic repository. The first set of calculations assumed one person directly ingested the entire quantity of a nuclide listed in the EPA criteria table. The resulting doses were then assumed to be population doses (in terms of man-rem). A conversion factor of 2×10^{-4} cancers per man-rem was used to convert whole-body doses to health effects. The resulting health effects ranged from 10^2 to 10^5 for the list of nuclides. The second set of calculations was performed assuming that the released nuclides were diluted in well water used for irrigation and human and animal consumption for 70 years. When the total diluting volume was taken to be sufficient to serve 200 persons (i.e., 50 wells, 5 gpm each, serving 50 farm families of four persons each), the calculated health effects were reduced to 1 to 10 with the exception of ^{99}Tc , which had a value of 0.01 health effects. It is very possible that the EPA used a more conservative (higher) value for the uptake of ^{99}Tc plants than the 0.25 used in PNL's code. ORNL had recommended a tentative value of 25 a few years ago, but has since found somewhat lower values in vegetation samples collected in the field.

A test data transfer to DITTY1 from AEGIS geotransport codes was begun. This work is necessary to develop the links between geologic simulation, hydrogeologic and transport and dose analysis necessary for an integrated evaluation of a repository.

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15. WASTE/ROCK INTERACTIONS TECHNOLOGY

R. J. Serne - Project Manager

The specific objectives of the Waste/Rock Interactions Technology (WRIT) program are to:

1. *identify and characterize the mechanisms of waste-form radionuclide release and subsequent geochemical interactions with engineered barriers and natural geologic media, e.g., leaching, solubility, and sorption*
2. *collect data and then develop and evaluate the effectiveness of models (i.e., the applications/limitations of each model) that predict leaching, sorption and release processes in the repository and surrounding media*
3. *obtain, through verification studies and documentation, the most acceptable test methodologies for sorption, leaching, solubility limitations, and waste package-geomedia interaction studies*
4. *support the National Waste Terminal Storage (NWTS) waste package, repository development, site characterization and selection, performance assessment and licensing program plans, specifically through data generation, analysis, predictive model formulation, and technical peer review.*

PROGRAM MANAGEMENT - R. J. Serne

Work focused on clarifying and updating the Technical Program Plan (TPP) during the first part of the quarter and in December. The tasks were reviewed in detail by management to provide information for the final revision.

During October, a WRIT information meeting was held in Seattle, Washington. It was attended by WRIT staff, Office of Nuclear Waste Isolation (ONWI) program managers, and principal investigators from each of the WRIT subcontracts, who gave presentations reviewing the work of FY 1980.

Other activities were as follows:

- A quality assurance plan was completed.
- A briefing was given to the National Academy of Sciences on December 2-3, 1980, at the request of ONWI.
- The annual NWTS Program Information meeting was attended and a presentation given on waste package tests and another co-

authored with N. Hubbard and J. Kircher on radionuclide retardation data.

MECHANISM STUDIES - G. L. McVay

Waste-Solution Interactions

Essentially all (only the 3-yr samples remain) of the static 25 and 75°C doped-glass leach tests were concluded, and actinide and elemental analyses have been performed. What follows is a comparison between ^{239}Pu releases for static (25°C) and modified International Atomic Energy Agency (IAEA) experiments (room temperature). The same doped-glass compositions (PNL-76-68) and surface area to volumes (0.1 cm^{-1}) were used in each test. Modified IAEA (M-IAEA) leaching of doped glass is described by Bradley et al. 1979. Figures 15.1 and 15.2 give normalized total releases (including plateout) for ^{239}Pu in deionized water and 0.03 M sodium bicarbonate

FIGURE 15.1. Release of ^{239}Pu from Doped Glass in Deionized Water. M-IAEA data is from Bradley et al. 1979 and solubility data is from Rai et al. 1980.

FIGURE 15.2. Release of ^{239}Pu from Doped Glass in 0.03 M NaHCO_3 Leachate. Solubility data applies to 0.0015 M CaCl_2 (Rai et al. 1980).

ground water. The M-IAEA curves represent cumulative releases into leachates which are replenished periodically. Static data represent release into leachates which are not changed. On the right-hand vertical axis a scale for molar concentration of ^{239}Pu has been provided that applies for static for data assuming the released material is water-soluble. Plateout on the leach container represented an average of 20% of the released ^{239}Pu in the bicarbonate leachate and an average of 25% in the deionized water leachate. Static release in deionized water as seen in Figure 15.1 is below that of M-IAEA release, conceivably due to solubility limitations. The shaded region on the concentration scale is the PuO_2 solubility at a pH of 8 in 0.0015 M CaCl_2 at room temperature (Rai et al. 1980). The solubility data for pH 8 and 9 are extrapolated using data obtained over the range of pH 3 to 7. Upper and lower bounds shown for solubility data are based on least-squares confidence limits provided by Rai. Leach measurements up to 32 days indicate a stable pH of ~8 is reached (alpha-radiolysis may lower the pH after long times, however). The maximum observed plutonium release agrees well with solubility-constrained release as predicted by Rai's data. Figure 15.2 shows ^{239}Pu release in the bicarbonate solution.

The discrepancy between M-IAEA and static experiments is much more dramatic. Again, solubility limits seem to be in effect. It should be mentioned that glass corrosion in static tests continues over the entire time period for both deionized water and bicarbonate leachates as indicated by increasing levels of matrix material (sodium, boron, silicon) in the leachates. The maximum release of plutonium in sodium bicarbonate (Figure 15.2) for the static test lies between that of PuO_2 or $\text{Pu}(\text{OH})_4$ solubility data

given at the measured leachate pH value of 9. Available plutonium solubility data are for very dilute CaCl_2 , and their use for the 0.03 M bicarbonate solution (Figure 15.2) is probably less reliable than in the deionized water leachate (Figure 15.1). This may be a factor in the more marginal agreement between solubility and maximum release in Figure 15.2.

Glass Corrosion and Gamma Radiation Effects

Studies of the corrosion of several glasses $\sim 1.6 \times 10^3$ years old unearthed near Jalame, Israel, are in progress. Glass fragments obtained consisted of broken sections of bottles or vessels in addition to larger masses of apparently unworked glass. These ancient Roman glasses are being analyzed to determine the extent and nature of their interaction with the underground environment. Additionally, unreacted sections from the interior of larger pieces of the Roman glass have been taken for evaluating them in the same way waste glasses are evaluated. These tests and analyses will provide some perspective in short-term evaluations of waste glasses. Currently, only the surfaces of the excavated glass have been completely analyzed. Evaluations of the durability and comparisons to waste glasses are in progress.

The excavated glasses were of three distinct colors: amber, green, and blue. All were basically of the same composition, as shown in Table 15.1; except for the addition of 2 to 3 wt% Al_2O_3 , this is similar to modern commercial soda-lime silicate glasses. To date, the origin of the colors has not been determined.

Exposed surfaces of the excavated glasses can be classified into at least three categories: 1) surfaces visibly free of corrosion, 2) surfaces covered with white scale,

TABLE 15.1. Ancient Glass Compositions, wt%

Material	Amber Glass	Blue Glass	Green Glass
Al ₂ O ₃	2.63	2.38	2.55
B ₂ O ₃	0.10	0.08	0.05
GaO	0.03	0.03	0.06
CaO	9.20	8.16	8.47
CuO	0.04	0.07	0.08
Fe ₂ O ₃	0.51	0.51	0.55
K ₂ O	1.03	0.78	0.7
MgO	0.70	0.50	0.59
MnO ₂	0.06	0.40	1.39
Na ₂ O	16.4	17.3	17.2
PbO	-	0.09	0.1
SiO ₂	69.8	69.1	67.2
SrO	-	0.06	0.06
TiO ₂	0.07	0.07	0.07
ZrO ₂	0.06	0.0	0.05
ZnO	-	-	0.07
	100.6	99.6	99.2

and 3) surfaces exhibiting considerable iridescence. Samples of each type were examined using x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS).

It should be noted, however, that although evidence for corrosion could be found, the glasses were essentially intact after 1.6×10^3 years of weathering. Glass fragments still exhibited relatively sharp edges and corners, sometimes covered with a corrosion layer, but indicating that most of the mass of the material still remained. Exposed surfaces visually free of corrosion were determined by SIMS analysis to be depleted of sodium to a depth of 3 to 5 μm and of calcium to a depth of 1 to 2 μm . No evidence for the adsorption of foreign material could be found.

The white scale found on some surfaces was high in calcium, carbon, and oxygen, as

determined by XPS analysis, and was likely to consist of calcium carbonate and calcium hydroxide. Calcium carbonate was identified in high concentrations in the surrounding soil. The use of limestone as a crucible material in the manufacture of the glass may account for some of the scale; transport of water is, of course, another possibility. The scale adhered tightly to the glass surfaces, resisting attempts at removal. Its presence probably protected glass considerably against further aqueous corrosion.

The iridescence observed on some glass surfaces was attributed to the presence of very thin scales on the surface. The scales could easily be removed mechanically and be examined on both the front and back sides. XPS analysis showed that both front and back surfaces were high in silica, with small amounts of calcium present. It was concluded that the scales were formed by repeated wetting and drying cycles, causing the reaction layer on the glass surfaces to spall off. Such behavior has been observed previously on other commercial soda-lime silicate glasses.

Gamma-irradiation was shown last year to affect the leaching of 76-68 glass. This effect is due to enhanced interaction of water and glass because of water radiolysis and to formation of nitric acid if air is present. The goals this year are to separate the effects of water radiolysis from those of nitric acid formation and to determine the temperature and dose rate effects on glass-water interactions in a gamma field.

Most experiments will be conducted on degassed water to eliminate nitric acid formation. Time experiments will be conducted at one dose rate (1.75×10^6 R/hr) at 50, 70 and 90°C. Dose rate effects will be evaluated from 10^4 to 10^7 R/hr. Currently, only

the 50°C time experiments have been completed. The following observations can be made from these results:

- The Si-O bond is preferentially attacked by products of water radiolysis, resulting in a threefold increase in the leach rate of silicon.
- If air is present, nitric acid is formed, which further enhances silicon leach rates due to the removal of protective reaction layers on the glass. The silicon leach rate enhancement can approach one order of magnitude, depending on the amount of nitric acid formed.
- Filtering of leachates through 18-Å filters shows no significant change in solution analysis for leachates containing small concentrations of elements. However when elemental concentrations in the leachate become large (>30 ppm Si), filtration significantly reduces the silicon, cesium, alkaline earths, and rare earths. This suggests colloidal silica with many elements attached. Many more experiments are needed in this area.
- If air has been removed from the leachate, the pH in a gamma field reaches 9.5 after 14 days due to enhanced leaching of the glass. The same time in a nonirradiation environment produces a pH of only 7.8.

Preliminary results indicate that temperature significantly influences effects of gamma-irradiation on glass leaching.

ROCK-RADIONUCLIDE RETARDATION STUDIES -

J. F. Relyea

Methodology Development and Application

At PNL the transport of tritium and technetium was studied by using a column of

Westerly granite (hand-crushed to eliminate metal chips from mechanical jaw crushers that may reduce pertechnetate ions) and flow rates ranging from 270 m/yr to 2800 m/yr. The maximum effectively porosity of the column was 90% of the total static porosity. Flow rate affected the transport of tritium minimally, but technetium was observed to elute in less volume as the flow rate was increased. The separation between tritium and technetium peaks, however, was <3 for all but the highest flow rate. Judging the position of a peak was found to be difficult because of peak dispersion (spreading). We found the centroid (elution of 50% of the spike) to be a more reliable measurement for determining retardation factors.

Retardation studies have been conducted at Los Alamos Scientific Laboratory (LASL) using a circulating column apparatus. The column is packed with rock, and spiked ground water is circulated through until a constant tracer concentration is observed. The rock material used was tuff, Climax Stock Granite, and Eleana Argillite. The K_d values obtained with this hydrid batch-column techniques compare very well with previously obtained column data. Contact times (26 to 49 days) and solution-to-solid ratio (20 ml of spiked ground water per gram of rock) are similar to the conditions utilized for batch sorption experiments. The differences observed between batch and circulating column K_d values indicate that solids are probably altered more in batch sorption tests by grinding than in experiments where the solids are stationary. Consequently, shaking speeds for batch-type experiments should be no greater than one oscillation per second to lessen the effects of grinding.

Retardation Mechanism Studies

At PNL, batch sorption isotherms for strontium, cesium, and technetium have been completed on a sample of unconsolidated sediment from a depth of about 1290 ft, and one-half mile south of the Oakwood salt dome, Leon County, Texas. The sample is a fine sand (mainly quartz and feldspars) with roughly 20 to 40% clay size particles (kaolinite has been identified in the clay fraction). Synthetic ground water was prepared according to the recipe supplied with the core sample from the Texas Bureau of Economic Geology. The sample was first washed with ground water to remove organic matter contamination that may have entered the sample because of the use of an organic polymer drilling mud. The first wash was analyzed and had 15 ppm organic carbon. The samples were then washed another four times with deoxygenated water in an attempt to remove any remaining organic matter.

Figures 15.3, 15.4, and 15.5 show the sorption isotherms for ^{137}Cs , ^{85}Sr , and ^{99}Tc , respectively. Nonradioactive strontium or cesium carriers were added to ground water to maintain concentration levels. For technetium, ^{99}Tc was used to maintain the concentration, but $^{95\text{m}}\text{Tc}$ was used for radiochemically determining the fraction adsorbed. The values for $K_d(\text{Cs})$ were found to keep increasing with decreasing cesium concentration in solution, while $K_d(\text{Sr})$ values (Figure 15.2) were fairly constant below about 10^{-7} M Sr. Solution chemical analysis has not been completed, but it appears that strontium from the sample itself may maintain a constant solution concentration of about 10^{-7} M. In this case K_d values for strontium may be taken as between 140 and 180 ml/g. For cesium the K_d value will depend on the solution cesium concentration and, because cesium

is so scarce in nature, $K_d(\text{Cs})$ will probably be >100 ml/g for this sample.

Technetium (Figure 15.3) also shows a decrease in K_d with an increase in initial solution technetium concentration; however, at the 10^{-7} M and 10^{-6} M concentrations, the average K_d value would be negative. The spread in data points at these concentrations means that they are not significantly different from zero. While the data at 10^{-8} and 10^{-9} M Tc apparently differ from K_d values of zero, there is no proof that these are valid K_d values. In other words, we cannot yet say whether the retardation of technetium is anion adsorption or reduction/precipitation. A K_d in the range of 1 or 2 ml/g should yield a retardation factor of <20; this will be checked in a short duration column experiment with the same sample material.

The computer code MINEQL was used at Lawrence Berkeley Laboratory (LBL) to predict uranium concentrations in solutions contacting quartz and montmorillonite clay. Concentrations were determined experimentally (as a function of pH and the NaCl and initial UO_2^{+2} concentrations) and compared with predictions based on thermodynamic data and an ion-exchange mechanism included in MINEQL. In almost all cases MINEQL overestimates solution uranium concentrations, but with one thermodynamic data set (Lemire and Tremain 1980) the error was seldom more than one order of magnitude.

Comparison of predicted and observed results indicates that UO_2^{+2} is dominant at $\text{pH} \leq 5$ and is probably adsorbed by an ion-exchange mechanism. Results also indicate that at higher pH values adsorption by ion exchange may not be as important. Neutral or negatively charged species may be the dominant solution species, but adsorption is much greater than predicted by an

FIGURE 15.3. Adsorption Isotherm for ^{137}Cs on Oakwood Dome Sample, Leon County, Texas

FIGURE 15.4. Adsorption Isotherm for ^{85}Sr on Oakwood Dome Sample, Leon County, Texas

FIGURE 15.5. Adsorption Isotherm for ^{99}Tc on Oakwood Dome Sample, Leon County, Texas

ion-exchange model. Two possible mechanisms may be responsible for the anomalous behavior at neutral and higher pH values: 1) formation of an unidentified solid phase may limit solubility and 2) adsorption of hydrolyzed species by some mechanism other than ion exchange (or electrostatic attraction).

The computer code has been useful thus far for making predictions under a wide variety of conditions that can be tested or verified experimentally. When solubility data seem to agree and concentrations still fall below predictions, we are forced to seek another mechanism for explaining and predicting the adsorption. The interactive nature of this process should also help when other easily hydrolyzed species are studied.

SOLUTION CHEMISTRY - D. Rai and R. Strickert

Solubilities of Key Compounds and Elements

The milestone report on $^{239}\text{Pu(VI)}$ polymer solubility was completed on schedule and has been submitted to Nuclear Technology for publication. The report deals with experiments conducted to determine the properties of the plutonium polymer under environmental conditions. The results indicate that the polymer suspensions are not stable at pH values >5 , and hence the polymer is not expected to be mobile in the lithosphere. The solubility of the polymer is intermediate between the solubilities of $\text{Pu(OH)}_4(\text{a})$ and $\text{PuO}_2(\text{c})$ (Figures 15.6 and 15.7) and is <10 ppb in air-equilibrated dilute salt solutions at pH 7.

FIGURE 15.6. Plutonium Solubility of Pu(IV) Polymer Suspensions in Nitrate Solutions

FIGURE 15.7. Plutonium Solubility of Pu(IV) Polymer in Chloride Solution

The oxidation state of the soluble plutonium was essentially all plutonyl [Pu(V) and/or Pu(VI)] as shown by TTA extraction. In addition, one of the filtered solutions with high plutonium concentration (pH 3.1) was analyzed by a spectrophotometric method (Rai, Serne, and Swanson 1980) and was found to contain Pu(V). The other solutions contained too little plutonium to use the spectrophotometric method, but because of the differences in stability fields of Pu(V) and Pu(VI) (Rai, Serne, and Swanson 1980), it is most likely that the predominant oxidation state in all these solutions is Pu(V). Such results agree completely with those reported by Rai, Serne, and Swanson (1980) for the oxidation state distribution of air-equilibrated $\text{Pu}(\text{OH})_4(\text{a})$ and $\text{PuO}_2(\text{c})$ suspensions. Pu(V) in these solutions is expected to be present predominantly as PuO_2^+ because 1) the relative tendency of plutonium ions to form complexes is $\text{Pu}(\text{IV}) > \text{Pu}(\text{III}) > \text{Pu}(\text{VI}) > \text{Pu}(\text{V})$; 2) the only anions present in these solutions in significant amounts are Cl^- and NO_3^- , which do not form strong complexes with PuO_2^+ ; and 3) the species PuO_2^+ does not exhibit further hydrolysis between a pH of 0 and ~8.

The solubility of the polymer in nitrate solutions was approached from the directions of both undersaturation and oversaturation (Figure 15.6). The close agreement in measured solubility values indicates that the soluble species was indeed at equilibrium with the solid phase. Polymer solubility in chloride solutions (Figure 15.7) was about 0.44 log units lower than the polymer solubility in nitrate solutions. Slight differences in ionic strength do not explain this difference. Rather, the difference in solubility may be due to the higher redox potentials observed in the nitrate solutions; the precision of measuring redox potentials with

a platinum electrode in nonpoised (unbuffered) air-equilibrated solutions is not high ($\approx \pm 50$ mV).

Finally, the results of the polymer solubility studies are consistent with the observations (Lloyd and Haire 1978) that polymer particles may be amorphous at first and may develop crystallinity on aging, and thus $\text{Pu}(\text{OH})_4(\text{a})$ and $\text{PuO}_2(\text{c})$ would then represent the extremes in solubility of the polymer, depending upon the degree of crystallinity of the polymer.

Preparation of the anoxic chamber to be flushed with argon gas was continued in the quarter. Lead-lined shakers and electrical connections are being installed for remote monitoring of pH and Eh values. The ability to remotely monitor these parameters in the anoxic chamber will save considerable time and allow the most efficient use of the limited space available. The anoxic chamber will be used for solubility studies involving several actinide compounds.

Solution Chemical Environment and Chemical Species of Redox-Sensitive Elements

The milestone report (Rai, Strickert, and Ryan 1980) on alpha radiation effects in solution was completed on schedule and has been accepted for publication in Inorganic and Nuclear Chemistry Letters. The alpha radiation studies, discussed in the third quarter executive summary report to ONWI, concluded that dissolved N_2 was converted to HNO_3 due to alpha radiolysis of suspensions of plutonium compounds. Although the intermediate reactions of HNO_3 production have not yet been identified, H^+ , NO_3^- and plutonyl ions were identified as the end products. It was also shown that the rate of H^+ production is proportional to the H^+ activity of the solution.

The importance of precipitation/dissolution behavior of actinide compounds under environmental conditions has been recognized by the waste management community (Rai and Stickert 1980). To gain a better understanding of equilibrium solubilities in the absence of complexing agents, actinide solubility behavior was calculated as a function of Eh and pH (Newton 1980). Actinide compounds were limited to oxides and hydroxides. Thus the solubility of an actinide is the sum of the concentrations of all species in equilibrium with it. This will include all the hydrolyzed forms of the various possible oxidation states. For these calculations, the various solubility products, hydrolysis constants, and redox potentials are needed. Unfortunately, almost none of the required data is available; instead, recently published estimates were used (Allard et al 1980). As an example, the results for $\text{PuO}_2 \cdot n\text{H}_2\text{O}$ are shown in Figure 15.8. The contour map shows lines of constant solubility as a function of pH and Eh. The solubility diagram is divided into two regions by a solid diagonal line; below the line the solid phase is the Pu(IV) hydrated oxide, while above the line the Pu(VI) hydroxide is stable. The dotted lines represent the stability limits of water. Three distinct principal solubility reactions are associated with the regions showing the diagonal, horizontal, and vertical lines, respectively. The diagonal lines show a slope of about -0.24 (-4×0.059) and represent the plutonium half reaction;

where the contours are horizontal, the half-reaction is

This result is consistent with the observation of Rai and coworkers (1980), who showed that where Pu(V) is the main solution species in contact with $\text{PuO}_2 \cdot n\text{H}_2\text{O}$, the solubility depends on the Eh but is essentially independent of pH. Where the contours are vertical, the plutonium reaction is

Such an analysis indicates that the only parameters that contribute significantly to the solubility of $\text{PuO}_2 \cdot n\text{H}_2\text{O}$ are

- the solubility product of $\text{PuO}_2 \cdot n\text{H}_2\text{O}$
- the Pu(III)/Pu(IV) redox potential
- the Pu(IV)/Pu(V) redox potential
- the fifth hydrolysis constant for Pu^{4+} .

One conclusion evident from the diagram is that careful measurement and control of Eh (and pH) is required for meaningful measurement of solubility. A good way of doing this is probably to use Eh moderators or buffers together with a potentiostat. Quinhydrone and Nile Blue have been used in the past. Inorganic buffers, if reversible and noncomplexing, may also be used. Newton (1980) has listed several possible organic redox buffers that may be useful over a broad Eh-pH range (Table 15.2).

Bondietti and coworkers (1980) have also investigated the control of the redox potential in conjunction with the work on technetium solubility. Their work included investigation of the Fe(II)/Fe(III) system for pH values greater than 7.5; the response of a platinum electrode was ~ 180 mV/pH unit. This corresponds to the $\text{Fe}^{2+}/\text{Fe}(\text{OH})_3\text{o}$ and/or $\text{Fe}(\text{OH})^+/\text{Fe}(\text{OH})_4^-$ couples. Between pH 6 and 7 the response was ~ 120 mV/pH unit, corresponding to the $\text{Fe}^{2+}/\text{Fe}(\text{OH})_2$ couple. Such results infer that the platinum electrode may be used to measure the redox potential of systems where the Fe(II)/Fe(III) redox reaction predominates.

FIGURE 15.8. Lines of Constant Log (Solubility versus Eh and pH) for Plutonium Hydrous Oxides

TABLE 15.2. Possible Organic Redox Indicators

Buffer	E_m^7 , mV ^(a)	pH Range
Induline Scarlet	-299	3.0- 8.6
Rosinduline 2G	-281	4.8-11.4
Lissamine Blue BF	-253	1-11
N,N'-dimethyl Viologens	-446	8.4-13
Indigo Carmine	-125	<9
Pyocyanine	-34	1-12

(a) E_m^7 (mV) is the formal redox potential at pH 7.

Experiments were conducted (Bondietti, Lee, and Hall 1980) to evaluate a Tc(VII)/ Tc(IV) redox couple as the controlling factor for technetium in solution. Using the Fe(II)/ Fe(III) couple to establish a measurable potential, known amounts of TcO_4^- were added to N_2 -purged solutions (0.01 M KCl). Eh and pH measurements were taken periodically along with technetium and Fe(II) con-

centration measurements in filtered (0.22 μm) aliquots of solution. Figure 15.9 briefly summarizes the results. Two concentrations of technetium were studied (4.2 μM below pH 8, 0.011 μM above pH 8). In general, where the Eh value was above the theoretical $\text{TcO}_4^-/\text{Tc(OH)}_4$ boundary, TcO_4^- was not lost from solution (regions N), or in some cases an initial marginal loss was not continuous

FIGURE 15.9. Summary of Experimental Data Obtained To Define Eh-pH Boundary for TcO₄⁻ Reduction. Equilibrium lines are at log TcO₄⁻ values initially present experimentally.

(regions M). When the experimental potentials were below the theoretical boundary, over 90% of the TcO₄⁻ was lost (regions R).

These experiments provide more definitive evidence that the Tc(VII)-Tc(IV) redox

$$\log[\text{TcO}_4^-] = (\text{Eh} - 0.710 + 0.0788 \text{ pH})/0.0197$$

is appropriate for inclusion in geochemical models evaluating the migration of technetium.

WASTE-PACKAGE INTERACTIONS MECHANISMS AND SYSTEMS PERFORMANCE - D. J. Bradley and J. W. Shade

Direct-Sampling Autoclave Tests

Preliminary data from the last FY 1980 series of direct-sample autoclave tests (series 3) were reported in the July-September 1980 Quarterly. The results of additional analyses from this series are

given in Table 15.3. Three tests were conducted utilizing 1) a minicanister and deionized water (DIW), (minicanister is defined as a 304L stainless steel cylinder 6.4 cm high and 1.9 cm in diameter filled with 76-68 g/l glass doped with ²³⁸U), 2) a minicanister in contact with Climax Stock granite and its equilibrated water, and 3) a minicanister in contact with Umtanum basalt and its equilibrated water. All minicanisters remained submerged in the liquid during the run, but the open end of the canister was exposed directly to the liquid rather than being surrounded with crushed rock media as in the earlier runs. The crushed rock material used in two of these tests amounted to 10 to 20% of the material used in previous tests. The purpose of the crushed rock material was to maintain rock-water equilibrium.

TABLE 15.3. Comparison of Solution Compositions, ppm, for Series III Package Tests, 250°C/200 psi

	Minicanister Only				Minicanister + Granite				Minicanister + Basalt			
	Weeks				Weeks				Weeks			
	0	5	6	8	0(a)	5	6	8	0(a)	5	6	8
DWI												
Si		312	348	375	10.8	295	308	343	26.8	565	580	585
Fe		0.5	0.6	0.4	0.3	1.0	0.1	0.2	0.8	0.1	0.1	0.2
Mg		0.1	0.2	0.5	1.4	N.D.	0.1	0.2	1.1	N.D.	N.D.	0.2
Ca		0.3	1.0	1.3	12.4	1.4	0.5	0.6	2.2	0.2	0.2	0.7
Na		325	400	485	11.5	285	325	469	13.1	230	263	344
K		1.4	1.3	4.4	13.2	20.3	22	32	3.5	31.3	30.4	28.4
Cs		17.0	21.0	25.5	0.0	15	17	24	0.0	3.7	3.8	5.5
B		135	161	209	0.9	134	160	234	1.6	117	140	200
Mo		82.5	103	130	0.0	43	60	120	0.2	58.5	72.5	110
Zn		1.2	0.6	0.6	0.0	1.5	0.6	0.6	0.0	1.1	0.9	0.6
pH	5.5	9.7	9.6	9.6	7.6	9.1	9.1	9.1	7.7	9.2	9.2	9.2

(a) Composition of rock-equilibrated water.

The changes in solution composition as a function of time for selected elements from these tests are compared in Table 15.3. These comparisons are probably more meaningful for the glass components (i.e., cesium, boron, molybdenum, zirconium) than those previously documented (Shade and Bradley 1980) because the present data are based on a solution volume-to-glass-surface area exposed in the minicanister that was essentially equal among the three tests. In general, the trends observed in these tests were similar to those in previous tests, but some of the magnitudes were different. It was assumed that redox conditions were fairly low because pyrite, present in the granite, did not seem to be altered. Boron and molybdenum are originally present only in the glass, and their release from the glass again seems unaffected by the rock media, as was previously observed. The silicon release from the basalt package

again is considerably higher than from either the canister alone or the granite package. This is expected because the silicon in the basalt packages is probably derived primarily from crushed, interstitial volcanic glass, which exists in the basalt, not the granite packages. The silicon in solution from the canister-only tests is about the same as in the granite package. Although more silicon would be expected from 76-68 glass, the surface area of glass exposed in the minicanister is only about 2.8 cm². The high silicon concentration in the basalt packages tends to cement the crushed basalt on cooling so that it is difficult to remove the canister. It was also observed that cesium release is inhibited by basalt, but not significantly affected by granite. This behavior may be related to the amount of silicon present in solution in basalt compared with granite, but at present the relationship is not understood.

The solution data again suggested that the rock systems were buffered by at least two alteration reactions. These are:

and

At a given alkali concentration, the solution pH is fixed by these equilibria, and as such, they appear to be among the major alkali-pH controlling reactions between 150 and 300°C. A limiting factor is the stability of zoisite relative to weirekite and also relative to calcite in high CO₂ systems. At present, it appears that these reactions may be useful for estimating the solution pH in the near-field environment for granite, basalt, or other alkali feldspar-rich rock.

The crushed rock materials from these tests as well as those from some of the previous tests are currently being examined by x-ray fluorescence in an attempt to determine changes in trace element concentrations between pre- and post-test rock media. The minicanisters are being examined by SEM to identify corrosion products. It is also planned to examine the effects of a montmorillonite clay (major bentonite component) in the presence of a feldspar-rich system. This mineral is not only a common alteration product of basalt, but is also a major component of several proposed backfill materials.

Intermediate-Scale PNL/Sandia Waste Package Test

During FY 1980, waste package tests on the WRIT program concentrated on using a minicanister (6.4 cm height by 1.9 cm diameter) made of 76-68 waste glass formed in a 304L stainless steel cylinder. Several series of tests, such as those described above, were completed using minicanisters in contact with crushed rock and an equilibrated rock solution.

Tests incorporating more of the barriers to be found in a typical waste package design for salt were to start in October 1980. Because of their interest in waste package tests, and experience in testing on salt environments and overpack materials, Sandia National Laboratory is a partner in these tests with the Pacific Northwest Laboratory. These tests have been termed intermediate-scale as they use a package that is roughly a factor of 10 larger than the minicanister tests and roughly a factor of 10 smaller than a typical full-scale waste package. This size allows us to incorporate all the barriers one wishes to study and have enough material for detailed analyses after the conclusion of the test. When assembled, the waste package occupies a volume of 19 l, which still allows for relatively easy handling.

There are two tests of this scale planned for FY 1981. Both utilize the same components and design; one will be with a simulated 76-68 waste glass doped with ²³⁸U. The second test will use a fully radioactive 76-68 waste glass.

The components of the test are:

- 38 cm (height) by 7.6 cm (dia) half-cylinder of 76-68 waste glass formed and annealed in a 304L stainless steel canister

- a Ti-code 12 titanium overpack
- a backfill mixture of 80% sand and 20% bentonite slurry prepared with a saturated salt brine
- a 53-cm (height) by 18.7-cm (dia) machined-out rock salt core with a 2.5-cm wall thickness.

The first three of the above components are assembled into the rock salt core to simulate a waste package emplaced in a bedded salt repository. The tests will be run at 2000 psi and up to 250°C and are intended to maximize interactions between the waste package components. Before starting the test, a test plan was written jointly by PNL and Sandia. This will be formalized prior to the fully radioactive test and will be used as the starting point for a methodology document for waste package testing. Expected results from the cold and fully radioactive systems test in a salt environment, based on previous minicanister tests, binary waste form/solution tests, and studies on overpacks and backfill materials, were postulated before the start of the test in terms of:

- solution properties and elemental/radionuclide redistribution
- radiolysis effects
- bentonite backfill properties
- metal corrosion.

The first test using ^{238}U -doped 76-68 glass waste form began on schedule in October and has operated ~70 days by the end of the first quarter. Two solution samples have been taken and are presently being analyzed. The first test will end in mid-January when our post-test analysis will be started.

We have already received part of the hot-cell autoclave system and have been notified that our 19-l autoclave, to be used for the fully radioactive PNL/Sandia test, will be shipped in mid-January. The schedule for

producing the high-level waste glass will be finalized in January.

SOURCE TERM MODELING - W. L. Kuhn

Waste Form Modeling

The release of constituents from borosilicate glasses during leaching is often said to "obey" the relation

$$(\text{amount released}) = a_0 + a_1 t^{1/2} + a_2 t$$

where a_0 , a_1 , and a_2 are constants, and t is elapsed time. These constants are then given the following interpretation:

a_0 : loosely bound material at the surface releases instantly and then contributes nothing more

a_1 : constituents diffuse from the glass matrix

a_2 : the glass matrix dissolves.

Actually, when the processes corresponding to a_1 and a_2 occur simultaneously, the release changes from the form $a_1 t^{1/2}$ initially to $a_2' + a_2 t$ at long times, where a_2' is related to a_1 and a_2 . This is discussed below.

Considering the behavior after any instantaneous release (a_0), this seems to explain the observation that releases increase first with the square root of time and then linearly with time.

A potential problem with the implied physical model, i.e., diffusion from the matrix, is that " $t^{1/2}$ " behavior is seen for large polyvalent ions, such as the actinides, which would be expected to exhibit extremely small diffusivities in the glass matrix. For example, results reported for the release of ^{137}Cs , ^{54}Mn , ^{154}Eu , $^{239+240}\text{Pu}$, and ^{244}Cm from radioactive borosilicate glass show that the amount released of each increases with the square root of time for about the

same time (10 to 20 days at room temperature), or in some cases longer for plutonium and curium, before beginning to increase linearly with time (Bradley 1978).

Also, the physical model presumes a homogeneous glass, whereas in fact borosilicate glasses are phase-separated, comprising sub-microscopic silicate- and borate-rich phases. The borate-rich phase is less durable chemically, and may be leached away from the surface to leave a chemically more durable silicate phase. This is the basis for producing Vycor® glassware.

Because of these inconsistencies, we have developed a simple leaching model based on the dissolution of two phases, with the dissolution of the less durable being controlled by the aqueous diffusion of dissolution products in pores left in the more durable phase, which connect the less durable phase with the surface. This presumes that dissolution of the less durable phase is reversible in the sense that accumulation of dissolution products at the phase interface somehow stops dissolution as the aqueous concentration there reaches some equilibrium value. Presumably, the aqueous concentration of a major constituent in the phase (e.g., boron) is controlling.

If the release of constituents is represented as

$$d = (\text{release depth}) = \frac{(\text{amount released})}{(\text{area})(\text{concentration in the solid})},$$

then both the "homogeneous" and "two-phase" theories predict

$$d \rightarrow d^* + vt \text{ as } t \rightarrow \infty,$$

where v is the velocity at which the (visible) surface recedes due to dissolution, and d^* is a characteristic contribution (a constant) originating from the " $t^{1/2}$ " process. Both theories also predict

$$d \rightarrow at^{1/2} \text{ as } t \rightarrow 0.$$

Using these common characteristics, the behavior predicted by either theory can be "normalized" by comparing $d - vt$ to d^* , and the time to that for which $at^{1/2}$ equals d^* . Hence, we define

$$\phi = \frac{d-vt}{d^*} \text{ and } \theta = t \frac{d}{d^*} \phi^2.$$

where ϕ is the normalized release and θ is the normalized time. Then both theories predict

$$\begin{aligned} \phi &\rightarrow \sqrt{\theta} \text{ as } \theta \rightarrow 0, \\ \phi &\rightarrow 1 \text{ as } \theta \rightarrow \infty. \end{aligned}$$

The two theories are compared in this form in Figure 15.10, which shows that they differ by no more than 5%. Therefore, the functional forms are so close that experimental data could be fit equally well by either theory by choosing two parameters: d^* and the initial slope of d versus $\sqrt{t}$.

We hope to determine a preference for one of the two theories by comparison to existing leach data for borosilicate glass.

Source Term Modeling

The source term for spent fuel in a basalt repository developed during the last quarter of FY 1980 is being used in support of a Reference Site Initial Analysis (RSIA) for a basalt repository by the Assessment of the Effectiveness of Geologic Isolation Systems

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FIGURE 15.10. Comparison of Theories for Dimensionless Release (ϕ) Versus Dimensionless Time (θ) for a Homogeneous and Two-Phase Glass, and the Asymptotic Behavior as $\theta \rightarrow 0$.

(AEGIS) program. The source term is a simplified analysis based on solubility constraints in an assumed oxidizing environment inside the waste package and assumes congruent leaching of spent fuel. To date we have not invoked the important constraints of the smaller solubilities of uranium and other elements in the strongly reducing conditions in basalt outside the waste packages; work is continuing to include these constraints.

GEOCHEMICAL MODELING – W. J. Deutsch

Code Development

The existing WATEQ family of computer codes enables the user to model speciation

and solubility of aqueous systems. WATEQ is being improved at PNL by a variety of programs including WRIT, Seasonal Thermal Energy Storage, and Compressed Air Energy Storage. Improvements made by one program will generally enhance the usefulness of the code to all. During this reporting period, WATEQ3 was rewritten to simplify the addition of new reactions and reduce computer dynamic memory requirements. Detailed documentation was completed on the source of available thermochemical data that will allow the addition of 24 minerals to the code. Additionally, available techniques are being assessed for estimating thermochemical data where data are complete.

The computer code EQ3/EQ6 is being developed at Lawrence Livermore Laboratory for WRIT applications. During the fourth quarter of FY 1980 data sets for the addition to the code of strontium, fluorine and phosphorus were completed. These sets contain data for all the reasonably expected major aqueous and mineral species. By the end of the quarter none of these data had been processed into the form necessary to support geochemical modeling calculations. A temperature extrapolation step is required to get the data to that level, and the necessary software to perform this function is now being written.

In further code development work, a feature has been added to EQ6 (the reaction path simulator) to overcome numerical problems encountered in systems unstable (ill-posed) with respect to the redox variable. This problem was typically encountered in ground waters with intermediate Eh values and now appears to be solved.

Model Applications

The initial phase has been completed in the geochemical modeling study of the basalt ground-water system of a portion of the Columbia Plateau. Based on the analysis of 16 geographically diverse water samples from the upper-confined aquifer system of the basalt, it is apparent that the dissolution of basaltic glass and formation of metastable secondary minerals are clearly continuing even though the basalts are of Miocene age (6-13 million years old) and presumably have undergone a long history of alteration. Most of these water samples are quite close to equilibria with amorphous silica, presumably from the continuing dissolution of volcanic glass, and the waters are variably oversaturated with regard to secondary clay

minerals. An indication that the formation rate of secondary aluminosilicate minerals lags the rate of volcanic glass dissolution is the near equilibrium with allophane, an amorphous aluminosilicate.

In certain respects (solubility limitations of dissolved constituents by metastable solid phases such as amorphous silica, amorphous aluminosilicate, and amorphous iron hydroxide) these basalt aquifer samples are analogous to water from snow melt and ephemeral springs in terms of solubility-limiting phases. This is remarkable considering that ground-water age dates are in the range of 10,000 to 30,000 yr, and it reflects the high chemical reactivity of the basalt. This high chemical reactivity of the bedrock would influence the transport of radionuclides released from a waste repository by controlling the concentration of major solute species in the ground water and the occurrence of secondary minerals that are formed and then serve as sorption substrates.

Repository and Breach Condition Support

The objective of this subtask is to provide an input to AEGIS safety assessments by estimating probable geochemical conditions for a nuclear waste repository. During this reporting period a study was completed on modeling transport of natural radionuclides, and Dr. Don Langmuir (Colorado School of Mines) carried out a simulation of uranite (UO_2) dissolution in various ground waters.

The dominant natural radionuclides in the geosphere are uranium, thorium, potassium-40, rubidium-87, radium and radon. To demonstrate the capability of modeling the movement of these elements in a natural system will be a step in validating our developing capability to geochemically model a waste repository. Based on available chemical

information on deep aquifers, it appears that the concentration in the ground water of all natural radioactive elements except radium should be limited by an input rate from the host rock. This rate may vary with the element because of the type of minerals the elements are concentrated in and because of the effects of radioactive decay on dissolution, but, given ground-water ages, the individual rates can be determined. From a knowledge of the uranium:radium ratio in the host rock and the input rate of uranium to the ground water, an average retardation coefficient for radium due to an exchange process can be determined between two or more boreholes.

The resultant geochemical model would simply consist of accumulation terms for each of the natural radionuclides. These accumulation terms would be linear with time and would be determined by measuring the concentration of an element at a number of selected sites for which ground water flow direction and age are known. For radium a retardation term would be estimated assuming its input rate is proportional to that of uranium (or some other element deemed more representative). This simple geochemical model can be tied to a hydrology model to

predict natural radionuclide concentrations across an aquifer's extent, with additional modification where necessary if the ground-water chemistry changes appreciably.

A comparison can be made between the natural situation and that of a nuclear waste repository for spent fuel. Given the inventory of the repository and a dissolution rate of its contents, it would be possible to compare natural radioactivity in an aquifer system to that of one influenced by a repository.

An important aspect in the modeling of a spent-fuel repository is chemical controls that influence the dissolution of the repository's primary component, uraninite. A computer simulation of uraninite dissolution in basalt, granite and tuff ground waters has been performed. Overall concentration of uranium in solution was limited by the precipitation of secondary uraninite as the spent fuel dissolved. Under the environmental conditions chosen and using available thermochemical data, it was found that solution concentrations of uranium do not approach maximum permissible levels, but, under certain conditions, the concentration may be at a level well above (10 to 100X) what is found in normal ground water.

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16. HIGH LEVEL WASTE FORM PREPARATION (HLWFP)

D. H. Siemens - Project Manager

The objective of this program is to characterize, prepare and ship the MWVP-2 waste log to the E-MAD Facility. At E-MAD, the waste log will be sealed in a storage canister and then shipped to Hanford, Washington, for storage in the Near-Surface Test Facility.

BACKGROUND AND SUMMARY

Two logs of vitrified high-level waste were produced during the Nuclear Waste Vitrification Project performed by PNL in the late 1970s. The second of these logs is slated for storage in the Near-Surface Test Facility (NSTF) as part of the BWIP Program being conducted by the Rockwell Hanford Company for the DOE. Before the waste log is placed in the NSTF, it will be transported to the Engine-Maintenance and Disassembly (E-MAD) Facility in Nevada, where it will be overpacked in a second canister. Prior to shipment of the waste log to E-MAD, it is being characterized to ensure that it is safe to ship and store and also to provide prestorage base data.

CHARACTERIZATION - D. N. Berger

Calorimetry tests that were performed indicate the waste log contains 500 watts of decay heat.

Core samples were taken at 10, 20 and 50 in. from the bottom of the waste log. All three samples consisted of homogeneous,

vitrified waste. After the samples were taken, the core holes were plugged and the plugs were seal-welded.

External dimensions of the waste log taken before and after filling with vitrified waste show that no appreciable changes in dimensions occurred during processing.

PREPARATION

Preparing the waste log for shipment will consist of welding a lid on, installing a bail and removing the external hardware. This work is now in progress.

CASK HANDLING

The National Lead Institute (NLI) truck cask has been selected for transport of the waste log to the E-MAD Facility. New equipment has been designed and, once approved, will be fabricated and tested. To protect the cask and waste log during shipment, a spacer will be designed and fabricated and inserted in the cask before the waste log is installed.

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17. DEVELOPMENT OF BACKFILL MATERIAL

E. J. Wheelwright - Project Manager

The objectives of this project are to define the optimum attributes of the backfill materials and to develop a single-component or multicomponent backfill material that most nearly satisfies the prescribed attributes.

SUMMARY

The major activities during this reporting period have been 1) acquisition of experimental quantities of candidate backfill materials, 2) continuation of radionuclide distribution coefficients with the materials, 3) initiation of compaction tests, and 4) design and construction of the permeability cell systems.

BACKFILL MATERIAL EVALUATIONS

Science Applications, Inc. (SAI) assisted PNL during FY 1980 in 1) defining and prioritizing the desired attributes of the backfill materials and 2) determining what quantitative data existed in the open literature on possible candidate backfill materials (Lester 1980). A list of candidate backfill components has been developed as follows:

- 10 to 30% sodium bentonite in quartz sand
 - Hydrophobic bentonite[®]
 - Bentone[®]
 - Cab-O-Sil[®]
- Natural and synthetic zeolites
 - Clinoptilolite

[®]Bentone is a registered trade name of NL Chemicals/NL Industries, Inc., Hightstown, New Jersey.

[®]Cab-O-Sil is a registered trade name of the Cabot Corporation, 125 High Street, Boston, Massachusetts.

- 13-X[®]
- AW-500[®]
- Zeolon-900[®]
- Ferrosand[®]
- Metal powders or fibers
 - Iron
 - Aluminum
 - Titanium
- Graphite
- Lead oxide
- Mineral Eh-pH buffers
 - Hematite $\longleftrightarrow$ magnetite
 - Magnetite $\longleftrightarrow$ siderite

Using these individual materials and homogeneous mixtures of two or more components, a program of laboratory testing has been initiated, testing three ground-water compositions and selected radioisotopes (Barney 1980).

Batch distribution (K_d) values were determined using bentonite clays (Volclay[®] and Accofloc-350[®]), several synthetic

[®]13-X and AW-500 are registered trade names of the Linde Molecular Sieves Division of the Union Carbide Co., 270 Park Ave., New York, New York.

[®]Zeolon-900 is a registered trade name of the Norton Chemical Process Products Division of Norton Co., Akron, Ohio.

[®]Ferrosand is a registered trade name of Hungerford & Terry, Inc., Atlantic Blvd., Clayton, New Jersey.

[®]Volclay and Accofloc-350 are registered trade names of the American Colloid Co., 5100 Suffield Court, Skokie, Illinois.

zeolites, glauconite (Ferrosand), and iron metal powder as examples of commercially available materials for backfill evaluation. Samples of each were contacted with a low-ionic-strength ground water (pH 8) containing ^{125}I , ^{85}Sr , ^{137}Cs , or ^{99}Tc . The samples were equilibrated for 7 days, the water fraction filtered with a $16\text{\AA}$ membrane filter cone, and the resulting samples counted for radionuclide content. The K_d results show that cesium and strontium are retained by the clays (2 to 5×10^3) and zeolites (10^3 - 10^6). Iodine, as expected, was not retained by any of the materials tested. Technetium was retained by the iron metal powder (10^3). Additional tests were started to obtain batch

distribution values for tuff, basalt, and salt brine ground waters and to determine the stability of various tracers in the above waters as a precursor to initiation of the dynamic flowthrough system. The results are shown in Table 17.1.

Backfill densities are being measured, as a function of pressing conditions, for individual clays and for compacted homogeneous mixtures of two or more materials. An air-hydraulic press is being used to obtain test pellets 1 to 5 cm in diameter. Powdered zeolites, quartz sand, metal powders, and clays are being mixed in various ratios for this test program. Compaction of as-received Volclay using 2, 6, 10, 14, and 18 T/in.²

TABLE 17.1. Batch Distribution Values for Backfill Candidates

	Distribution (K_d), ml/g ^(a)				Final pH
	Cs	Sr	I	Tc	
Volclay (smectite)	5.2E3	2.0E3	6.3	14.5	7.96
Zeolon-900 (mordenite)	3.4E5	>1.6E6	<0.3	4	8.51
13-X (faujasite)	7.8E3	>1.6E6	1.4	6	8.52
Ferrosand (glauconite)	7.0E4	2.1E3	4.9	15	7.08
Iron (metal powder)	8	1.1E2	7.6	2.5E3	9.96
Accofloc-350 (Na bentonite)	2.4E3	3.6E3	<0.4	10	8.37
Zeolite 4A [®] (Type A)	8.5E3	8.6E3	<0.4	<0.4	9.52
AW-400 (Erionite)	1.9E4	4.4E3	<0.4	19	8.28
Blank	--	--	--	--	7.84

$$K_d = \frac{\text{Standard} - \text{Aqueous}}{\text{Aqueous}} \frac{\text{Sample volume (20 ml)}}{\text{Weight of solid (0.5 g)}}$$

Standard = filtered blank or filtered acid sample.

Aqueous = filtered aqueous count rate - background count rate.

[®]Zeolite 4A is a registered trade name of Norton Chemical Process Products Division of Norton Co., Akron, Ohio.

has resulted in compaction densities of 1.92, 2.08, 2.14, 2.16, and 2.20 g/cm³, respectively. Physical measurements of the individual clays and compacts, i.e., thermal conductivity, as a function of density will be initiated.

CONSTANT-VOLUME PERMEAMETER-CELL SYSTEM

The system to measure water and radionuclide migration through candidate backfill materials has been designed, and the components are being fabricated and assembled. Calculations based on Darcy's law for flow in porous media indicate that a pressure of about 34 MPa (5000 psi) will be needed to force 1 ml/day of water through a disk, 5 cm in dia by 1 cm thick, of compacted bentonite clay (~2 g/cc density). The system has been designed to withstand these high pressures. Figure 17.1 shows the components of this system.

Water will be forced through the system by a high-pressure liquid chromatography pump capable of flows of 0.01 ml/min at pressures of 42 MPa. A back-pressure relief valve will actually control the pressure within the system and will vent excess flow back to the reservoir. System pressure will be measured by a transducer ahead of the permeability cell. For very impermeable materials, flow

rates will be measured by collecting in a capillary tube the water that has passed through the backfill. Larger volume collectors will be needed for more permeable backfill candidates.

Figure 17.2 shows the permeameter cell itself. Water enters through the bottom

FIGURE 17.2. Schematic of Permeability Cell

FIGURE 17.1. Schematic of Water/Radionuclide Migration System

piston and is distributed on the backfill sample face by a porous metal disk. The sample itself will be 5 cm in diameter, but the height can be varied between 0.5 and 5 cm. After passing through the sample, the water is recollected and flows out to the capillary tube. A thermocouple near the top of the sample will monitor the temperature of the test, and a load-cell will measure the swelling pressure developed in backfill materials as they are saturated with water.

All wetted parts of the system were fabricated from stainless steel, sapphire (pump

pistons), Kel-F, or Teflon to prevent changes in the water chemistry. Tests under anoxic conditions should require little, if any, modification to the system.

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18. DEVELOPMENT OF STRUCTURAL ENGINEERED BARRIERS

R. E. Westerman - Project Manager

The objective of this project^(a) is to develop materials for the structural engineered barrier components of high-level nuclear waste packages. Structural barriers include the canister, the overpack, and the hole sleeve. The barrier elements must contribute substantially to a barrier system that will hold radio-isotope release rates to near-zero values for time periods of ~1000 years.

SUMMARY

Candidate barrier element materials are being evaluated by means of corrosion screening tests, using Hanford ground water at 250°C. The most promising candidates will be subjected to in-depth enviromechanical testing.

A dynamic autoclave facility is being constructed for exposing specimens simultaneously to gamma radiation and high-temperature corrosive environments. A slow-strain-rate test facility also is being constructed to determine the susceptibility of metals to embrittlement in repository environments.

APPROACH

The selection and evaluation of materials for long-lived waste package barrier elements involve anticipation of material failure modes (e.g., general corrosion, pitting, stress corrosion cracking); screening of a

large number of candidate materials in relatively inexpensive tests; and finally rigorous in-depth testing of the best performers under the conditions of temperature, pressure, water chemistry, and radiation closely simulating those expected in the repository.

Corrosion screening tests are currently under way. Construction of a facility to permit exposure of specimens simultaneously to a high-temperature corrosive environment and gamma radiation is in progress. An apparatus for testing slow strain rate is also under construction.

SCREENING TESTS

A number of iron-, nickel-, copper-, titanium-, and zirconium-base alloys are undergoing corrosion screening tests in a simulated Hanford (basalt) ground water at 250°C. Feedwater, made up to the appropriate groundwater chemistry, is pumped into an autoclave held at 250°C. Before the water passes over the specimens it flows upward through a bed of crushed basalt contained in the bottom of the autoclave. The specimens are in U-bend configuration, and each specimen contains a simulated weldment.

The oxygen fugacity is a variable in the tests. Three-month tests have been run in the past at dissolved oxygen levels of ~1 ppm and ~50 ppb. A test discharged this

(a) This project has been under way at PNL in essentially the same form, and with the same basic objectives, since January 1979. It is now sponsored by the Office of Waste Isolation. Until the current fiscal year, however, it was funded by the Division of Waste Products and was reported on as part of the High-Level Waste Immobilization Program. A recent document (Westerman 1980) describes the project results prior to October 1980.

quarter used an oxygen level of ~7 ppm. Detailed weight change data for the last test are not yet available, as the specimens are currently being descaled. However, as in the past studies, the titanium alloys appear to have outstanding resistance to corrosion, and the cast irons once again appear to exhibit the highest corrosion rates.

RADIATION-CORROSION FACILITY

To predict with any certainty what the corrosion rates of barrier materials will be under actual geologic repository conditions, it is essential that the effects of temperature, pressure, environment chemistry, and radiation be brought to bear simultaneously on the candidate barrier material(s), which would be maintained in some appropriate flawed and stressed state.

To date, an autoclave test apparatus in a radiation facility has not been available for our program. To remedy this situation, such a facility is currently being constructed. The radiation will be provided by ^{60}Co sources in an existing Hanford Engineering Development Laboratory radiation facility. Provision is being made for isothermal heating by a steam source; dynamic flow conditions; complete chemical charac-

terization of influent and effluent liquids; and electrochemical monitoring of the specimens and the environment within the reaction vessels.

The three autoclaves required for the facility have been ordered, and the preliminary safety assessment has been completed. We expect to have a usable facility by July 1981.

SLOW-STRAIN-RATE APPARATUS

A slow-strain-rate test facility is also under construction. This facility will eventually have three pressure vessels and three constant-elongation-rate loading mechanisms. Rupture of metallic specimens under slow-strain-rate conditions in repository-relevant environments, with subsequent fractography and stress-strain analysis, is expected to further define susceptibility of candidate barrier materials to environmentally induced degradation. This facility is expected to be operational in January 1981.

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Westerman, R. E. October 1980. Investigation of Metallic, Ceramic and Polymeric Materials for Engineered Barrier Applications in Nuclear Waste Packages. PNL-3484, Pacific Northwest Laboratory, Richland, Washington.

19. ONWI DISPOSAL CHARGE ANALYSIS

L. L. Clark - Project Manager

The objective of this program is to determine the sensitivity of the disposal charge to geologic and institutional factors, including disposal of defense wastes.

Work was completed on the analysis of the cost impacts of storing defense wastes in a commercial spent fuel repository. The results of this analysis showed that such an option would cost on the order of \$100 million to \$2 billion in 1980 dollars, depending on the degree of volume reduction in waste treatment and the extent to which defense wastes are recovered.

Factors that significantly affect the charge were determined to be:

- discount rate provisions
- uncertainty in expenditure projections
- timing of expenditures and collection of fees
- whether or not an additional contingency factor is included and
- institutional factors.

Other factors that affect the disposal charge less significantly are the levelizing period over which the charge is calculated, cost allocation mechanisms to distribute costs related to both away-from-reactor storage and disposal, and allocation of R&D and other overhead costs to other transuranic wastes besides spent fuel.

As a result of the above analysis, it was determined that the discount rate provisions and institutional effects should be studied in more detail since these may be subject to controversy. At the same time we will begin gathering data on the cost variances as a function of geologic media.

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20. SPENT FUEL AND FUEL POOL COMPONENT INTEGRITY PROGRAM

A. B. Johnson, Jr. - Project Manager

The objectives of this program are to develop and conduct a surveillance program for nuclear fuel stored in spent fuel pools to determine whether degradation of cladding or fixtures is occurring; also to examine selected spent fuel pool components for evidence of degradation; monitor similar studies going on in other countries; and cooperate in international information exchanges.

PROGRAM MANAGEMENT

A. B. Johnson, Jr., presented a paper at the International Atomic Energy Agency (IAEA) Specialist Meeting on Spent Fuel Storage Alternatives, Las Vegas, November 17-20, 1980: A. B. Johnson, Jr., W. J. Bailey, E. R. Bradley and D. L. Langstaff, "Significance of Shippingport and Connecticut Yankee Fuel Examinations to Extended Water Storage of LWR Fuel."

INTERNATIONAL

The draft of a report, World survey of Spent Fuel Storage Experience, was reviewed by members of the consultant group who attended the Las Vegas IAEA Meeting. Recommended revisions to the report are being incorporated. When these are complete, the report will be sent to the 19 contributing nations for review before public distribution. The world survey is sponsored jointly by the IAEA and the BEFAST^(a) committee, which operates under OECD.^(b)

(a) BEhavior of Fuel Assemblies in Storage.

(b) Organization for Economic Cooperation and Development, based in Paris.

SPENT FUEL ACQUISITION AND EXAMINATION

Hot-Cell Examinations of Shippingport Fuel Rods

Hot-cell examinations of Zircaloy-clad fuel rods from two bundles of Shippingport PWR Core I fuel were initiated and nearly completed in FY 1980. These fuel rods were selected for examination in the present program because they had been in pool storage for more than 16 years and detailed metallurgical examinations of similar fuel rods had been made immediately after reactor discharge. The results from prior examinations are necessary to provide a direct basis for assessing the effects of extended pool storage on the integrity of Zircaloy-clad fuel rods.

Comparisons of data from the present examinations to those obtained immediately after reactor discharge were presented at the IAEA Advisory Group/Specialist Meeting on "Spent Fuel Storage Alternatives," Las Vegas, Nevada, November 17-21, 1980. The general conclusion from these comparisons is that extended pool storage had produced no significant changes in the Zircaloy cladding

of these fuel rods. This conclusion was based on the following specific comparisons:

1. No measurable changes in the external oxide thickness occurred during storage.
2. No measurable change in the hydrogen content of the cladding occurred during storage.
3. No measurable change in the burst strength of the cladding occurred during storage.
4. No significant changes in the diameters or ovality of the fuel rods occurred during storage.
5. No measurable change in fission gas release occurred during storage.
6. Bare Zircaloy surfaces that were produced during the hot-cell examinations in 1960 showed no evidence of corrosion after 20 years of exposure to the water environment.

Results from detailed visual examinations, leak testing, or eddy-current tests have not produced any definite evidence of defective cladding. Water vapor was detected in four of the eight fuel rods examined, which suggests that defects may exist in these rods. However, this is not consistent with the results from leak testing or the burst tests, and we think the water vapor was introduced from an external source during rod puncture and gas collection.

Hot-Cell Examinations of Connecticut Yankee Fuel Rods

Hot-cell examinations of stainless steel-clad (Type 304L) fuel rods from Connecticut Yankee (Haddam Neck) Qualification Fuel Assembly S004 were initiated in FY 1980. The S004 fuel assembly was selected because it contained fuel rods with high burnup, had been stored for a significant time in water, and was well characterized. The results from previous characterization served as a

basis for evaluation of the current examination results. This program will eventually include results from a few stainless steel-clad (Type 304) fuel rods from each of two other Connecticut Yankee fuel assemblies that have higher burnups but shorter storage times than S004.

The results of the nondestructive post-irradiation examination (PIE) and the cladding metallography have shown that the fuel rods are sound and that no obvious degradation has occurred after 5 years of storage in borated water. These PIE results were presented at the IAEA Advisory Group/Specialist Meeting on "Spent Fuel Storage Alternatives," Las Vegas, Nevada, November 17-21, 1980.

Analyses of the results from fission gas analysis, fuel ceramography, fuel burnup, fuel density, and cladding mechanical properties are under way. Analysis of irradiation histories and PIE results for fuel rods from the other two Connecticut Yankee fuel assemblies is under way. This analysis is to support selection of rods for reconstitution in the S004 assembly as part of the long-term surveillance program for pool storage of spent fuel.

MECHANISM STUDIES – S. M. Bruemmer, J. R. Divine, and R. H. Jones

Stress Corrosion Studies

The intergranular stress corrosion cracking (IGSCC) of 304 SS in high-temperature (288°C) water has been studied extensively. Extrapolation of this work and of the limited work at low temperatures (<100°C) suggests that as the temperature is reduced the environment is considerably less aggressive and propensity for SCC is minimal. However, some cases of IG cracking have occurred in

spent fuel pool system piping. The material and environmental factors that control this low-temperature cracking are under investigation. An experimental matrix was formulated to determine these factors, with primary emphasis on parameters that are known to be important from experimental results on 304 SS in high-temperature water.

In general, three major factors are essential to induce IGSCC of 304 SS in high-temperature water:

- sensitization
- environment: oxygen and chloride content
- stress: residual or applied.

These areas will be systematically investigated, with primary emphasis on determining the material (degree of sensitization) and environmental (oxygen, chloride, etc.) conditions necessary for IGSCC to occur at low temperatures.

The primary cause of sensitization in austenitic stainless steels is the depletion of chromium at the grain boundary regions from the precipitation of chromium-rich carbides. The extent of the depleted zone determines the degree of sensitization and susceptibility to intergranular attack. To study a range of sensitized conditions, commercial 304 SS containing various levels of carbon (0.01 to 0.09 wt%) are being evaluated. Sensitization will be produced both by isothermal heat treatments and welding. The degree of sensitization will be determined electrochemically with polarization techniques (EPR), by standard ASTM corrosion tests (A262-B, and A262-C), corrosion tests, and chemically by analytical electron microscopy (AEM). The latter analysis will document not only chromium concentration profiles across and along the grain boundary, but also will characterize the precipitate morphologies and chemistries. Two of four standard ASTM test cells for establish-

ing the degree of sensitization have been completed, and the initial tests to correlate heat treatment and sensitization have been started.

Segregation of impurities such as sulfur, phosphorus, and silicon may also have an effect on the susceptibility to IGSCC. The enrichment of impurities and alloying elements at grain interfaces will be analyzed with Auger Electron Spectroscopy (AES). Design of a slow-strain-rate fracture device for the AES apparatus is under way. This device is necessary to obtain intergranular fracture within the high-vacuum system and grain-boundary chemistries obtained.

The main test method to investigate material and environmental effects on IGSCC will be constant-load experiments in solution. Four constant axial-load apparatuses with environmental cells (shown schematically in Figure 20.1) have been constructed with an interlinked computer system for continuous data analysis of load, displacement, temperature, pH, electrochemical potential, and oxygen content. Constant-load SCC experiments on furnace-sensitized 304 SS have been started. Initial tests will establish stress levels for determining SCC susceptibility. An environment of air-saturated water with 13,000 wt ppm H_3BO_4 + 15 ppm Cl^- was selected to coincide with experimental results on samples removed from a welded pipe-elbow section of the Three Mile Island Unit No. 1 Spent Fuel Pool system (PNL-3000-6). The presence of 15 ppm Cl^- was necessary to induce IGSCC under constant extension rate test conditions. These results have also indicated that crack initiation may be a major limiting step in reproducing the service failure in the laboratory. Therefore, compact tension specimens with a fatigue precrack will also be tested.

FIGURE 20.1. Test Cell for Static Load Investigation of Stress-Corrosion Cracking

Although the initial tests are in a more complex solution, the base environment for the full series SCC tests will be deionized water at 35°C. A series of additions will be made to determine the importance of oxygen and chloride ions that have proven critical in the high-temperature case. The effect of pH, boric acid, fluoride and sulfate or sulfide ions of IGSCC will also be studied. For the material-environment combination shown to induce IGSCC, the temperature dependence of the phenomenon will be mapped from 20 to 100°C. If the mechanism and critical parameters are not evident from these tests, then the specimens will be polarized anodically during testing to accelerate the corrosion process.

Because of the large number of tests that will be needed to screen the numerous mate-

rial and environmental parameters discussed above, bend tests will be used in many cases. The time for crack initiation and the crack depth after a fixed time will be monitored as indications of IGSCC susceptibility. In addition, straining electrode tests (SET) will be performed to supplement the determination of conditions that induce IGSCC. For welded samples, electron channeling patterns (obtained using a scanning electron microscope) will be employed to locate the regions of maximum residual stress; this will be done in order to relate the residual stress to the initiation and propagation of intergranular cracks. Thus a wide range of material and environmental variables will be examined for their effect on IGSCC. The program will attempt to both identify the parameters responsible and define fabrication limits such as material chemistry, welding conditions, and water chemistry for the present and future application of austenitic stainless steels. The results will be useful to spent fuel pool designers and operators. They also will provide a basis for responding to questions in spent fuel pool licensing hearings regarding materials behavior.

REFERENCE

- Johnson, A. B., Jr. 1980. "Spent Fuel and Fuel Pool Component Integrity Program." Nuclear Waste Management Quarterly April Through June 1980. A. M. Platt and J. A. Powell, comps. PNL-3000-6, Pacific Northwest Laboratory, Richland, Washington.

21. ANALYSIS OF SPENT FUEL POLICY IMPLEMENTATION

M. K. White - Project Manager

The objective of this project is to provide analytical support to the Director of Spent Fuel Storage and Transfer and the Spent Fuel Project Office (DOE/SR) in evaluating alternative methods of providing spent fuel management services, determining the cost of providing those services, and calculating an appropriate charge for spent fuel storage and disposal.

SUMMARY

A presentation summarizing the output of this task was presented at the Spent Fuel Storage Program Contractors meeting in Augusta, Georgia, on October 22. These results were also included in a report on the spent fuel program submitted to Congress by DOE.

The draft and final fee update reports are to be issued in June 1981. The reports will include data which will not be available until April. The methodology description for the fee report was started.

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22. ANALYSIS OF POSTULATED CRITICALITY EVENTS IN A STORAGE ARRAY OF SPENT LWR FUEL

L. R. Dodd - Project Manager

The objective of this program is to calculate the progress, consequences, and eventual shutdown mechanisms for postulated criticality events in an away-from-reactor storage facility.

SUMMARY

Efforts during the quarter have concentrated on implementing calculational capabilities to be used to model postulated criticality events in AFR storage facilities.

MODEL DEVELOPMENT

The objectives of this program require the capability to model the time-dependent neutronic and thermal-hydraulic behavior of a system comprised of an array of spent fuel in a nonpressurized water environment. The two-dimensional, time-dependent neutronics program TWIGL and the thermal-hydraulic analysis code COBRA were selected for use in the analysis. The two codes were modified and combined into one during the previous quarter. The resulting program has been undergoing debugging and enhancement this

quarter. Testing and modifications to the program are expected to be essentially completed early in the next quarter.

CRITICALITY ANALYSIS

Preliminary calculations were performed during the previous quarter to determine the excess reactivity available as a result of incidents associated with selected scenarios. New rack design information has since been received from the sponsor. The excess reactivity calculations will be performed again using the more recent designs. Neutronic and thermal hydraulic parameters required for dynamic analysis are currently being developed. The dynamics of reactivity excursions associated with selected scenarios will be analyzed during the next two quarters.

23. ASPHALT EMULSION SEALING OF URANIUM TAILINGS

J. N. Hartley - Project Manager

The overall objective of this project is to investigate the use of asphalt emulsion sealants to contain radon and other potentially hazardous materials in uranium tailings, including development of the supporting technology and engineering criteria for full-scale sealing of uranium mill tailings piles.

SUMMARY

Results of FY 1980 laboratory and field studies were presented for a project review held December 17 and 18, 1980, at PNL, Richland, Washington. The review committee consisted of J. C. Petersen, Laramie Energy Center; J. Dybalski, ArmaK Co.; R. E. Kallio, University of Illinois; and J. D. Nelson, Colorado State University. Because the Nuclear Regulatory Commission representative was unable to attend the project review and his input is very important, we plan to visit NRC in February 1981 and present the results of our work. A draft 1980 annual report was prepared and distributed for comment.

Monitoring of the Grand Junction field test site for radon exhalation continued to show the effectiveness of the admix seal. Radon fluxes in November averaged about $0.6 \text{ pCi m}^2\text{-sec}$. Laboratory radon diffusion measurements were completed on samples of hot rubberized asphalt. Diffusion coefficients were about $10^{-7} \text{ cm}^2/\text{sec}$ for a specimen 60 mm thick. Laboratory seal stability tests were started, including temperature cycling tests (freeze-thaw) and aqueous leaching and oxidation studies. After eight cycles of freeze-thaw (-12°C to 38°C), no degradation or failure occurred to specimens containing 22 wt%

residual asphalt and sand. A review of microbial attack on asphalt indicates that this mechanism of degradation should present no problem to the long-term stability of the admix seal. Some microbiological experiments are planned to further verify that this mechanism is not important.

LABORATORY STUDIES

Tailings Characterization - M. R. Elmore

Tailings samples from the Grand Junction field test plot were analyzed. The chemical compositions of the tailings samples shown in Table 23.1 were determined by x-ray fluorescence, and the radium content was determined by direct counting.

Since the environment surrounding the admix seal will potentially affect the long-term stability of the seal, the water-soluble salt content of the tailings was determined. The analytical results of these tests will be presented in the next quarterly.

Plans for characterizing a test site for a proposed joint field test were started. These include plans for determining water-soluble salts, chemical and radionuclide composition, and particle size distribution.

TABLE 23.1. Chemical Composition of Grand Junction Tailings at Test Site(a)

Element	Range, wt%
K	0.3 - 0.6
Ca	0.3 - 1.4
Fe	0.2 - 1.0
	Range, ppm
Ti	80 - 760
V	900 - 1600
Cr	35 - 66
Mn	13 - 45
Cu	10 - 42
Zn	67 - 163
Se	25 - 74
Rb	3 - 15
U	35 - 848
Sr	40 - 215
Y	1 - 15
Nb	1 - 4
Mo	1 - 32
²²⁶ Ra(b)	32 - 1600 pCi/g

(a) Data obtained by x-ray fluorescence analysis. Range of composition of 20 samples of tailings.

(b) Radium content was determined by direct counting.

Seal Formulation - R. L. Dunning (Petroleum Sciences, Inc.)

The goal of the emulsion studies during the last quarter has been to demonstrate that the set times can be controlled from immediate set to no set through formulation techniques, and that certain of these emulsions could be mixed with dry aggregate.

One anionic and several cationic emulsions were prepared and mixed with a dense-graded -3/8-in. aggregate that contained 11.6% -200-mesh fines. A 35 wt% emulsion was mixed with aggregate containing 4% water in all the tests except one that did not have water. The emulsions mixed well.

With the anionic slow-set emulsion, no water was added to the aggregate, which was quite dry. Although dry mixes were not tried with some of the other emulsions, the Indulin W-3® and 50:50 Tyfo® blends probably would also mix with dry aggregate. Since the emulsion supplies water to the aggregate, dry mixing should not be harmful in compaction if mixing is adequate. Also, it is evident that varying the formulation ratio of Tyfo A and Tyfo B allows a large range of set times.

Further testing will include mix tests with dry aggregate, helium leak tests on emulsions, and analyses of hot asphalt macadam mixes.

Radon Diffusion Measurements - H. D. Freeman

Studies were conducted to determine the effective diffusion coefficient of rubberized asphalt. Two rubberized seals, 0.95 cm and 0.59 cm thick, were run for 480 hr while samples were taken periodically of the radon concentration below and above the seal. These data were used to estimate effective diffusion coefficients for the two seal thicknesses. Effective diffusion coefficients on the order of 10^{-6} to 10^{-7} cm²/sec were calculated. These values, however, are questionable because of fluctuations in the radon concentration under the seal. Therefore, we ran duplicate tests to determine whether the radon fluctuation was a serious problem. As these revealed that the radon was fluctuating with time, we are now altering the radon generator to eliminate these fluctuations.

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Seal Stability - D. A. Nelson and
P. L. Koehmstedt

The leaching experiment conducted last quarter with admix seals was terminated after 3 months of brine exposure. No aqueous discoloration was noted in the brine reservoir. Fungal growth, however, did occur on the admix surface. This experiment was modified to avoid the influence of bacteria on test results. A brine solution containing 21 salts at pH 1.6 was prepared that simulates the composition of the slimes fraction of the Grand Junction tailings. Twelve polycarbonate cylindrical cells were prepared as the experimental drop chambers. Admix seals (10 cm dia x 3.8 thick) were buried in acid-washed sand in the 15.2-cm-dia cells to eliminate photocatalytic oxidation. All components, including solutions, were sterilized to eliminate fungal or bacterial contamination. Half of the cells were exposed to the brine and the other half to distilled water. The exposure to brine, with time, should provide worst-case conditions of the asphalt-tailings interface. The exposure to distilled water should provide the effects of water leaching alone and thus indicate the effects of meteoric (rain) water on the asphalt-overburden interface. This, of course, does ignore the salts that could be solubilized from the overburden. These two sets of six cells were further divided into two groups: half are being exposed to air and half to nitrogen atmosphere. This is an attempt to isolate the leaching phenomenon from potential asphalt oxidation. After 2 months no change in leachate color has been observed. The leachate will be solvent-extracted after 6 months to determine whether asphalt degradation has occurred by this route.

Investigation of bacterial degradation of asphalt was begun this quarter. Thin films of asphalt are currently being exposed to known pure culture strains of bacteria. These organisms are grown in flasks containing sterile salt solutions with no added nutrients except the asphalt. Thus the organisms will receive nutrients only by degrading the asphalt coating (thin film) in the flask, and the rate of growth of the culture will be proportional to that of asphalt degradation. The growth rate is being measured by the increase of turbidity as well as standard cell counting procedures. Once the standard growth curves are established for the pure cultures, natural communities isolated from the Grand Junction overburden will be grown under the same regimen.

We are currently measuring the oxygen levels, both dissolved and gaseous, at an asphalt-overburden interface under 1 m of Grand Junction clay soil. The overburden compaction level was calculated because the oxygen level will be quite dependent upon it.

A series of experiments based upon the uptake of oxygen by asphalt has been started, with the ultimate goal of determining the relative rate of asphalt oxidation. The initial experiments involve the barometric measurement of oxygen over asphalt for long periods. (Calculations based on similar work in 1955-1962 by Shell, in Holland, indicated that the depth of oxygen penetration can also be obtained.) The results of these experiments will be confirmed by Raman-infrared spectroscopy, which can measure the concentration of oxygen above the asphalt surface in a sealed vessel. The Raman-IR measurements will be started in April when the instrument is available to us.

A test program was started to determine the susceptibility of various asphalt-emulsion admix seals to temperature cycling (freeze-thaw). The test used is similar to that developed by Plancher et al. of DOE's Laramie Energy Research Center. Test specimens (4.1 cm dia x 2.2 cm) containing asphalt emulsion and sand (~22 wt% residual asphalt) are placed on a stress pedestal and submerged in water. The specimen is then held at -12°C for 24 hr. Next the specimens are thawed rapidly in hot water ($\sim 38^{\circ}\text{C}$) and then placed in an oven at 38°C for 23 hr. This constitutes one cycle.

Initial test specimens were heated in the oven to 60°C , but this caused them to slump and fail. Since the admix seal would not see a 60°C temperature extreme, 38°C was selected as a maximum case for heating. Under this condition none of the specimens has failed in up to 8 cycles of freeze-thaw. Testing is continuing on various asphalt emulsions and concrete sand.

FIELD STUDIES - H. D. Freeman

Grand Junction Field Test Site Monitoring

The Grand Junction test site was again monitored during November to determine the condition of the asphalt seal applied in August. Radon measurements were made on 30 test sites on 0.3 to 1 m of overburden to determine the effectiveness of the seal after 2 months of environmental exposure. Results of these measurements and of corresponding

measurements taken in September are shown in Table 23.2. In most cases the November measurements were slightly higher than the September measurements. This was to be expected because the radon flux did not have enough time to reach equilibrium by the first of September. The fluxes were still quite low, with a $0.6 \text{ pCi/m}^2\text{-sec}$ average. There were two exceptions to the low fluxes: test areas 16B and 18B, on the edge of the sealed areas. Because the measurements were made on $\approx 0.3 \text{ m}$ of overburden, the radon from the unsealed tailings was able to diffuse through the overburden to the radon measurement systems. These test areas, therefore, were not taken into account when computing the average.

Radon measurements were taken in conjunction with Argonne National Laboratory in order to compare two different radon measurement systems. Selected test areas were measured by both systems and the results compared. Further joint testing is planned so that both systems can be tested under various conditions.

In addition to the radon flux monitoring, temperature-moisture probes were put in place during November. These probes were placed in drill holes at various depths so that a temperature and moisture profile through the overburden could be obtained throughout the year. Currently, measurements are being taken weekly. They will be used to determine whether freezing and thawing of the seal could be a potential problem under $\sim 1 \text{ m}$ of overburden.

TABLE 23.2. Radon Fluxes Before and After Seal Application
at Grand Junction Test Site, pCi/m²-sec

Sample	Before Seal	After Seal	
	Aug. 1980	Sept. 1980	Nov. 1980
6A	938	0.3	0.9
B	948	0.6	2.0
7A	1101	0.5	0.4
B	1046	0.3	0.7
8B	470	0.3	0.3
9A	196	0.6	0.5
10A	200	0.4	0.7
11A	129	0.008	0.6
C	199	0.041	0.5
D	324	0.036	0.5
12A	143	0.6	1.1
D	545	0.1	0.7
13A	205	0.3	0.5
C	459	0.1	0.4
D	687	0.2	0.6
14C	347	0.3	0.6
D	184	0.1	0.4
15B	94	0.2	0.9
C	157	0.2	0.8
16A	116	0.0	0.4
B	134	0.2	55.8 ^(a)
C	189	0.02	0.6
17B	139	0.008	0.4
C	183	0.022	0.3
18B	143	0.4	231.6 ^(a)
C	183	0.1	0.4
19A	137	0.014	0.3
B	184	0.2	0.6
D	172	0.0	0.6
20A	258	0.2	0.4
C	313	0.025	0.4
D	341	0.1	0.4

(a) Measurements taken on the edge of the seal
atop ≈ 0.3 m of overburden.

24. LINER EVALUATION FOR URANIUM MILL TAILINGS

J. L. Buelt - Project Manager

The objective of the liner program is to evaluate prospective materials for preventing moisture transport of radionuclides and hazardous chemicals from uranium mill tailings over a long-term period. The approach embodies conducting a tailings site characterization study to determine the liner exposure conditions and evaluating the effectiveness of the liner through field studies and accelerated laboratory tests.

SUMMARY

A selection study was performed to identify eight liner materials for laboratory testing under accelerated exposure conditions. The results of these tests will determine the most likely material or composite of materials for field testing in the summer of 1981. Also, characterization of surface samples of the tailings at the Durango, Shiprock, and Salt Lake sites have been completed. The results of these analyses will provide the data base for determining the exposure conditions in the laboratory tests representative of a thousand years.

LINER SELECTION STUDY

An exhaustive search identified a number of promising lining materials. The material properties were evaluated in accordance with their long-term compliance with proposed regulatory requirements. Basically, the assumed liner criterion was to maintain a permeability of $<10^{-7}$ cm/sec over a thousand-year period. The categories of materials considered in this selection study were clays locally available to proposed sites, sodium-saturated bentonites, various soil treatments, asphalt concrete and mem-

branes, cement-based concretes designed for impermeability, and synthetic membranes.

In these categories, the following eight liner materials were chosen for laboratory study:

- natural soil amended with sodium-saturated montmorillonite (Volclay®)
- typical local clay with an asphalt emulsion radon-suppression cover
- typical local clay with a multibarrier radon-suppression cover
- rubberized asphalt membrane
- hydraulic asphalt concrete
- chlorosulfonated polyethylene (Hypalon®) or high-density polyethylene
- bentonite, sand and gravel mixture
- catalytic airblown asphalt membrane.

The sodium-saturated montmorillonite offers good resistance to ion exchange, which reduces the clay's swelling capabilities. The locally available clays, which offer considerable economic incentives, will be tested in conjunction with proposed radon-suppression covers. The rubberized and hydraulic

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asphalts are the two most viable asphalt candidates. High-density polyethylene or Hypalon are the best synthetic membrane candidates for this application. The final two materials are included to correlate the laboratory test results with data collected on these materials in the field.

EXPOSURE CONDITIONS

The program's current thrust is to identify the exposure conditions for the eight liners. The data base for determining these conditions is taken from surface samples of tailings at Durango, Shiprock, and Salt Lake City. Chemical conditions destructive to liners were analyzed. The range of calcium available for ion exchange in clay liners

extended as high as 45,000 ppm. Both alkaline and acid leach processes were used among the sites, giving a pH range from 2.9 to 10.0. Chloride concentrations were as high as 1300 ppm, but no trace of organic solvents (kerosene) was detected. Selected samples also underwent a gamma scan to determine the radionuclide content.

DIRECTION

The results of these analyses are now being evaluated with reaction kinetics to determine the exposure concentration and temperature representative of 1000 years. They will then be exposed in test cylinders, currently under construction, for a 3-month period.

25. MULTILAYER BARRIERS FOR SEALING OF URANIUM TAILINGS

G. W. Gee - Project Manager

The objective of this project is to investigate the use of multilayer earth materials to contain radon diffusion from uranium mill tailings.

SUMMARY

Diffusion model results based on considerations about air-filled porosity indicate the need for multilayer covers in order to achieve the required radon flux control. Based on measured parameters for cover and tailings, >7 m of a single-cover material would be required to attenuate the highest bare surface flux ($1900 \text{ pCi m}^{-2} \text{ sec}^{-1}$) to $<2 \text{ pCi m}^{-2} \text{ sec}^{-1}$ at our test site. This compares with <2 m total cover thickness when a properly designed multilayer system is used. The measurements of water content in our multilayer cover at Grand Junction and at Hanford indicate that the designed capillary barrier is effective in isolating the wet clay/gravel layer from the dry overburden cover material, and thus in maintaining a relatively low air-filled porosity-radon control layer. The field results indicate that air-filled porosities of <0.1 can be achieved by surface wetting of the compacted clay/gravel layers. Model results suggest that the clay/gravel layer thickness will need to be increased to achieve the $2 \text{ pCi m}^{-2} \text{ sec}^{-1}$ limit if the average air-filled porosity of the control layer is much greater than 0.02.

Field measurements of radon flux at the Grand Junction, Colorado, test site were continued through December. Results to date show continued increases in radon flux from the test plots. With few exceptions, the

measured radon flux levels exceed the $2 \text{ pCi m}^{-2} \text{ sec}^{-1}$ limit set by the Nuclear Regulatory Commission. Additional water was added to the clay/gravel layer on three subplots in December. The effect of the added water on these subplots will be monitored during subsequent months.

A computer code has been developed that determines the minimum cost of multilayer covers under user-specified constraints. Thus economic analysis can be made for a variety of single or multilayer cover designs. Multilayer cover diffusion test columns have been assembled in the laboratory for use in verifying the radon diffusion portion of that code. Field measurements of moisture distributions in non-mined areas adjacent to five western U.S. mill tailings sites are continuing.

MATERIAL TESTS AND MODELING - R. W. Nelson, G. W. Gee, C. Oster, D. W. Mayer, and C. S. Simmons

Modeling of radon diffusion through air-filled pore space in cover materials and tailings has allowed us to calculate the seasonal and long-term effects of climate on radon flux from covered tailings. Water storage in the cover was shown to vary significantly throughout the year. The radon flux changes calculated from the changes in water storage in the cover were similar to observed climate (rain)-induced radon flux

changes reported in the literature. The model results also clearly demonstrate the effect of cover compaction on radon diffusion. In contrast to reported relationships that depend significantly on cover moisture content alone, the model results suggest that tightly compacted covers can be more effective radon barriers than wet, low-density clays or silt materials.

Table 25.1 lists the average values and range of measured parameters for cover and tailings at the Grand Junction test site. Based on these measured parameters, we calculated the required single-cover thickness needed to reduce the radon flux below $2 \text{ pCi m}^{-2} \text{ sec}^{-1}$. The cover thickness ranged from 3.2 to 8.2 m, corresponding to measured surface radon fluxes of 43 and $1900 \text{ pCi m}^{-2} \text{ sec}^{-1}$, respectively. When a multilayer system with a compacted clay/gravel layer was used, the corresponding cover thickness (including an overburden cover 1 m thick) ranged from 1.4 to 2.6 m.

FIELD TESTS - B. Opitz, R. R. Kirkham, and M. E. Dodson

Test plots were monitored for radon flux in November. Table 25.2 shows the variety

of clay/gravel characteristics for each test plot. The average thickness for the clay/gravel layer was about 15 cm. Table 25.3 compares the initial surface radon flux values (determined in September) with the November measurements. Significant increases in radon flux were observed as expected because the initial measurements were made within a few days after the cover was placed on the tailings and the radon flux had not equilibrated in the cover material. On December 16 and 17, water was subsequently added to the east half of plots 1, 2 and 3. Each plot received $18.2 \times 10^6 \text{ l}$ (4800 gal) of water. On each plot, water was applied at one point through a 25-cm-dia PVC pipe directly to the clay/gravel layer. The water was allowed to gravity-feed for ~5 hr. These sites will be monitored in February to determine the effects of the added water on the surface radon flux.

COMPOSITE COVER OPTIMIZATION - Rogers and Associates Engineering (RAE)

The FORTRAN computer code (entitled MULCOP for Multi-Layer Cover Optimization Program) has been completed. This code provides a

TABLE 25.1. Material Characteristics of Cover Materials and Tailings at Grand Junction Test Site

Layer	Layer Type	Characteristics				
		Radium Content, pCi/g	Emanation Factor	Bulk Density, g/cm ³	Volumetric Water Content, cm ³ /cm ³	Air-Filled Porosity, cm ³ /cm ³
1	Earth fill cover	0	0	1.46 (1.3-1.6) ^(a)	0.11 (0.07-0.22)	0.37 (0.20-0.47)
2	Capillary barrier	0	0	1.6 (1.52-1.64)	0.01 (0.008-0.01)	0.39 (0.37-0.42)
3	Compacted clay gravel	0	0	2.0 (1.8-2.1)	0.20 (0.18-0.25)	0.06 (0.03-0.15)
4	Tailings	1600 (200-2500)	0.2	1.23 (1.10-1.50)	0.19 (0.05-0.27)	0.36 (0.19-0.56)

(a) Represents range of measured values.

TABLE 25.2. Physical Properties of Clay/Gravel Layer Materials
Used at Grand Junction Test Site

Plot	Cover Designation	Composition, wt%	Field Density, g/cm ³	Max(c) Density, g/cm ³	Max Water Content, (c) cm ³ /cm ³	Min Air-Filled Porosity, cm ³ /cm ³
1	A-	3/4 Roadfill(a) plus GJC(b) (86/24)	2.05	2.22	0.151	0.017
2	A+	3/4 Roadfill plus bentonite (86/14)	1.97	1.91	0.239	0.053
3	B-	Pea gravel/sand/GJC/ (29/29/42)	2.00	2.20	0.147	0.036
4	B+	Pea gravel sand/GJC/ bentonite (29/29/29/14)	1.66	2.05	0.169	0.071

(a) 3/4 roadfill--a standard roadbase aggregate mix with a maximum aggregate diameter 1.9 cm (3/4 in.).

(b) GJC--earth fill-silty clay loam soil; 32 to 40 wt% clay (<0.002 mm). Unified soil classification--CL.

(c) Based on ASTM D-1557-70, modified Proctor Test.

fast, accurate analysis of the radon concentration and flux at any position within a multilayer tailings cover system and the costs associated with implementing a given tailings cover system. It also will, under specifiable constraints of radon flux limits, tailings cover thickness, and site-specific cost factors, determine the tailings cover system that minimizes the cost of emplacement. Architect-engineering cost data pertinent to typical tailings sites are being collected, and sample cost optimization studies will be made.

To characterize the radon flux attenuation characteristics of multilayer tailings covers, 11 test columns are being monitored for radon flux, radon concentration profiles, and moisture contents. Related experiments are also being conducted to evaluate and improve the accuracy of the flux measurement methods and to make certain there is no significant radon leakage through materials used in the columns and measurement devices. The latter quality-control experiments will ensure the high degree of accuracy needed

to properly characterize the multilayered covers.

Construction of the test columns was completed with the addition of various cover materials. The columns are presently equilibrating with respect to their radon distributions. The addition of the cover materials to the 61-cm-high tailings sources was delayed from the original schedule because of corrosion by the tailings through the galvanized steel walls of the original columns. The corrosion breakthrough occurred after the bare tailings sources had been characterized for radon flux. Subsequently, the 61-cm-by-30-cm-dia tailings sources were transferred to new PVC plastic pipes of equal diameter after cutting away the corroded metal containers. The tailings sources were re-equilibrated and monitored for radon flux before the cover materials were added.

The present test configuration includes five columns containing cover materials from the proposed Vitro disposal site in Utah. Two of these are identical and contain a 30-cm clay layer, followed by a 152-cm layer

TABLE 25.3. Radon Flux in pCi m⁻² sec⁻¹ at the Grand Junction Multilayer Test Site

Plot	Site	Aug 11-15, 1980	Sept 19-20, 1980	Nov 4-7, 1980
1 (A-)	1	406	-	5.5
	2	229	4.9	3.1
	3	283	-	1.4
	4	175	6.2	1.6
	5	529	-	13.5
	6	452	-	26.8
	7	509	2.3	10.2
	8	496	-	38.0
2 (A+)	1	232	-	1.1
	2	254	2.2	19.5
	3	290	2.7	33.8
	4	137	4.9	29.3
	5	471	10.0	19.3
	6	361	-	4.3
	7	698	2.4	10.5
	8	548	-	1.8
3 (B-)	1	43	-	6.6
	2	93	0.6	7.1
	3	53	-	9.8
	4	153	3.6	3.5
	5	363	14.0	33.9
	6	775	-	26.3
	7	1360	17.4	80.4
	8	1454	-	11.6
4 (B+)	1	246	-	6.6
	2	818	4.3	88.9
	3	759	32.9	8.8
	4	795	25.0	122.8
	5	1527	19.9	73.3
	6	1722	-	12.8
	7	1911	-	211.6
	8	1643	-	11.7
5 (no clay/gravel layer)	1	1441	15.7	97.7
	2	1504	63.0	142.5
	3	1429	-	116.0
	4	1406	36.6	178.4
	5	1873	35.5	85.5
	6	1818	-	12.5
	7	1842	291.7	286.3
	8	1715	-	14.9

of soil. One will be used as a control when moisture will be added to the other columns. A third column contains identical materials but has the clay layer placed from 15 cm to 45 cm from the top of the soil cover instead of beneath it. Fourth and fifth columns contain single layers of the soil and clay materials, respectively.

The remaining six columns include two with Durango materials, one with Shiprock materials, one with Riverton materials, and two with the aggregate composite cover materials used by PNL at the Grand Junction test

site. The Durango columns contain Mancos shale and wet and dry clay layers in differing orders to test for layer-order effects on radon diffusion. The columns of Shiprock and Riverton materials contain layers of local clay and soil compacted on top of Vitro tailings.

Field moisture gradients are being monitored using moisture/temperature probes buried to depths of up to 240 cm at proposed disposal sites for Vitro, Durango, Shiprock, Grand Junction and Riverton tailings. Although significant changes in temperature

profiles have been noted, the moisture profiles have thus far shown little variation. Grab samples have also been collected at the various sites and have been used to calibrate the moisture probes. Parameters at the Vitro site are being monitored monthly, and those at the other sites are being monitored quarterly.

Local climatological data, including rainfall and temperature, are being obtained from local sources for possible correlation with the moisture profiles. We also expect that useful information will be derived from local soil survey data on soil water retention and drainage characteristics.

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26. APPLICATION OF LONG-TERM CHEMICAL BIOBARRIERS FOR URANIUM TAILINGS

J. F. Cline - Project Manager

The objective of this project is to develop and evaluate the effectiveness of physical and chemical barriers designed to prevent the breaching of uranium tailing containment systems by plants and animals for extended periods of time.

SUMMARY

Three new polymers in sheet forms were combined with 10% trifluralin, and two pelletized PCD systems were formed and combined with 10 and 25% trifluralin. Release rates of trifluralin from these systems were measured. The effective life of the pellets loaded with 25% trifluralin was estimated to be 100 years or more.

The minimal concentrations of trifluralin in soil required to prevent root penetration of a barrier ranged from 0.3 to 12 ppm in nine plant species tested. Trifluralin reached equilibrium concentrations in soils in 30 days and remained in a steady state during the rest of a 60-day study. Preliminary studies show that longitudinal movement of trifluralin from placement is <6 cm.

A pelletized PCD system was placed at various spacings in growth containers that were then planted to Russian thistle, barley, and tansy mustard. These plants will be harvested, and plant root relationship with the barrier and seals will be determined in February.

DEVELOPMENT OF POLYMERIC CARRIER/DELIVERY (PCD) SYSTEMS - W. E. Skiens

During this quarter we continued to develop PCD devices that maintained release of

trifluralin for longer periods than earlier devices. Two methods were used; first, various types of polymers were tested and, second, different configurations of the devices were developed. Four polymers as sheets with 10% trifluralin loadings were produced and tested (Table 26.1). Two groups of pellets, the preferred configuration for field application, were produced. The first group was made from PS-1600 polypropylene loaded with 10% trifluralin and ranged in size from 1 to 3 mm in diameter and 2 to 7 mm long. The second group was made with the same polymer, but loaded with ~25% trifluralin and fabricated as cylinders

TABLE 26.1. Release Rate of Trifluralin
from Polymer Sheets

<u>Polymer Type</u>	<u>Release Rate, $\mu\text{g}/\text{cm}^2/\text{day} \pm \text{SD}$</u>
EVA® (ethylene vinyl acetate)	13.1 ± 0.6
EVA Microthene sandwich®	9.2 ± 0.7
Polyethylene Microthene MN 711-20®	1.5 ± 0.2
Polyethylene Microthene MN 710-20®	15.9 ± 2.9

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~9 mm in diameter and 15 mm long. The above PCD systems were submitted to analytical laboratory to determine release rates of trifluralin.

DETERMINATION OF TRIFLURALIN RELEASE RATES FROM PCD SYSTEMS - F. G. Burton

Using a continuous flow system, we determined the release rates from the sheets loaded with 10% trifluralin as shown in Table 26.1.

During this quarter we also determined the release rates for the two groups of pellets. The release rate from the smaller 10% trifluralin-loaded pellets was $19.8 \mu\text{g/day/g} \pm 2.4 \text{ SD}$ at controlled temperature of $13^\circ\text{C} \pm 1$.

The determination of the release rate from the larger pellets loaded with 25% trifluralin is continuing, but initial information suggests that their release rate will be $<6 \mu\text{g/day/g}$. With a 25% loading, these pellets would release at this rate for more than 100 years.

Based on the above data, we estimate that requirements of the project can be met, that is, the development of a device that will prevent plant root intrusion of uranium tailings for 100 years or more. The pellets described may not be the best possible device or solution, but we believe we have a successful experimental system. We are continuing to test additional polymeric systems that may have significantly longer effective lives.

PHYTOTOXICITY AND DEGRADATION STUDIES - D. A. Cataldo

We determined the minimal effective concentrations of trifluralin that are required to prevent root penetration of the biobar-

rier. Nine of 23 plant species were tested that may be used for revegetation of the Grand Junction uranium tailings site. At the point of root growth cessation the minimal concentrations ranged from 0.3 to 12 ppm. These results are being used in the final design criteria of our PCD system.

The cumulative half-life of trifluralin in a silt loam was determined to be ~50 days. These losses were regulated by microbial decomposition, chemical degradation, and volatilization of the trifluralin in the soil. We are starting similar studies to determine cumulative half-lives of trifluralin in sand and in clay soils.

A study to determine the accumulation rate of trifluralin in soil from a promising PCD system, made from Profax PS-1600-PP[®] polymer, is nearly complete. Three densities of pellets were placed in soil and have been incubated for 60 days to date. At this time, we estimate that concentrations of trifluralin reached equilibrium in the soil around the pellets in 30 days and remained in a steady state during the remainder of the 60-day study period.

Preliminary studies show that longitudinal movement of trifluralin in soil is <6 cm from the point of placement. Detailed studies are being initiated to verify this measurement.

GREENHOUSE AND FIELD STUDIES - J. F. Cline

A promising pelletized PCD system made from Profax PS-1600-PP was placed in the soil profiles of nine growth containers. The pellets were placed in a thin layer 2 ft below the soil surface at spacings of 0, 1, 4

[®] Profax is a registered trademark of Hercules, Inc., Polymers Dept., Wilmington, Delaware.

TABLE 26.2. Placings and Spacings of (PCD) Pellets in Plant Containers in the Greenhouse

<u>Treatments,</u> <u>g pellets/box</u>	<u>Pellet Spacings,</u> <u>Pellets/in.²</u>	<u>Seal Type</u>	<u>Number of</u> <u>Containers Used</u>
0	-	Asphalt	1
0	-	Clay layer	1
Q	-	None	1
4	1	None	2
16	4	None	1
16	4	Asphalt	1
64	16	None	1
64	16	Clay	1

and 16 pellets per square inch. The experimental design is shown in Table 26.2. Each container was planted in separate rows with seed of Russian thistle, barley, and tansy mustard. These plants will be allowed to grow until they develop root systems deep enough to test the various biobarriers. At harvest the plant tops will be removed and the soil removed from around the roots to determine the relationship of the roots with different pellet spacings and seals.

The results of the study will be used to estimate the density of pellets needed to prevent root intrusions of the uranium tailings seals.

ANIMAL INTRUSION STUDY - K. A. Gano

During the last quarter, a manuscript was prepared describing the burrowing habits of the rodents that may inhabit uranium tailings sites. The paper describes the maximum recorded burrowing depths and other information on the habitats of mammals that are capable of disturbing seals over uranium tailings. The manuscript recommends how sites may be designed to deter these burrowing animals.

The rough draft was prepared and edited, and the final draft is being prepared for publication.

No data have been collected from the animal enclosure studies at Hanford because the ground squirrels are dormant for the winter. The enclosures will be evacuated and the barriers inspected when the animals emerge in February 1981.

PUBLICATIONS

A manuscript entitled "Biobarriers Used in Shallow Burial Ground Stabilization," by J. F. Cline, D. A. Cataldo, W. E. Skiens, and F. G. Burton, was prepared and submitted for publication to the Journal of Nuclear Technology.

A manuscript entitled "Application of Controlled Release Technology of Uranium Mill Tailings Stabilization," by F. G. Burton, D. A. Cataldo, J. F. Cline and W. E. Skiens, was prepared for presentation at the American Nuclear Society Topical Meeting on Waste Management, February 23-26, 1981, in Tucson, Arizona.

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27. REVEGETATION OF INACTIVE URANIUM TAILINGS SITES

L. L. Cadwell - Project Manager

The objective of this program is to select and test revegetation strategies, including choice of species and methods for revegetation, that are compatible with sealant/barrier systems and are suited to soils and climates at inactive uranium mill tailings sites.

SUMMARY

Test plot studies under way at the Grand Junction, Colorado, site will evaluate the interaction between remedial action cover technologies and selected revegetation strategies. Contouring, fertilizing, mulching and seeding of the site have been completed. Soil moisture blocks and neutron probe access ports are in place. An irrigation system has been designed and should be operational for the 1981 growing season.

Selection of plant species involved compiling site-specific information on climate and suitable species. Climatic data were gathered primarily from NOAA (National Oceanic and Atmospheric Administration). The Plant Information Network (PIN) was used to compile plant species lists pertinent to sites in Colorado, Wyoming and North Dakota.

TEST PLOTS - P. A. Beedlow, L. L. Cadwell, J. R. Skalski, R. H. Sauer, and M. A. Simonds (Century West Engineering Corp.)

Revegetation studies are being conducted on the inactive mill tailings pile located at Grand Junction, Colorado, in conjunction with the UMTRAP^(a) projects testing sealants, biological barriers, and liners. The

revegetation project will examine the relationships between vegetation and technologies for containing radon. Interaction between vegetation and the herbicide barriers intended to limit plant root penetration into sealant systems will also be studied. The effects of soil depth on plant rooting are being investigated to determine minimum planting requirements. Soil moisture responses to plant cover and the sealants will be monitored to assess the effects of the cover systems on soil water. This will provide a basis for evaluating potential cover treatment impact on revegetation success.

Planting

The test plots and surrounding disturbed areas were seeded in early November. The seeded area was first mulched and fertilized using a commercial fertilizer spreader. Jacklin grass fiber mulch was applied at a rate of ~1 ton/acre; fertilizer (20N:20P:20K) at ~120 lb/acre, and seeds at 18 to 20 lb of pure live seed per acre.

The plant species used to seed the site were chosen for their adaptation to the local

(a) Uranium Mill Tailings Remedial Action Program

environment, proven success in revegetating disturbed areas, and availability. The species chosen and their proportions in the planting mix are shown in Table 27.1. Twenty-five pounds of additional seed were also planted at a rate of 5 lb/acre. The additional seed mix contained about equal proportions, by weight, of each species (Table 27.1). A garden plot was sown with the major species to provide reference specimens to aid in identifying immature plants. Seed quality specifications and collecting locations are shown in Table 27.2.

Soil Moisture Sampling

A primary objective of the Grand Junction test plot work is to evaluate the influence of asphalt emulsion, multilayer earth and

root barrier herbicide treatments on the establishment of a stabilizing vegetative cover. Soil moisture regimes are likely to be influenced by tailings cover treatments. Since soil moisture is critical to the establishment and maintenance of vegetation on disturbed sites in arid and semi-arid regions, it is an important parameter for study on the test plot.

Three hundred eighty-two soil moisture blocks, previously calibrated in the laboratory, were installed in the treatment plots during October and November. The blocks were placed at 0.1-m, 0.3-m, 0.6-m and 1.2-m depths, as permitted by the depth of soil cover. Comparisons will be made among soil treatments and among soil depths.

The soil moisture experimental design (Table 27.3) includes plain soil (S), soil

TABLE 27.1. Plant Species and Their Proportions in Seed Mixtures Planted at Grand Junction

<u>Major Seed Mix</u>	<u>Wt%</u>
<i>Atriplex canescens</i> (fourwing saltbush)	9
<i>Atriplex confertifolia</i> (shadscale saltbush)	21
<i>Ceratoides lanata</i> (winterfat)	12
<i>Sphaeralcea coccinea</i> var. <i>disecta</i> (scarlet globemallow)	1
<i>Oryzopsis hymenoides</i> var. <i>Palana</i> (Indian ricegrass)	12
<i>Puccinellia lemmoni</i> (Lemmon's alkaligrass)	12
<i>Agropyron cristatum</i> (crested wheatgrass)	12
<i>Agropyron dasystachyum</i> (thickspike wheatgrass)	9
<i>Amaranthus retroflexis</i> (redroot pigweed)	12

Additional Seed Mix (approximately equal proportions)

Ceratoides lanata (winterfat)
Oryzopsis hymenoides var. *Nezpar* (Indian ricegrass)
Melilotus officinalis (yellow sweetclover)
Atriplex canescens (fourwing saltbush)
Atriplex cuneata (Nuttall's saltbush)
Ephedra viridis (Mormon tea)
Hilaria jamesii var. *Viva* (galleta grass)
Sporobolus airoides (alkali sacaton)

TABLE 27.2. Specifications for Seed Used to Plant the Grand Junction Test Plot

Major Seed Mix Species	% Purity	% Germ	Origin	% Inert	% Other Crop	% Dormant Seed
Fourwing saltbush	95.1	54% full(a)	Nevada-Utah	4.62	-	-
Shadscale saltbush	85.32	40% full	Montello area 700 ft Mesa Co.	14.67	00	15
Winterfat	5.39	88	Gunnison Delta Co.	94.31	12	-
Scarlet globemallow	95	90	Mesa Co.	-	-	-
Indian ricegrass	95.26	85	New Mexico	4.60	14	-
Alkaligrass	99.65	89	Oregon	-	0.20	-
Crested wheatgrass	93.97	88	So. Dakota	5.09	0.45	-
Thickspike wheatgrass	89.54	92	Mesa Co.	9.48	0.78	-
Redroot pigweed	99.22	34	Montrose Co.	0.29	-	28

Additional Seed Mix

Fourwing saltbush	14.84	54% full	Nevada
Indian ricegrass	14.34	90 T2	Washington
Yellow sweetclover	12.46	40% full	South Dakota
Mormon tea	12.44	95 T2	Idaho/Utah
Nuttall's saltbush	11.72	40% full	Colorado
Galletta grass	6.50	68	New Mexico
Alkali sacaton	6.21	87	New Mexico
Winterfat	3.86	90	Utah

Other crop: 0.08%

Inert: 17.42%

Weed: 0.13%

(a) A seed cut test was conducted on fourwing saltbush and shadscale. Seeds filled with endosperm are considered viable. A tetrazolium test was used to determine dormant seed on the shadscale and pigweed.

TABLE 27.3. Coefficients for Orthogonal Contrasts

Treatments	S	A	A-H	M	M-H	Hypothesis
Contrast #1	4	-1	-1	-1	-1	No difference between plain soil and more advanced preparation
#2	0	1	1	-1	-1	Asphalt vs. multilayer
#3	0	1	-1	1	-1	Main effect herbicide
#4	0	1	-1	-1	1	Interaction herbicide and preparation

over asphalt (A), soil over asphalt plus herbicide (A-H), soil over multilayer earth (M), and soil over multilayer earth plus herbicide (M-H). The asphalt and plain soil treatments consist of an uppermost mounded soil cover ranging in depth from ~0.3 m to 1.4 m. The soil over the multilayer earth plot is ~0.75 m deep. Soil preparation and seeding, as described in the preceding section, are the same for all cover treatments.

Comparison of Types of Cover Treatments

All treatments will be compared at the 0.6-m depth to eliminate confounding of soil treatment and depth of overburden. Moisture readings among vertically placed moisture blocks may be highly correlated, preventing simultaneous analysis of the 0.1-m, 0.3-m, and bottom depths using analysis of variance. Separate analyses may be performed, or multivariate analysis of the trivariate data (0.1 m, 0.3 m, and bottom moisture) may be used to compare treatments. Assuming balanced data sets, orthogonal contrasts may be used to test the hypotheses listed in Table 27.3.

Comparison of Soil Depths

Analysis will depend on the assumption of independence among vertically placed moisture blocks; either one or several analyses of variance for a one-way experimental design will be used to analyze blocks at the 0.1-m, 0.3-m, 0.6-m and 0.9-m depths. Orthogonal contrasts will be used to determine whether moisture is equal for blocks at a specified depth in soils of various overburden depths. Interactions between soil moisture patterns and soil treatments will be (S, A, A-H) tested.

Irrigation System Design

Preliminary design for an irrigation system was completed by Century West Engineering Corp. The system is designed to allow irrigation of the entire site in one set (without moving handlines) at an application rate of ~0.1 in./hr. Sprinkler spacing and pressure were selected to give adequate overlap and uniform application.

The design assumes that irrigation water will be available from the Colorado River below the site. However, other water sources could be employed with slight modification.

The availability of water rights for use on the test plot is under continuing investigation. Ownership of Colorado River water rights for the site has been traced, and efforts are in progress to obtain a water use permit. The following alternative sources of water for test plot irrigation were also investigated:

- purchase water from Grand Valley Irrigation District
- purchase city water
- use irrigation drainage water
- use onsite well water.

PLANT SPECIES SELECTION - M. C. McShane, N. R. Hinds, and P. A. Beedlow

During the first 3 months of FY 1981, the chief accomplishment of the Plant Species Selection Task was a compilation of data received on the individual uranium tailings sites. Detailed and site-specific climatological information needed for choosing plant species for revegetation was obtained for each state containing uranium-tailings sites. Annual summaries of climatological data were ordered from NOAA. Temperature and precipitation data collected at weather stations throughout the state were available

in the summaries; in nearly all cases a station was close to an inactive tailings site. Well-established stations provided average monthly temperature and precipitation values based on years of data. But from the newer stations the monthly data over the past 5 yr had to be averaged to estimate climatologic patterns at the tailings sites. The NOAA reports also furnished data on the number of frost-free days and on annual maximum and minimum temperatures. Our analysis shows that the average annual precipitation of the tailings sites ranges from <6 in. to 36 in. The number of frost-free days varies from a few days a year at the high elevation sites in Colorado to nearly 300 days at the Texas site.

Another resource recently utilized more fully was the Plant Information Network (PIN). PIN is a data base developed for the U.S. Fish and Wildlife Service by Colorado State University. It contains information on all native or naturalized vascular plants in Colorado, Wyoming, Montana, and North Dakota. A list of plant species received from PIN for counties in Colorado, Wyoming and North Dakota with uranium tailings sites included information on their erosion control potential, establishment requirements,

long-term revegetation potential, and growth on various soil types. For example, galleta grass (*Hilaria jamesii*), found in Gunnison County, Colorado, is easily established, has high potential for erosion control, and has moderate long-term revegetation potential. It grows well on dry sites with loam or clay-loam soils but grows poorly on sodic, saline or acidic soils.

One milestone for the Plant Species Selection Task was to establish criteria for choosing species for revegetation.

Literature reviews and discussions with experts over the past few months were used in selecting the criteria. The criteria for choosing species, in order of importance, are listed below. The plants chosen will:

1. be tolerant of local environmental conditions
2. have properties that will aid in erosion control
3. have propagules that are readily available
4. be relatively easy to establish
5. be perennials or
6. be annuals with good reproductive capabilities
7. have minimal rooting depth requirements
8. be of low food value and/or palatability
9. have low value as habitat for wildlife.

28. VERIFICATION INSTRUMENT DEVELOPMENT

R. L. Brodzinski - Project Manager

The objective of this research program is to organize, apply, and develop as required, instrumentation for assaying the radionuclide content of waste packages received by land burial operators, both to verify the data provided by the generator/shipper and to provide the most accurate records possible of buried materials.

SUMMARY

This is a new program, and the first quarter has been largely devoted to planning and organization. Site visits have been arranged at the Nevada Test Site (NTS) and at Beatty, Nevada. Optimization of an existing passive neutron counter for application to package TRU assay has been initiated.

WASTE RECEIPT INSTRUMENTATION DEVELOPMENT -

R. L. Brodzinski and E. A. Lepe

This is a new program, and the first quarter has been largely devoted to organization and planning. Options for execution of the program plan have been evaluated, and some relevant literature has been reviewed.

Arrangements have been made to visit Steve Carpenter at the NECO disposal operation (Nuclear Engineering Co., Inc., since

changed to U.S. Ecology, Inc.) in Beatty, Nevada, and Gene Kendall at the REECO (Reynolds Electrical and Engineering Co., Inc.) disposal operation at the NTS. These visits will establish the communication lines to these two low-level waste disposal operations and obtain information about monitoring and assay restrictions and requirements as regards the scope of this program.

Some efforts have been applied toward optimizing a passive neutron TRU package assay system. It is anticipated that the onsite analysis of waste receipts for transuranic activities at the 10 nCi g^{-1} level will be one of the major technological problems encountered. Consequently, the potential of this TRU assay technique will be determined for comparison to the potential of TRU assay techniques currently under development at LASL.

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