Nuclear Waste Management Quarterly Progress Report July Through September 1981

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

December 1981

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NUCLEAR WASTE MANAGEMENT
QUARTERLY PROGRESS REPORT
JULY THROUGH SEPTEMBER 1981

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

December 1981

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington

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 April Through June 1981, PNL-3000-10.

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1. HIGH-LEVEL WASTE PROCESS DEVELOPMENT

D. E. Larson, C. A. Knox and S. C. Slate - Project Managers

The objectives of the High-Level Process Development Program are as follows:
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;
2) to develop the basic technical information for the design of waste containers, emphasizing the reference canisters for waste glass and including conceptual designs and material data for canisters for alternative waste forms and for barrier canisters; and 3) to analyze and document PNL-developed waste vitrification technology and the condition of the dismantled liquid-fed ceramic melter.

SUMMARY

All corrective action items identified by DOE to recover from the two incidents were completed. Permission was requested and was received to restart hot cell operations.

Several reports were issued, and work continued on the barrier canister concept.

RADIOACTIVE PROCESS DEVELOPMENT

The investigation was completed of the two incidents that occurred when contaminated solution was detected in piping in the operating gallery. The corrective action items were 1) installation of non-adjustable 5-min timers to prevent insufficient air purges upon completion of a steam jet transfer; 2) installation of separate key switches for every steam jet in the hot cell complex to prevent use of an incorrect steam jet due to common keys; and 3) modification of all operating procedures to reflect these changes. All of these corrective actions have been completed. Permission was requested of, and received from,

DOE to restart hot cell operations. The facility has been operability-tested and is operational.

HIGH-LEVEL WASTE CANISTER DEVELOPMENT

During this quarter we issued two topical reports and one informal report, which fulfilled the remaining project milestones. The definition report for commercial high-level waste (CHLW) glass was issued and was distributed to other waste management programs to serve as the basis for their CHLW studies. A final report on the results of our glass-cracking study was issued. This report identified the levels of glass cracking, the causes of cracking, and methods for crack reduction. The informal report, issued to the HLW Lead Office, described seven conceptual designs for AWF canisters.

Work continued on evaluating the concept of a barrier canister. A draft report on this concept was prepared this quarter, and corrosion tests were continued into FY 1982. The final report on this work will be issued in FY 1982.

A new project plan for the continuation of work into FY 1982 was prepared. The main study areas for next year are barrier canisters, a commercial alternative waste forms definition, and analysis of impact-tested canisters.

DOCUMENTATION OF PROCESS DEVELOPMENT

The following documents were published during the fourth quarter:

Miller, F. A. June 1981. Design and Performance of a Full-Scale Spray-Calcliner for Nonradioactive High-Level Waste Vitrification Studies. PNL-3742, Pacific Northwest Laboratory, Richland, Washington.

Barnes, S. M. and D. E. Larson. September 1981. Materials and Design Experience in a Slurry-Fed Electric Glass Melter. PNL-3959, Pacific Northwest Laboratory, Richland, Washington.

Chick, L. A. et al. September 1981. The Effects of Composition on Properties in an 11-Component Nuclear Waste Glass System. PNL-3188, Pacific Northwest Laboratory, Richland, Washington.

Lukacs, J. M., L. L. Petkus and G. B. Mellinger. September 1981. Evaluation of Defense Waste Glass Produced by Full-Scale Vitrification Equipment. PNL-3550, Pacific Northwest Laboratory, Richland, Washington.

Petkus, L. L., D. E. Larson, W. J. Bjorklund and L. K. Holton. September 1981. Development of In-Can Melting Process and Equipment, 1979 and 1980. PNL-3957, Pacific Northwest Laboratory, Richland, Washington.

2. 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 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.

SUMMARY

The plasma spray system was used to apply 17 different single/duplex coatings to simulated TDS-211 composition glass marbles. Coatings that appeared to be high quality (thick, low-porosity coatings) have been subjected to MCC-1 static leach tests.

Thirty-three deposition runs have been completed by General Atomic Company (GAC) using plasma-activated chemical vapor deposition (CVD) to apply carbon coatings on glass particles. Out of these coating runs, 15 were judged suitable for further evaluation at PNL.

Investigation has been concluded on the interaction of molten lead with 76-68 glass. Heat treatment in an air atmosphere between 500 and 550°C has indicated an enhanced crystallization in the glass at the glass/metal interface. The activation energy related to the diffusion of lead in glass 76-68 was determined to be 34.8 kcal/mole.

Leaching of waste glass is inhibited when a lead container is used. Other metals investigated exhibit interactive effects but not to the same magnitude as lead. This phenomenon suggests that syner-

gistic interactions in the waste package are important.

Compacts containing glass beads and rock salt embedded in a carbonaceous matrix have been fabricated at GAC for evaluation by PNL.

Water-permeability tests of graphite matrix rods produced at GAC have continued to look encouraging. Sodium was not leached from a graphite matrix rod containing NaCl pellets during a 14-day test at 90°C.

Several cesium-containing materials were neutron-irradiated in April 1979 to convert a portion of the cesium to ^{134}Cs (the average conversion was 12%), 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 6% of the cesium had transmuted to barium at the time of the most recent measurements. There have been some small changes in density, crystallinity, and leach rates.

The effects of several different processing steps were evaluated for preparation of zircon powder precursors from an aqueous

solution of zirconyl nitrate and colloidal silica. For preparing zircon (ZrSiO_4), it was concluded that the solution-gelation (or coprecipitation) methods are superior to simple gelation or boil-down techniques.

All corrective action items identified by DOE have been completed for D-Cell, 324 Building. Permission has been received to restart hot-cell operations to produce high-level waste calcine.

COATED-PARTICLE WASTE FORMS

Thermal Spray Coatings - K. H. Oma and L. E. Peterson

Various coatings consisting of metals, metal alloys, and ceramics have been applied to simulated TDS-211 composition glass marbles using the plasma spray process. The waste marbles were agitated in a drum mixer to allow all surfaces to receive a uniform coating. Following is a list of the coatings applied:

- lead
- tin
- nickel
- titanium
- Inconel®
- 316 stainless steel
- nickel/chromium/molybdenum
- self-fusing molybdenum
- chromium oxide/silicate composite
- zinc silica
- silica/lead oxide
- spinel
- mullite
- aluminum/alumina duplex

® Inconel is a registered trademark of Huntington Alloys, Huntington, West Virginia.

aluminum/titania duplex

aluminum/lead duplex.

Except for tin, zinc and lead, all the metallic-based coatings were applied with little difficulty. The tin, zinc and lead coatings were oxidized to a high degree during spraying. Selection of a coarse powder as feed permitted lead eventually to be sprayed satisfactorily. The silica, silica/lead, spinel and mullite coatings were found to be extremely dependent on the technique used. Once applied, these coatings would require a fusion step to seal off the interconnected porosity. The three duplex coatings all appeared to be of high quality.

Plasma-Activated CVD Coatings - J. L. Kaae (GAC)

Thirty-three deposition runs have been completed using plasma-activated chemical vapor deposition (CVD) to coat glass spheres supplied by PNL. Of these coating runs, 15 were judged suitable for further evaluation. The spheres used for the coating studies were doped with simulated fission products for leach testing in the subsequent evaluations. Various coating conditions were utilized. Among the coating parameters that were changed from run to run were: the pressure in the reaction tube; the position of the sample holder relative to the induction coil; the radio frequency power; the temperature of the glass sphere; and the degree of agitation of the glass sphere. In some cases rough carbon coatings were produced, and in other cases smooth carbon coatings were produced. The coating smoothness appeared to be increased as the agitation of the glass sphere during coating increased.

MATRIX WASTE FORMS

Metal Matrix Interactions - J. W. Wald

Investigation has been concluded on the interaction of molten lead with 76-68 glass in the temperature range of 500 to 550°C. Distinct interaction was observed in all tests where heat treatment was conducted in an air atmosphere. The interaction was typified by a band within the glass at the metal interface that was divided into what appeared to be a simple diffusion zone and a reaction or crystallization zone. Crystallization appears to occur in the glass after a finite lead concentration level is attained. Since glass 76-68 has not been previously reported to undergo devitrification at these low temperatures, it must result from the influx of lead. X-ray diffraction has identified the crystallization products as $\text{Pb}_5\text{B}_2\text{SiO}_{10}$ and $\text{Pb}_8\text{FeSi}_6\text{O}_{21}$, with a possible simple lead silicate such as $\text{Pb}_3\text{Si}_2\text{O}_7$ also present.

The diffusion coefficients for lead migration into 76-68 glass have been estimated from the width of the diffusion plus reaction zones according to the equation $D = X^2/4t$ and are listed in Table 2.1.

The diffusion coefficient as a function of temperature can be represented by the equation $D(T) = D_0 \exp(-Q/RT)$, and in the present case $D_0 = 3.6 \times 10^{-11} \text{ cm}^2/\text{sec}$ and $Q = 34.8 \text{ kcal/mole}$. This activation energy is similar to values reported elsewhere for

TABLE 2.1. Diffusion Coefficients of Lead in 76-68 Glass

Temperature	D, cm^2/sec
500°C (773°K)	5.6×10^{-11}
525°C (798°K)	1.2×10^{-10}
550°C (823°K)	3.1×10^{-10}

both oxygen and lead diffusion in lead silicate glasses.

Matrix Cell Leach Tests - C. Q. Buckwalter

A continuation of investigations of the synergistic interactions of glass/matrix/water shows significant differences in the chemical durability of a borosilicate waste glass. Leaching of the glass was decreased one order of magnitude when an aluminum container was used and more than two orders of magnitude when a lead container was used. Tin, copper, and titanium exhibit no significant effects on the leach rate (see Figure 2.1).

Figure 2.2 shows scanning electron microscopy (SEM) cross sections of the waste glass leached in the indicated containers. Samples leached in tin, copper, titanium, and Teflon® containers have depleted regions of $\sim 9 \mu$. Glass leached in aluminum shows an $0.8\text{-}\mu$ layer, and the sample leached in lead has a layer beyond detection limits. All samples were leached in deionized water at 90°C for 28 days. Similarly depleted regions have also been identified by secondary ion mass spectrometry (SIMS) data.

Table 2.2 shows x-ray photoelectron spectroscopy (XPS) results of the analysis of the inside of the containers and the corresponding glass surfaces. All containers except Teflon, aluminum, and lead show a considerable amount of dissolved glass constituents sorbed to the walls. The surfaces of the glass samples leached in aluminum and lead show container material that is not evident with the other container materials. Lead crystallites predominate on the surface of glass samples as shown in Figure 2.3.

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FIGURE 2.1. Leachate Analysis of Silicon by Inductively Coupled Plasma Emission Spectroscopy (ICP). Analysis of leachate from the lead container shows no evidence of glass dissolution.

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FIGURE 2.2. Cross Sections of Waste Glass Samples Show Depleted Layers. The aluminum container sample exhibits a leach layer of 0.8μ , while the sample depleted layer is not detected in the sample leached in the lead container.

TABLE 2.2. Concentration, atom percent, from XPS Analysis

	<u>Al</u> <u>Container</u>	<u>Glass</u> <u>Leached</u> <u>in Al</u>	<u>Cu</u> <u>Container</u>	<u>Glass</u> <u>Leached</u> <u>in Cu</u>	<u>Pb</u> <u>Container</u>	<u>Glass</u> <u>Leached</u> <u>in Pb</u>	<u>Sn</u> <u>Container</u>	<u>Glass</u> <u>Leached</u> <u>in Sn</u>	<u>Ti</u> <u>Container</u>	<u>Glass</u> <u>Leached</u> <u>in Ti</u>	<u>Teflon</u> <u>Container</u>	<u>Glass</u> <u>Leached</u> <u>in Teflon</u>
Al	29.9	8.0	--	--	--	--	--	--	--	--	--	--
Cu	--	--	24.6	--	--	--	--	--	--	--	--	--
Pb	--	--	--	--	30.8	25.0	--	--	--	--	--	--
Sn	--	--	--	--	9.7	6.4	12.2	--	--	--	--	--
Ti	--	--	--	--	--	--	--	--	20.5	--	--	--
B	--	12.1	--	--	--	--	--	3.6	--	--	--	--
C	--	--	--	--	--	--	--	--	--	--	62.9	--
Fe	--	8.8	--	2.0	--	--	--	3.0	2.7	3.5	--	3.7
Ni	--	2.4	--	0.2	--	--	--	1.0	--	1.6	--	1.9
Si	--	8.0	13.9	19.5	--	7.9	16.2	17.0	8.3	23.5	1.4	20.6
Zn	--	15.6	--	28.6	--	--	7.8	25.8	3.1	10.1	--	9.6
Zr	--	0.5	--	--	--	--	--	0.2	0.4	--	--	0.4
O	20.1	44.6	61.5	49.5	59.6	60.7	56.0	49.4	65.1	61.4	5.0	63.5
F	--	--	--	--	--	--	--	--	--	--	62.9	--

81H531-1

FIGURE 2.3. Surface of 76-68 Waste Glass Exhibits Growth of Lead Crystallites

Graphite Matrix Development - R. E. Bullock (GAC)

During waste encapsulation work in FY 1980, it was found that carbonaceous matrices containing simulated nuclear wastes made by heat-treating organic binders to temperatures above 800°C were permeable to water. It is not mandatory that waste compacts have such a high temperature capability, however, and lowering the heat-treatment temperature markedly decreases the porosity of the matrix material. Therefore, during FY 1981 organic-based waste compacts were fabricated at 400°C. Preliminary work at PNL has shown that waste-free compacts made from two types of matrix material are

impermeable to water following 400°C heat treatment. Similar compacts containing glass beads and rock salt to simulate nuclear wastes have been supplied to PNL for evaluation of their permeability.

Graphite Matrix Evaluation - W. J. Gray

The prior quarterly progress report (PNL-3000-10) describes the results of heating some of the General Atomic Company's (GAC) matrix rods to 400°C at the rate of 67°C/hr. Those rods that were pure binder (i.e., contained no graphite filler) were badly pitted after machining. It was thought that a slower heating rate might give better results. Only one pure binder

rod (M12) remained; it and a few other rods were heated at 50°/hr to 100°C and then at 3°/hr to 400°C. Rod M12 partly melted during heat treatment and, after machining, was badly pitted. Thus the slower heating rate did not help.

Permeability tests were performed on some of the rods heated at the slower rate. Table 2.3 shows the results, which have simply been added to the table used in the previous progress report.

The permeability tests have been run for arbitrary times of 16 to 24 hr. Because of the nature of the process, it has not seemed necessary to run them for longer periods. That is, the permeability tests would seem to be much like porosimetry measurements except that the liquid is in contact with only one side of the sample during the former. Just as with porosimetry measurements, penetration into the pores should occur very quickly if the pressure is high enough; otherwise, penetration never occurs. In practice, water has been observed to penetrate through the samples during permeability tests in an hour or less in most cases or has not penetrated at all after periods up to 24 hr. There was one exception where water penetrated a sample in about 8 hr. To further test the possibility that water might penetrate a sample after a much longer time, Rod M20 was tested for 7 days at 1000 psi, during which time there was no water penetration. This same rod had previously been tested at 1000 psi for 21 hr with no penetration.

Because the permeability tests for pure matrix materials looked favorable, GAC prepared eight matrix rods containing glass beads or NaCl pellets for permeability and leach testing, respectively. All the rods had on the outside a skin about 1 mm thick that was free of beads and pellets. Some

of the rods were received at PNL in the green state, and others had been heat-treated at 400°C. The bond between the center region and the skin was so poor that permeability tests could not be performed. A leach test was conducted on the green rod that contained sodium-chloride pellets. No sodium was detected in the leach solution after a test of 14 days at 90°C.

The work at GAC is now aimed at improving the bond between the central and skin regions of similar rods.

RADIATION EFFECTS

Transmutation - W. J. Gray

The third round of post-irradiation examinations of samples irradiated in the high-flux isotope reactor (HFIR) is nearly completed. About 6% of the cesium has now transmuted to barium. Optical microscopy results were reported in the April-June Quarterly Progress Report (PNL-3000-10). No changes in microstructure were observed.

Table 2.4 lists results of density measurements on the materials irradiated in the HFIR together with results for two non-radioactive reference materials. Densities have increased slightly for four of the materials, including pollucite (No. 7). The largest increases are for the two high-cesium glasses (Nos. 2 and 3), particularly the one without curium (No. 3). Increases for the other two materials (Nos. 4 and 7) are statistically significant, but just barely. Additional measurements a year or so from now will be required to definitely establish a trend.

Leach rates are shown in Table 2.5. Results for the second round of leach tests appear to be in error, particularly for materials 2, 3, and 8. An exception is the

TABLE 2.3. Permeability and Heat Treatment Results for GAC Matrix Rods

Binder Type	Rod No.	Wt% Filler	Density, g/cm	Permeability ^(a)	Condition After Heat Treatment	Condition After Machining	Permeability ^(a)
A-240 Pitch	M1	40	1.423	Extruded			
	M43	65	1.669		Cracked(c)	Good	Shattered
	M30	75	1.759	Extruded	Good	Good	Shattered
MC-600 Polyimide	M19	0	1.092	Good	Good(b)	Badly pitted	
	M15	45	1.350	Good	Badly cracked(b)		
	M28	55	1.470		Good(c)	Good	Good
	M6	60	1.655				
	M5	70	1.731	Poor	Good(b)	Good	Good
	M20	75	1.613		Good(c)	Good	Good
Resinox-755 Phenolic	M32	0	1.251	Good	Good(b)	Badly pitted	
	M34	40	1.511		Good(b)		Poor
	M37	60	1.645				
	M33	65	1.749				
	M16	70	1.719		Good(c)	Good	
	M36	70	1.765	Good	Good(b)	Good	Slightly permeable
	M31	75	1.671		Good(c)	Good	Poor
Resinox-755 + Resinox-754	M12	0	1.226		Partly melted(c)	Badly pitted	
	M4	70	1.722				
QX-322 Furan Resin	M13	0	1.254	Good	Good(b)	Badly pitted	
	M18	60	1.645		Good(b)		Shattered
	M23	65	1.735				
	M17	70	1.750		Cracked(c)	Good	Slightly permeable
	M21	70	1.759	Good	Good	Good	Poor
QX-322 + Resinox 755	M39	70	1.762				

(a) Permeability tests were run at 1000 to 1500 psi for about 18 hr.

"Good" means no water penetrated the specimen; flow rate $<10^{-9}$ mL/sec.

"Poor" means water did penetrate the specimen; flow rate $>10^{-6}$ mL/sec.

"Slightly permeable" indicates 10^{-9} mL/sec $<$ flow rate $<10^{-6}$ mL/sec.

Specimens containing A-240 pitch were too soft and were "extruded" through the sample holder.

Specimen "shattered" into small pieces (almost a powder) when pressure was applied.

(b) Rods were heated at 67°/hr to 400°C and held for 10 hr.

(c) Rods were heated at 50°/hr to 100°C, then at 3°/hr to 400°C and held for 6 hr.

TABLE 2.4. Density of HFIR Samples and Nonradioactive Standards

Number	Material Type	Density, g/cm ³ (a)		
		6/79	2/80	6/81
Std. 3		3.209 ± 0.007	3.203 ± 0.004	3.214 ± 0.007
Std. 5		2.689 ± 0.009	2.690 ± 0.000	2.691 ± 0.007
1	Simulated waste glass	1.993 ± 0.018	1.990 ± 0.010	1.992 ± 0.004
2	High Cs glass (with Cm)	2.704 ± 0.015	2.727 ± 0.007	2.731 ± 0.005
3	High Cs glass	2.835 ± 0.021	2.857 ± 0.018	2.911 ± 0.028
4	High Si glass	2.362 ± 0.005	2.360 ± 0.000	2.381 ± 0.015
5	High Al glass	2.315 ± 0.004	2.310 ± 0.000	2.309 ± 0.007
7	Pollucite	2.970 ± 0.020	2.970 ± 0.000	2.994 ± 0.003
8	Supercalcine	4.207 ± 0.022	4.208 ± 0.010	4.199 ± 0.010

(a) Errors listed represent two times the standard deviation of the mean.

molybdenum results for supercalcine (No. 8), where the results in 5/79 appear out of line. The only materials for which there appears to be a consistent trend are the simulated waste glass (No. 1) and for pollucite (No. 7). The increases observed in the leach rates for these materials, although significant, are still relatively unimportant since the increase is only a factor of about three.

Some preliminary x-ray diffraction results have been obtained on a sample of pollucite using the new shielded diffractometer. Peak intensities are only about 25% of those obtained on a nonradioactive pollucite sample. No other crystalline phases are present, and the lattice parameters appear essentially unchanged. Additional work is being done to more fully characterize the material.

Metamictization – R. E. Haaker and
R. C. Ewing (University of New Mexico)

The effects of several different processing steps were evaluated for preparation of zircon powder precursors from an aqueous solution of zirconyl nitrate and colloidal silica. For the preparation of zircon (ZrSiO_4), it was concluded that solution-

gelation (or coprecipitation methods are superior to simple gelation or boil-down techniques.

Sintering periods of 24 hr at 1450°C were required to produce excellent yields of zircon from the coprecipitation methods. Zirconia (ZrO_2) was still present in samples sintered under similar conditions but produced from other powder-precursor methods.

Hot-Cell Activities – C. A. Knox

The investigation was completed regarding the incidents that occurred when contaminated solution was found in gallery piping. The corrective action items identified were the installation of nonadjustable 5-min timers to prevent insufficient air purges upon completion of a steam jet transfer; the installation of separate key switches for every stream jet in the hot-cell complex (so the incorrect jet could not be used in the future because the key was the same for all jets); and the revision of all procedures to reflect these changes. All of these corrective actions have been completed. Permission was requested from, and granted by, DOE to restart 324 Building, D-Cell operations.

TABLE 2.5. Leach Values of Materials Irradiated in HFIR

Material	Percentage of Element Leached in 7 Days at 90°C in Deionized Water(a)					
	Boron			Silicon		
	5/79	4/80	8/81	5/79	4/80	8/81
1	ND ^(b)	0.93 ± 0.17	1.61 ± 0.22	0.57 ± 0.36	1.00 ± 0.12	1.36 ± 0.31
2	23.6 ± 17.6	15.0 ± 6.6	22.7 ± 3.0	7.8 ± 3.4	5.7 ± 2.3	10.3 ± 0.4
3	27.6 ± 2.6	14.5 ± 2.8	24.3 ± 8.9	7.0 ± 0.7	6.5 ± 1.9	7.6 ± 0.6
4	ND	0.46 ± 0.20	0.61 ± 0.07	0.13 ± 0.00	0.15 ± 0.03	0.12 ± 0.03
5	ND	0.31 ± 0.33	0.31 ± 0.15	0.43 ± 0.22	0.61 ± 0.19	0.57 ± 0.22
7	(c)	---	---	0.70 ± 0.30	1.15 ± 0.06	1.25 ± 0.12
8	---	---	---	3.1 ± 0.3	2.23 ± 0.07	2.97 ± 0.14

Material	Molybdenum			Cesium		
	5/79	4/80	8/81	5/79	4/80	8/81
1	0.11 ± 0.04	ND	0.62 ± 0.26	0.52 ± 0.12	0.89 ± 0.19	1.56 ± 0.22
2	16.5 ± 15.8	9.5 ± 3.6	14.1 ± 3.1	15.3 ± 9.5	5.59 ± 2.21	16.5 ± 3.6
3	18.6 ± 0.9	8.8 ± 1.9	16.4 ± 7.5	29.9 ± 1.3	13.8 ± 2.8	28.6 ± 6.2
4	---	---	---	0.36 ± 0.03	0.38 ± 0.02	0.58 ± 0.07
5	---	---	---	0.53 ± 0.24	0.34 ± 0.10	0.38 ± 0.14
7	---	---	---	1.25 ± 0.51	1.68 ± 0.36	2.58 ± 0.34
8	0.71 ± 0.11	0.09 ± 0.02	0.08 ± 0.04	2.95 ± 0.16	0.57 ± 0.26	1.98 ± 0.65

(a) Errors listed represent two times the standard deviation of the mean.

(b) ND = element not detected.

(c) --- = element not present.

3. TMI ZEOLITE VITRIFICATION DEMONSTRATION PROGRAM

D. H. Siemens - Program Manager

The objectives of this program are to 1) establish the technical feasibility of vitrifying zeolite as a means of immobilizing high specific-activity-level accident wastes and to provide preliminary characterization of the vitrified waste form; 2) provide a vitrified radioactive waste form for analysis and disposal demonstration; and 3) perform special studies as requested by DOE/TMI.

SUMMARY - D. H. Siemens

Four nonradioactive zeolite vitrification demonstrations were successfully completed this quarter. Several zeolite compositions were processed into glass to include a mixture of 40% Linde Ionsiv A-51[®] and 60% Linde Ionsiv IE-96.[®] This mixture has also been selected as the blend to be used initially in the TMI (Three Mile Island) submerged demineralizer system (SDS).

The vitrification system developed for use during the nonradioactive demonstration portion of the Zeolite Vitrification Demonstration Program is relatively simple and easy to operate. The glass formers and zeolite are premixed for homogeneity of glass product and ease of introduction into the canister, where the glass is formed.

The rate of feed addition to the canister is controlled by a star valve. The canister temperature of 1050°C is maintained by a vertical furnace. The off-gas system consists of sintered stainless steel filters followed by a condenser and venturi scrubbers. No significant amounts of cesium and strontium were found in the off-gas system downstream of the filters.

The final glass product is an amber, transparent borosilicate glass with a melting point of about 1050°C. Soxhlet leach tests indicate that it is of good quality with a leach rate similar to those of borosilicate glasses developed for high-level waste programs.

GLASS FORMULATION - G. H. Bryan and L. J. Ethridge

The glass-former composition selected to vitrify the TMI zeolite is shown in Table 3.1. All the formers except for SiO₂ were combined and pelletized to allow easier mixing with the zeolite. The addition of SiO₂ as a third component allows the ratio of Linde Ionsiv IE-96 and A-51 to be changed with an adjustment only in the SiO₂ content (necessary to achieve a constant glass formulation). A 60 wt% zeolite loading in the glass has been achieved with the 60% IE-96 and 40% A-51 mixture selected for initial use in the TMI SDS system.

PROCESS EQUIPMENT - G. H. Bryan, C. A. Knox and D. N. Berger

The system devised for the vitrification of TMI SDS zeolite is shown in Figure 3.1. The system is of a simple design, and very

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TABLE 3.1. Glass-Former Composition

Component	Wt%
SiO_2	25
Li_2CO_3	22
Na_2CO_3	17
TiO_2	12
$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (Borax)	24

few operational problems were encountered. One major change from the original concept was the use of sintered stainless steel filters rather than a cyclone in the off-gas line. The filters were found to be very effective in the removal of particu-

late matter from the off-gas system. A canister length of 9 ft instead of the originally designed 8 ft was also used with Runs 2, 3 and 4 to permit cooling of the feedline to less than 400°C . Higher temperatures at the canister interface cause melting of the glass formers and eventual plugging. It was also necessary to heat the off-gas line and filters to prevent water condensation.

ZEOLITE - G. H. Bryan and C. A. Knox

The zeolite compositions varied during the first three runs, as shown in Table 3.2. Runs 3 and 4 used the mixture selected for

FIGURE 3.1. Zeolite Vitrification System

TABLE 3.2. Zeolite Description

	Run 1	Run 2	Run 3	Run 4
Composition	100% IE-95	67% IE-96 33% A-51	60% IE-96 40% A-51	60% IE-96 40% A-51
Drying temperature	~100°C	250°C	350°C	350°C
Water content	14%	10%	7%	7%

use in the SDS liners. It is necessary to dry the zeolite prior to mixing with glass formers as the excess water will be drained off only just prior to shipment. A 250°C drying temperature was found to produce a reasonably dry zeolite (see Table 3.2) that does not add excessive amounts of water to the off-gas. Heating the zeolite to higher temperatures (350°C) results in marginal water removal.

GLASS PRODUCT - L. J. Ethridge, C. A. Knox and G. H. Bryan

The glass produced during the four non-radioactive demonstration runs was an amber, transparent borosilicate glass with a melting point of about 1050°C. The zeolite waste loading was 60 wt%, except for the first run with an average cesium content of about 0.3 wt% and an average strontium content of about 0.04 wt%, as shown in Table 3.3. Soxhlet leach tests indicate

glass is of a high quality that compares favorably with borosilicate glass developed for the high-level waste programs. Analysis of the glass and off-gas system shows the cesium and strontium retained by the glass.

OFF-GAS - R. W. Goles and G. H. Bryan

Analysis of the off-gas system shows extremely small amounts of particulate matter downstream of the sintered stainless steel filters (see Table 3.4) except in the case of Run 1, where a cyclone was used. The CO₂ and H₂O contents of the gas are high due to the decomposition of the glass formers in the canister. Less than 0.03 wt% of the cesium and 0.6 wt% of the strontium was found in the entire off-gas system during any one run.

Further analysis of the off-gas is under way to identify particulate composition and size range.

TABLE 3.3. Glass Product Data

	Run 1	Run 2	Run 3	Run 4
Waste loading	70%	60%	60%	60%
Cs content, wt%	0.27	0.33	0.62	0.45
Sr content, wt%	0.03	0.04	0.03	0.03
Soxhlet leach _{test} results, g/cm ² /day	5 x 10 ⁻⁵	4 x 10 ⁻⁵	4 x 10 ⁻⁵	3 x 10 ⁻⁵

3.4

TABLE 3.4. Off-Gas Data

	<u>Run 1^(a)</u>	<u>Run 2^(b)</u>	<u>Run 3^(b)</u>	<u>Run 4^(b)</u>
CO ₂ , avg.% molar composition	~1	~20	~37	12
H ₂ O, avg.% Molar composition	~24	~12	~7	4
Particulate, g/L	0.015	<10 ⁻⁶	<10 ⁻⁶	<10 ⁻⁶
Total Cs in off-gas system, wt%	0.03	0.01	0.03	0.01
Total Sr in off-gas system, wt%	0.3	0.3	0.6	0.4

(a) With cyclone

(b) With filter

4. 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 first edition of the Nuclear Waste Materials Handbook, DOE/TIC-11400, was issued at the end of this quarter. It contains the two test methods, MCC-1 and MCC-2, that have been approved on a provisional basis by the MRB. Full distribution of the Handbook, which has a loose-leaf format, will not be made until about 6 weeks later, in the expectation that MCC-6 and MCC-11 test methods will have received MRB provisional approval and can then be included.

In addition to the four test methods mentioned above, eight other test methods have now been submitted to MRB by the MCC and are in various stages of review. Thus, at the end of FY 1981 the MCC has proposed 11 test methods for waste forms and one for structural barriers and submitted them to the MRB.

LONG-TERM MCC-1 TESTING - D. M. Strachan and B. O. Barnes

At the close of FY 1981, the MCC completed two 1-yr tests by using the MCC-1 Static Leach Test Method. Since the start of this testing predated the final version of MCC-1, there were minor deviations from MCC-1P, as ultimately approved by the MRB. These deviations, in the cleaning of

Teflon® and the preparation of specimens, are not expected to affect the results significantly. The long-term tests were performed at 40°C and 90°C using specimens of PNL 76-68 simulated waste glass.

Representative data for the leaching of cesium, strontium, and silicon in the three reference MCC-1 leachants, deionized water, silicate water, and brine, at 90°C are plotted in Figure 4.1. Relatively similar leaching behavior was observed in the deionized water and silicate water leachants. The concentration of cesium in the leachant reached an apparent steady-state after about 200 days. The rate of increase in the concentration of silicon appears to be tending toward steady-state, but steady-state had not been achieved at 364 days. As usually observed in these leachants with the MCC-1 procedure, the release of strontium was very low. This is attributed to a pH effect; the pH goes to about 9.6 within a few days when 76-68 glass is contacted with the reference DI water or silicate water leachants at 90°C. In contrast, the concentration of strontium in the brine continued to increase at almost a constant rate throughout the 364-day test. The pH of the brine remained about 6 throughout the test.

FIGURE 4.1. Results of 1-Year MCC-1 Leach Test of 76-68 Glass

The only unexpected difference between the 90°C data and the 40°C data was the enhanced strontium leachability. However, this is most easily explained by the lower pH in the 40°C leachates. After 1 yr the pH was equal to 8.6 versus the 9.5 at 90°C.

Photomicrographs and analyses by SEM-EDX (scanning electron microscopy and energy-dispersive x-ray fluorescence) show that a magnesium silicate compound forms on the glass surface in brine at 90°C. The solubility of this compound apparently limits

the silica concentration in the brine to a relatively low value. The compound does not form a protective layer, however, as shown by the continued leaching of strontium and cesium at relatively high rates even after the silica has saturated.

Analyses show that a zinc silicate alteration phase forms on the surface of 76-68 glass in deionized water and silicate water at 90°C. It is believed that this alteration phase may have a clay-like structure that adsorbs cesium, creating a saturated

boundary layer at the glass surface that very effectively slows the leaching of cesium. Examination of the surface of the specimens leached for 1 yr at 40°C shows similar results but significant decreases in the leach depth and phase alteration.

Depth profiles have not yet been obtained for these specimens. When these analyses are performed, a more complete interpretation of the data should be possible.

5. TRU WASTE IMMOBILIZATION

W. A. Ross - Project Manager

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

SUMMARY

The draft of the report on comparison of alternative immobilization systems has been completed. Tests on the basalt-glass ceramic waste form have indicated that the ceramic continues to have improved matrix durability over the parent glass for times out to nearly 100 days. Static leach tests have been completed on the six comparative samples. Cement forms continue to have the highest pHs and lowest plutonium releases. Preliminary desorption tests on cast cement waste forms indicated that up to 14 wt% of the initial mixing water can be desorbed to rock salt. Process tests were conducted on cast cement, pressed cements, and in-can melting.

COMPARATIVE REPORT

An interim draft report on the comparison of alternative TRU immobilization systems has been completed. The draft report is undergoing review and comments, with publication planned for next spring.

BASALT GLASS CERAMIC CHARACTERIZATION -

L. A. Chick, L. E. Thomas and R. O. Lokken

Development and initial characterization of basalt glass ceramics (BGC) containing

simulated TRU waste were reported previously. Longer term static leaching and scanning transmission electron microscopy (STEM) are now complete.

Normalized elemental release rates for the BGC reported last quarter appeared to be increasing between 14 and 28 days. This was attributed to a simultaneous increase in the solution pH from acid to slightly basic. Longer term leaching tests were begun to learn whether the increased release rates would continue and eventually reduce the difference between the BGCs and the parent glasses. The 50 wt% waste-loaded materials, parent glass, BG-50, and glass ceramic, BGC-50, were chosen for these tests. Figures 5.1 and 5.2 show the results. Data from the 41-day test on BG-50 were rejected as an outlier.

Figure 5.1 illustrates the resulting solution pHs. The pH of the BGC-50 solution continued to rise after 28 days and appeared to level off at about pH 8. The pH of the parent glass, BG-50, decreases from its initial maximum to the same level as that of the glass ceramic. It might be expected that the levels of the major elements in solution would control the pH and that, therefore, the cumulative releases of the two samples would be nearly equal. This is not the case, however, as illustrated in Figure 5.2.

FIGURE 5.1. Solution pH from a Parent and a Crystallized Basalt-Glass-Ceramic

FIGURE 5.2. Normalized Cumulative Releases of Calcium, Silicon, and Sodium from a Parent and Crystallized Basalt-Glass-Ceramic

The silicon release for BGC-50, shown in Figure 5.2, rises at a moderate rate until it is about one-quarter that of the parent glass at 56 days. Subsequently, its re-

lease rate seems to taper off. Aluminum release, which is not shown, is similar to silicon release.

The sodium release appears to become nearly linear for both the parent glass and the glass ceramic. However, the rate of sodium release for the parent glass remains slightly higher than for the glass ceramic.

Calcium release and magnesium release (which behaves similarly to calcium release) for BGC-50 rise slowly and level off below 1 g/m^2 at about 60 days, while release rates of these elements for the parent glasses appear to be increasing between 28 and 56 days.

Overall, it can be concluded that the glass ceramics retain their moderate advantage in elemental release over those of the parent glass. The glass ceramics have released from 1/3 to 1/6 as much into solution at 56 days, and these improvement factors would probably be maintained for at least 100 days or longer. The fact that the two materials reach a similar equilibrium pH of 8 seems to have little relation to their elemental releases.

Although STEM characterization revealed some differences between the several BGC phase compositions, the analyses shown in Table 5.1 for BGC-50 are typical enough to represent these materials. The first three columns show the range of the weight percents of oxides found in several analyses

of each of the three major crystalline phases, a titaniferrous hematite, an Fe-Al-Mg-Na-Ca silicate, and a Ca-Mg-Al-Fe silicate (augite). Three other phases were found among the several glass ceramics, but their total weight percent was minor. The glass matrix was also analyzed in several spots, and the ranges of oxides observed in it are shown in the fourth column. The fifth column shows the bulk composition of the material as determined by inductively coupled plasma spectroscopy (ICP). Comparison reveals that the formation of the crystal phases results in enrichment of the glass matrix in SiO_2 , Al_2O_3 , and Na_2O . Previously it was thought that the matrix was depleted in Na_2O . However, despite some difficulty with determination of sodium due to its apparent mobility in the sample during analysis, we are fairly certain that Na_2O is indeed enriched in the glass matrix.

Since the glass matrix composition is expected to control leaching, we conclude that the beneficial effects of enriching Al_2O_3 and SiO_2 and depleting CaO during crystallization outweigh the detrimental effect of enriching Na_2O and that they cause the improved leaching behavior observed after crystallization.

TABLE 5.1. Phase Compositions in BGC-50 by STEM, wt%

Oxide	Titaniferrous Hematite $\text{Fe}_{2-3}\text{TiO}_x$	Fe-Al-Mg- Na-Ca Silicate	Ca-Mg-Al-Fe Silicate (Augite)	Glass Matrix	Bulk Composition by ICP
Fe_2O_3	65 to 67	28 to 58	9 to 10	5 to 14	15.4
TiO_2	22 to 25	3 to 13	2 to 4	2 to 5	4.2
CaO	0.5 to 1.5	2 to 6	16 to 18	3.5 to 8	8.8
P_2O_5	0.5	0.5 to 4	0.5 to 1.5	0 to 4.5	2.7
SiO_2	1 to 5	18 to 38	44 to 49	55 to 60	46.1
Al_2O_3	1 to 3	9 to 12	7 to 8	11 to 14	10.1
MgO	2 to 3	5 to 8	13 to 14.5	2 to 3.5	5.4
Na_2O	1 to 3	4 to 5.5	1 to 3	3.5 to 15	5.2

STATIC LEACH TESTS - J. H. Westsik, Jr.,
F. P. Roberts and C. O. Harvey

The MCC-1 leach tests on the comparative samples were completed with data at 91 and 182 days. Trends noted previously (Roberts, Westsik and Harvey 1981) have continued. Normalized mass losses (g/m^2) based on plutonium and several nonradioactive components of the waste forms were calculated. After leaching, the surface of each waste form was examined with the scanning electron microprobe (SEM) with energy-dispersive x-ray attachment.

Figure 5.3 shows the normalized mass losses for plutonium, silicon, and calcium and pHs as a function of time for each waste form leached in deionized water at 90°C. The observed plutonium releases are the lowest in all the forms.

COMPARATIVE STUDY - J. H. Westsik, Jr.,
F. P. Roberts, C. O. Harvey, R. E. Thornhill
and J. E. Gose

Plutonium releases are lowest from the cast and cold-pressed cements. This is due in part to the high pH attained by the leachant in contact with the cements. However, releases of calcium, sodium, and aluminum are much higher than for the glasses or ceramics. The basalt glass-ceramic and the cold-pressed sintered ceramic show the highest releases of plutonium. The correlation with pH again shows the pH was lowest for these two waste forms although it is increasing slowly with time.

In general, for all waste forms the release of plutonium is highest in the brine leachant. This trend is more evident in

the 90°C tests than in the 40°C tests. The only exception is for the aluminosilicate glass, where the releases of plutonium are highest in the silicate leachant and the release to the brine is similar to that in deionized water.

A cross section of each waste form leached 182 days in deionized water at 90°C was examined with the scanning electron microscope (SEM). Each of the waste forms except the cold-pressed sintered ceramic showed some kind of reaction layer. The cast cement had a reaction layer roughly 50 μm thick. The outermost portion of the layer looked somewhat like coral and was depleted of iron, titanium, and magnesium. The inner portion of the layer contained some iron and titanium but no magnesium and appeared structurally more like the bulk material.

The cold-pressed cement had a reaction layer roughly 20 μm thick. This layer was also depleted of iron, titanium, and magnesium, but some parts contained sodium that was not observed in the bulk material.

The reaction layer on the borosilicate glass was $\sim 13 \mu\text{m}$ thick. The layer was depleted of sodium and potassium and showed some variation in calcium and magnesium concentrations.

The aluminosilicate glass had a reaction layer 2 μm thick, with some fingers extending 6 μm into the bulk glass. Sodium and potassium were missing from the reacted zone.

The reaction zone observed on the basalt glass ceramic consisted of fingers extending up to 13 μm into the bulk material. These reaction layers appeared slightly depleted in silicon (or enriched in the other components).

FIGURE 5.3. Leach Results for TRU Waste Forms Leached in Deionized Water at 90°C

DESORPTION OF WATER FROM CEMENT WASTE FORMS - W. A. Ross

One of the unresolved questions about use of cement waste forms for TRU immobilization is the fraction of pore water that may desorb into the repository salt. To evaluate this behavior, a series of tests has been conducted with fresh cement and ground rock salt. The cement forms were prepared with 35 wt% cold sludge, 65 wt% portland cement, and a water-to-solids ratio of 0.43. The cements were aged for 11 and 28 days in a 100% humidity environment and then surrounded by an equivalent weight of freshly ground -100 mesh rock salt, obtained from a commercial mine near the WIPP site. After the salt and cement combinations had aged at room temperature for various periods, samples were separated and reweighed to determine the water transfer between cement and salt. The results

are shown in Figure 5.4. While trends were established for the first few days, longer-term results became somewhat random, but showed a general value between 3 and 5 wt% loss from the cement. This means that up to 14 wt% of the initial water is desorbed to the rock salt. The salt with the addition of desorbed water was agglomerated and not free flowing. No water pockets were formed.

The tests indicate that water is desorbed from cast cement when in contact with rock salt; however, the quantity of water, which may be 3 to 5 wt% of the waste form, does not appear to cause a serious problem with the salt.

TRU PROCESS TESTING - C. L. Timmerman and J. G. Carter

Several cement test runs were performed to gain experience with the batch mixer and

FIGURE 5.4. Weight Loss from Cement in Powdered Rock Salt

to produce larger ($\sim 2 \text{ ft}^3$) products and samples. All tests were made with a 35% simulated waste and 65% cement solids mixture. The waste consisted of a sludge and ash mix or of 100% sludge. Various quantities of water were added to obtain a flowable mix, but a 0.37 to 1 water-to-solids ratio appeared to be most satisfactory. The final products from these runs showed no residual water on the surface, an indication of no excess water. Some holdup problems were experienced with the mixer after product discharge, due probably to the stickiness of the product. Simply flushing with water removed most of this holdup material.

An in-the-die mixing technique was tested to form pressed cement pellets. Cement and sludge were dry-mixed and charged to the die assembly of a hydraulic press. Then water ranging from 0.1 to 0.5 water-to-solids ratio was added. The test was to demonstrate the feasibility of mixing water with the cement and waste in the die, which may greatly facilitate the processing of cement pellets. In all cases the final amount of water remaining had a water-to-solids ratio of ~ 0.1 ; however, the test made with a 0.1 ratio produced a pellet with incomplete mix-

ing. The other test pellets, though, were all of quality appearance. All pellets were pressed to 25,000 psi.

An in-can melting test run was performed to obtain a larger scale glass sample along with glass processing performance data. The melt mixture used in the run consisted of 50% frit, 37.5% chemically simulated sludge, and 12.5% chemically simulated ash. The test run was performed in a 6-in.-dia Inconel 690® canister. Operating temperatures of 1100 to 1200°C were required to achieve a good melting rate. Approximately 30 kg of glass were produced. The physical quality of the glass appeared to be very acceptable, with little porosity.

®Registered trademark of Huntington Alloys, Inc., Huntington, West Virginia.

REFERENCE

Roberts, F. P., J. H. Westsik, Jr., and C. O. Harvey. 1981. "Static Leach Tests of Comparative-Study Samples." Nuclear Waste Management Quarterly Progress Report April Through June 1981, T. D. Chikalla and J. A. Powell, compilers. PNL-3000-10, Pacific Northwest Laboratory, Richland, Washington.

6. 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 continued with the complete disassembly, sectioning and decontamination of a plutonium-contaminated glove box in 1 wk. Assembly and calibration was completed on three ^3He neutron detectors for the criticality safety system. Routine use of the MEGAS system for counting low-density waste began. A technology exchange visit was made to the United Kingdom and the Federal Republic of Germany to assess available technology in decontamination and size reduction and to interact with the technical contacts for these exchange areas. A series of load tests were conducted using the 12-ft³-capacity annular vibratory finisher to determine the dimensions of sectioned waste for maximum loading and optimum vibratory finisher performance.

PROCESS DEMONSTRATION

A major milestone, the processing of a plutonium-contaminated glove box within a 1-wk period, was completed. The processing included the disassembly, sectioning and decontamination of all the materials from the glove box (except the HEPA filters) as well as the treatment of the resulting secondary waste. The initial volume of the glove box was $\sim 100\text{ ft}^3$. After size reduction and decontamination, the resulting vol-

umes were 27 ft^3 of non-TRU waste and only 4 ft^3 of TRU waste; this included all the secondary waste produced by the sectioning/decontamination work plus the unprocessed HEPA filters from the glove box, which occupied 1.3 ft^3 . This means that the volume reduction factor was greater than 95% for the TRU waste and more than 70% for the resulting low-level waste.

The glove box (Figure 6.1) was basically 3 ft high by 4 ft wide by 7 ft long, with an airlock and HEPA filter housing protruding from the box. The box was constructed primarily from 3/16-in. stainless steel, with three large Plexiglas® windows along the front. It was heavily painted on the inside with epoxy paint and on the outside with enamel. It contained numerous welded service pipes running the length of the glove box and several shelves located inside.

The glove box was processed using our standard preparation, disassembly, sectioning, and decontamination procedures. The noncontaminated external hardware was removed before the glove box was placed in the sectioning/pretreatment facility. In this facility the HEPA filters and all other material inside the glove box were removed and the interior surfaces of the

®Plexiglas is a registered trademark of Rohm & Haas Co., Philadelphia, Pennsylvania.

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FIGURE 6.1. A Plutonium-Contaminated Glove Box That Was Completely Sectioned and Decontaminated in 1 Week

glove box precleaned and coated with a fixative. The glove box was then disassembled, the material sectioned using the web press, nibblers and saws, and decontaminated by vibratory finishing. As usual, all components from the glove box, including the stainless steel frame, Plexiglas windows, Neoprene® gaskets, Hypalon® gloves and vinyl bag-out bags were successfully decontaminated.

® Neoprene and Hypalon are registered trademarks of E. I. du Pont de Nemours Co., Wilmington, Delaware.

Sectioning is the most time-consuming segment of glove box processing, requiring more than half of the total processing time. Consequently, the greatest potential for time savings is in this area. One new tool and several new techniques were used during the sectioning of this glove box, permitting the accomplishment of the 1-wk processing milestone.

The new tool was the hydraulic web press, shown in Figure 6.2 and discussed in an earlier report (Allen 1981). This tool,

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FIGURE 6.2. Modified Web Press Used To Section Plutonium-Contaminated Glove Boxes

which is used as a nibbler for thick material, was useful in two areas. First, the web press was used to remove the lip around the glove box windows, which previously had

to be removed with reciprocating saws, a slow and laborious process. Second, the web press could be used to cut holes in the stainless steel glove box panels to provide

start and stop points for the hand-held nibblers.

The hand-held nibbler is the fastest-cutting mechanical sectioning tool we have found. However, it has some limitations. It can cut only flat, smooth sheet, and it can cut only in a forward direction, requiring start and stop points. Combining the use of the web press with the nibbler significantly expanded the usefulness of the nibbler and substantially reduced sectioning time.

Another technique that expanded the role of nibblers for sectioning was cutting the corners off glove boxes. The corners were sawed off using reciprocating saws, thus providing additional start and stop points for the nibbler. Additionally, nibbler cuts were carefully planned to intersect each other, providing additional stop points.

Finally, a different approach was used for sectioning the Plexiglas windows. The Plexiglas was shattered by repeated blows from a hammer while the windows were still in place in the box. This technique is the most rapid of all that have been tried, which included use of special saws, hot knives and mechanical breaking devices.

CRITICALITY SAFETY/CONTAMINATION MEASUREMENT STUDIES

The multi-energy gamma assay system (MEGAS), shown in Figure 6.3, was checked for proper calibration and used to monitor several bags of waste. This system, used to screen low-density TRU waste, was assembled and installed under a subcontract with Los Alamos National Laboratory. Many of the bags of waste that were examined contained wet rags, which severely attenuated the plutonium L x-rays and resulted in

inaccurate readings from the MEGAS. Such L x-ray attenuation can be easily detected by looking at the pulse height analysis spectrum; this can indicate which bags have attenuation characteristics significantly different from the standard bag and require special calibration factors for accurate assay.

Three additional ^3He neutron slab detectors for the acquisition of criticality safety data were assembled and calibrated. The ^3He neutron slab detectors included a three-tube detector for the sump in the sectioning/pretreatment facility, a five-tube detector for the liquid waste evaporator, and a three-tube portable detector.

DECONTAMINATION STUDIES

Load tests were conducted using the 12-ft³-capacity annular vibratory finisher to determine the dimensions of sectioned waste for maximum loading and optimum vibratory finisher performance. Based on these tests, we now can predict the size of the pieces that are likely to jam as well as the areas in the process channel of the vibratory finisher that are susceptible to jamming. We found that the diagonal dimension of the rectangular pieces must be less than the smallest dimension of the vibratory finisher process channel (12 in.) to avoid jamming and to maximize the amount of material that can be processed in the vibratory finisher.

The tests were conducted by loading 3/16-in.-thick steel coupons of a given size into the vibratory finisher until the normal action of the vibratory finisher process tub ceased. Two abnormal conditions were observed. The first was jamming that occurred near the discharge gate for the larger coupons, those 12 to 18 in. long.

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FIGURE 6.3. MEGAS Counting System Used To Segregate Low-Density TRU Waste

The second problem occurred when the amount of material in the vibratory finisher (coupons and media) rose above the level of the discharge chute, prematurely forcing coupons out of the vibratory finisher. This condition occurred when large volumes of the smaller coupons were run.

The test results are listed in Table 6.1. The total amount of material that could be processed increased substantially when the coupon size was reduced to preclude jamming, but leveled off as the coupons became square. Additional sectioning again increased the amount of material that could be processed. This is shown graphically in Figure 6.4.

TABLE 6.1. Effect of Coupon Size on Processing Capacity for a 12-ft³ Annular Vibratory Finisher

Coupon Size, in.	Solid Volume of Load, ft ³
18 x 6 x 3/16	0.11
16 x 6 x 3/16	0.15
14 x 6 x 3/16	0.15
12 x 6 x 3/16	0.19
10 x 6 x 3/16	0.68
9 x 6 x 3/16	0.95
6 x 6 x 3/16	1.38
3 x 6 x 3/16	1.38
1 x 6 x 3/16	2.67

Applying this information to the process demonstration work using the 12-ft³ annular vibratory finisher shows that the feed material should be sectioned to give pieces with a maximum linear dimension <12 in. The target size for sectioned material for the subsequent hot tests will be ~6-in. squares. This will give reasonable loading in the vibratory finisher while minimizing the amount of time-consuming sectioning. This load capacity should be sufficient to process about one standard glove box, 4 by 4 by 8 ft, in two 1-hr decontamination cycles.

TECHNOLOGY TRANSFER

During September 1981, R. P. Allen of PNL visited the United Kingdom (UK) and the Federal Republic of Germany (FRG) as part of a formal information exchange tour sponsored by the TRU Waste Management Program. The purpose of the visit was to assess technical progress in the areas of size reduction, materials preparation, and decontamination. This trip also provided an opportunity to establish working relationships with the technical contacts in the UK and FRG, identify objectives for future technology exchange activities, and define areas for cooperative R&D programs and exchange of personnel. Sites visited in the UK included the Atomic Energy Research Establishment at Harwell, the Atomic Weapons Research Establishment at Aldermaston, the Windscale Nuclear Power Development Laboratories, and the British Nuclear Fuels Ltd. Windscale Works. In the FRG, visits were made to ALKEM and NUKEM at Hanau and the Karlsruhe Nuclear Research Center.

FIGURE 6.4. Relationship of Coupon Length to Loading Capacity of 12-ft³ Annular Vibratory Finisher

Other technology transfer activities during the year included publication of four papers and two topical reports summarizing progress in the vibratory finishing and sectioning studies, preparation of three video tapes, and hosting of more than 30 individual visitors and two tour groups numbering more than 50 people. The visitors to the PNL decontamination facilities represented the Department of Energy, several Department of Energy sites, Department

of Defense, and several commercial companies. Included were 16 foreign visitors from the Federal Republic of Germany, Belgium, Japan, the United Kingdom, and Mexico.

REFERENCE

Allen, R. P. 1981. "TRU Waste Decontamination." Nuclear Waste Management Quarterly Progress Report April Through June 1981, T. D. Chikalla and J. A. Powell, compilers. PNL-3000-10, Pacific Northwest Laboratory, Richland, Washington.

7. KRYPTON IMPLANTATION

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

Attempts to reduce the cost and improve the mechanical properties of high-krypton-content, amorphous alloys are under way. One such alloy tested (80 at.% Ni - 20 at.% U) contained only 0.7 at.% krypton. Further work will, therefore, focus on those nickel-lanthanum alloys that efficiently trap krypton during sputtering. Krypton release measurements on the nickel-lanthanum alloy containing 30 to 34 cm³ Kr (STP)/g of deposit show a temperature coefficient of 71.5 kcal/mole, with a total release of about 0.5% of the krypton in the first 10 years if the maximum temperature reached is 350°C. At the lower temperature predicted for dry-well storage, the release will be negligible.

ION IMPLANTATION OF KRYPTON IN SPUTTER-DEPOSITED GLASSY METALS - E. D. McClanahan, G. L. Tingey, R. W. Moss and J. M. Lytle

Alloy Development

We have previously shown (Tingey et al. 1979) that sputtered deposits with very small crystallite sizes and appearing largely amorphous to x-rays trap larger quantities of krypton and do so at lower substrate voltages than do crystalline

metals. Several binary metal alloys have been tested and shown to satisfactorily contain implanted krypton. Economic factors, however, provide the incentive to examine a few other potential alloy systems. In the most recent quarterly progress report (Tingey 1981), we described results from implanting krypton in an amorphous nickel-lanthanum alloy. This alloy exhibited an unusually high sputtering rate and contained about 10 at.% krypton. Furthermore, the cost of the rare earth metal lanthanum was far less than that of yttrium, which had previously been used. In an effort to further reduce the cost and to improve the mechanical stability of the deposit, we examined other low-cost alloys. We postulated that uranium, with an atomic size comparable to that of lanthanum, would give an amorphous deposit with high krypton contents and might yield some improvement in properties. An experiment was, therefore, devised to examine the validity of this hypothesis. A nickel target was drilled and plugs of depleted uranium inserted into the holes in an array calculated to yield a homogeneous deposit containing about 20 at.% uranium. The target was then sputtered with a target potential of -2500 V and a substrate potential of -250 V. From this experiment we obtained a very smooth, highly adherent deposit containing about 28 at.%

uranium as determined by x-ray fluorescence measurements. The krypton content, however, was disappointingly low at a value of about $1.5 \text{ cm}^3 \text{ (STP)/g}$ of deposit, or about 0.7 at.% krypton. X-ray diffraction studies conducted on the deposit show very broad diffraction lines, indicative of a nearly amorphous deposit.

The results of this experiment emphasize the fact that the properties of metal deposits required to trap large quantities of krypton are not well understood. Previously it had appeared that almost any alloy that deposited in an amorphous structure could be expected to trap krypton effectively. The nickel-uranium experiment shows that more is required than merely having a disordered structure. To clearly understand this process will require further evaluation and is beyond the scope of this program. The major effort in the future will focus on alloys already shown to be effective in trapping krypton. Some work will continue on alloy development, but the emphasis will be on improving mechanical stability, which can be achieved by adjusting some of the sputtering parameters and by matching the properties of the deposit with the substrate material.

Kinetics of Krypton Release

The ultimate goal of our effort to trap krypton in solid matrices is to develop a material that will contain the radioactive gas for periods approaching 100 years with only a minimum of release to the environment. With this goal in mind, we have measured the kinetics of krypton release. Data from several alloys were reported earlier (Tingey et al. 1979). The release of krypton from a nickel-10 at.% lanthanum alloy containing about 30 to 34 cm^3 of krypton (STP)/g of deposit was initially measured

as a function of temperature as the temperature was increased from 200 to 1300°C over a period of 4 to 6 hr. The data reported here were obtained by isothermal treatment at a selected temperature for several days and are thus much more precise. Such isothermal treatments have thus far been completed on the sputtered nickel-lanthanum alloy in the temperature range from 250 to 450°C . Krypton release rates were determined by measuring the gas pressure generated by heating in vacuum and then analyzing the gas by gas chromatography. At all temperatures the total krypton release increased linearly with the square root of time after an initial period required to establish a steady-state krypton concentration profile characteristic of that temperature. Arrhenius plots of the release rate show a temperature coefficient within this temperature range of 71.5 kcal/mole, somewhat higher than observed on other amorphous alloys. Extrapolation of release rates to 10 years yields an estimated release of about 1.2% of the krypton at a constant temperature of 350°C .

A more realistic total release is obtained by using data from Klett of Sandia Laboratories (private communication 1981) on the temperature-time relationship of a deposit containing ^{85}Kr stored in dry wells. In this medium, the temperature would reach its maximum temperature after about 2 years' storage and then decrease as the ^{85}Kr concentration decreases. Using this time-temperature estimate and the release rates as a function of temperature, the total release from a sample that reaches a maximum temperature of 350°C would be about 0.5% of the krypton in the first 10 years. Furthermore, the estimated maximum temperature for a sputtered deposit 1 cm thick will be below 250°C . Under these conditions, the release of krypton would be negligible.

REFERENCES

Tingey, G. L. 1981. "Krypton Solidification," Nuclear Waste Management Quarterly Progress Report April Through June 1981. PNL-3000-10, Pacific Northwest Laboratory, Richland, Washington.

Tingey, G. L., E. D. McClanahan, M. A. Bayne and R. W. Moss. 1979. Entrapment of Krypton in Sputter Deposited Metals--A Storage Medium for Radioactive Gases. PNL-2879, Pacific Northwest Laboratory, Richland, Washington.

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8. 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 fuel*
2. *evaluate the use of thermal outgassing using various sweep gases or vacuum outgassing for the removal of ^{14}C , ^{129}I , ^{85}Kr , and ^3H*
3. *apply the information obtained from both experiment and theory to spent fuel reprocessing, interim and long-term storage, and to reactor safety.*

SUMMARY

Two thermal vacuum outgassing tests have been completed. The first test consisted of two sections of zirconium-clad Shippingport UO_2 blanket fuel heated at 1500°C for 2 hr. The second test involved crushed fuel pellets (separated from the cladding) heated in a vacuum at 1575°C for 3 hr. About 15 to 17% of the xenon and 26 to 36% of the krypton was released during the tests, respectively. Sweep-gas studies were conducted at 1250°C and 1500°C to determine xenon, krypton and tritium gas release data as a function of time. Glen Benedict of the General Atomic Company (GA) spent 2 days reviewing the Thermal Outgassing program at PNL. Preparation of the literature survey document on thermal treatment continued during the quarter.

THERMAL SWEEP-GAS OUTGASSING - D. L. Baldwin
(HEDL) and L. A. Bray

Sweep-gas studies were repeated at 1500°C to duplicate previously reported results, and at 1250°C to determine xenon, krypton and tritium release values as a function of

temperature. The analysis of residual gas for these tests has been delayed by repair of analytical equipment. A Matheson flow meter was installed on the test equipment to provide better control through the tube furnace.

THERMAL VACUUM OUTGASSING - C. A. Hinman
(HEDL) and L. A. Bray

The second vacuum outgassing test (BNW-02) was successfully completed in July in G-Cell at the 327 Building. Approximately 17% of the xenon and 26% of the krypton was released during the 3-hr test. These results compare favorably with a previously reported test (BNW-01) in which 15% of the xenon and 36% of the krypton was released from two sections (each 0.9 cm dia by 1.27 cm long) of zirconium-clad fuel heated under vacuum at $200^\circ\text{C}/\text{min}$ and held at 1500°C for 2 hr. The second test involved Shippingport UO_2 fuel separated from the cladding. The crushed fuel pellets (8.69 g) were placed in an Al_2O_3 crucible with a molybdenum lid and heated at $200^\circ\text{C}/\text{min}$, and held at 1575°C for 3 hr. Total pressure and partial pressures were

8.2

monitored with pressure transducers and a mass spectrometer during the anneal. Five gas samples taken during the run were analyzed for tritium, xenon, and krypton. The in-line spectrometer and the first gas sample showed that all of the tritium release occurred during the first 5 min of heating. Residual values for tritium have not been obtained to confirm the results. Krypton and xenon were found in the first four gas samples. Residual gas values for adjacent fuel pin segments and for the heated fuel were obtained to confirm the xenon and krypton results.

OTHER - L. G. Morgan, C. L. Matsuzaki, L. L. Burger and L. A. Bray

Preparation of the literature survey document on thermal treatment continued during the quarter. This report in draft form will be reviewed and issued in final form in FY 1982. Glen Benedict, Head of the Technical Group, Separations Development, General Atomic Company, San Diego, spent 2 days reviewing the Thermal Outgassing program at PNL. Mr. Benedict is preparing an outline of work to be initiated by GA in FY 1982 to assist PNL in the preliminary economic and engineering evaluation of thermal outgassing.

9. 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 shipment, and for permanent isolation. The technologies must be related to all phases of the nuclear fuel cycle.

SUMMARY

Silver iodide in cement has proven superior to other iodine forms in leach tests. The amount leached was decreased by a factor of 10^3 compared to barium iodate in cement.

In our studies on the sorption reaction of elemental iodine by silver sorbents, we found that water enhanced the reaction for AgZ and that iodine sorbed by Ag⁰Z was at least partially converted to silver iodide.

L. L. Burger presented an invited paper, "Iodine Fixation Studies at the Pacific Northwest Laboratory," at the Iodine Specialists' meeting in Brussels, Belgium, and R. D. Scheele presented a paper, "Characterization of Iodine Loaded Silver Zeolites," at the American Chemical Society's national fall meeting in New York City. A draft of a report on waste-form characterization entitled Selection of a Form for Iodine-129 Fixation has been written and is now being edited.

New samples of iodine-containing sodalite indicate that the material synthesized with kaolinite clays gives a superior product over that made with laboratory reagents.

WASTE-FORM LEACHABILITY - R. D. Scheele

One of the most important factors in selecting a fixation form for ¹²⁹I is the

leachability. In past quarterly progress reports, most recently PNL-3000-9, we discussed the results of our two types of leach tests used for evaluating different iodine compounds and forms in cement.

One form that appeared especially promising at the end of March was AgI in cement; the normalized fraction leached was $<10^{-5}$ cm in 14 days, which was our detection limit (the normalized fraction leached is calculated by multiplying the fraction leached by the geometric-volume-to-geometric-surface-area ratio, about 0.5 cm for our samples). AgI in cement has proven to be superior to all other forms except iodine sodalite, which was comparable. In the simulated dynamic test AgI in cement was a factor of 10^3 better than Ba(IO₃)₂ in cement. The results for the simulated dynamic test are presented in Figure 9.1. It may be noted that the actual leach rate at the end of the test period is about an order of magnitude less than the cumulative rate (averaged over the test period).

In another test a 0.4-mmol Ba(IO₃)₂-cement monolith was encapsulated in 1 cm of cement, and no iodine was found in the leachate after 42 days. Cement encapsulation appears to be an effective method to reduce the high initial leach rates but must be considered only a delaying action.

FIGURE 9.1. Simulated Dynamic Leach Test of AqI in Portland Type III Cement, 0.8 mmol AgI/g Dry Cement (cement-equilibrated distilled water leachate)

To date, the most effective fixation forms for iodine are silver iodide, barium, calcium, strontium, mercuric iodates in cement, and sodalite. Despite the much lower solubility of $\text{Ba}(\text{IO}_3)_2$ compared to $\text{Ca}(\text{IO}_3)_2$, the leach rates of the Group 2 iodates are roughly equivalent. Calcula-

tions show that the excess sulfate in the cement can produce such a leveling effect.

Our waste-form characterization studies are discussed more fully in a document to be published in the near future, Selection of a Form for Iodine-129 Fixation, PNL-4045.

SILVER SORBENT CHARACTERIZATION

To provide a better understanding of the iodine-capture process by silver-containing solid sorbents, we have studied the iodine sorption reaction using differential scanning calorimetry (DSC), and various iodine-loaded silver sorbents using DSC, thermogravimetric analysis (TGA), and surface analysis techniques (Auger and electron scanning microscopy). Earlier studies are detailed in prior quarterly reports, most recently in the April-June 1981 report, PNL-3000-10.

DSC studies for this period included the reaction of silver mordenite (AgZ) with elemental iodine in the near-absence of water vapor ($\sim 4 \mu\text{mol H}_2\text{O/L}$), and the reaction of silver and reduced silver mordenite with elemental iodine.

The effect of water is shown in Figure 9.2; the reaction at dry conditions is

compared to that at ambient conditions ($\sim 500 \mu\text{mol H}_2\text{O/L}$). The reaction at $\sim 4 \mu\text{mol H}_2\text{O/L}$ is significantly less exothermic than the other and occurs at a higher temperature. Also while AgI formation was indicated in the wet run, the two endothermic peaks at 146 and 556°C correspond to a crystal change and to the melting point, only a slight indication exists in the dry run. The presence of water enhances the reaction between I_2 and AgZ.

Figure 9.3 presents a comparison of the Ag and AgZ reactions with elemental iodine. Both reactions were similar, except for the large endotherm at 180°C, and the formation of AgI was indicated in both cases.

The studies show that the equilibrium water content of AgZ affects the sorption of elemental iodine by AgZ. A high water content enhances the reaction. Elemental iodine reacts with AgZ similarly to Ag with some formation of AgI.

FIGURE 9.2. Effect of Zeolite Water, DSC 10°C/min

FIGURE 9.3. DSC Studies Comparing the Reaction of Ag and Ag²O with Elemental Iodine

PAPERS AND PRESENTATIONS – L. L. Burger,
 R. D. Scheele and K. D. Wiemers

During this quarter R. D. Scheele presented a paper, "Characterization of Iodine Loaded Zeolites," PNL-SA-9510, at the American Chemical Society's national meeting, and L. L. Burger presented an invited paper, "Iodine Fixation Studies at the Pacific Northwest Laboratory," PNL-SA-9829,

at the Iodine Specialists' meeting sponsored by the Commission of European Communities.

A draft copy of a document, Selection of a Form for Iodine-129 Fixation, PNL-4045, is in preparation and will be published in the near future. This document makes recommendations for an iodine-129 fixation form based on solubility, thermal and chemical stabilities, cost and availability, and leach resistance.

SODALITE PREPARATION STUDIES – R. G. Johnson
(Rockwell Hanford Operations)

Synthetic sodalites containing iodine were prepared using commercial kaolinite clays. Three kaolinites of differing purities were used. The procedure involves mixing the clay with NaI or HI plus NaOH, gently heating to dryness and grinding to a fine powder. The final step is hot-pressing of the powder up to 1000°C at 34.5 MPa (5000 psi). X-ray diffractograms of the powders showed that up to 75% conversion to sodalite occurred during the aqueous reaction step when the kaolinite/clays were used in place of reagent chemicals SiO_2 and NaAlO_2 . Iodine losses during hot-pressing where final conversion to sodalite occurs were 1.4 to 7.6%. This loss repre-

sents iodine that must be recycled, and efforts are under way to minimize this by increasing the conversion during the first step of the process. It has been observed that the less pure kaolinites give a better product.

Leach resistance using a modified IAEA room temperature test was examined over a 96-hr period. The better samples gave leach rates on the order of 10^{-5} fraction per day ($\sim 2 \times 10^{-6}$ cm/day) cumulative. Terminal rates were considerably lower.

Iodine proved to be more difficult to incorporate into the sodalite structure when added as HI. No explanation has yet been found. Further efforts will be aimed at optimizing the sodalite preparation procedures and minimizing the volatilization of iodine.

10. NWVP OFF-GAS ANALYSIS

M. S. Hanson - Project Manager

The objective of this project is to investigate the behavior of high-level waste vitrification effluents by analyzing the sintered stainless steel filters used in the spray calciner and the off-gas system samples taken during the Nuclear Waste Vitrification Project.

SUMMARY

Microprobe analysis of the filters from the spray calciner used during the Nuclear Waste Vitrification Program (NWVP) has indicated that a significant amount (0.27%) of the ruthenium processed in the high-level waste (HLW) is trapped in the filters. Radiochemical analysis of a representative set of off-gas samples gave preliminary high-level waste feed to condensate decontamination factors of $\sim 10^5$ for ruthenium and 1.65×10^4 for technetium.

TECHNICAL PROGRESS

Fission product loadings have been determined on two of the sintered metal filters. The loadings determined must be considered semiquantitative due to the size of the samples and the counting accuracy. The analysis of nine filter samples gave a mean value of $0.2 \mu\text{m}/\text{cm}^2$ for ^{106}Ru , the fission product of concern. Integrating the mean value across the $15,567 \text{ cm}^2$ of total surface area gives an estimated total ^{106}Ru filter loading of 3.18 mg. Based on the ruthenium fed to the calciner in the 87 hr of operating time, 0.27% was trapped in the filters. Ratioing the ruthenium content to the europium content and assuming europium is non-

volatile, then 97% of the ruthenium in the filters was of a volatilized form.

Radiochemical analysis of a representative set of off-gas system liquid samples was completed. Samples from the quench scrubber, the condensate evaporator, and the acid fractionator were analyzed for a variety of elements, including ^{60}Co , ^{102}Ru , ^{125}Sb , ^{134}Cs , ^{137}Cs , ^{144}Ce , and ^{154}Eu . Activity levels of the samples are relatively low, since the discharge date for the fuel, which was the source of the processed HLW, was April 1974. The low activity levels allow for easier handling of the samples, yet sufficient activity is present to permit statistically accurate analysis by radiochemical means for most isotopes of concern. Activity levels for ^{106}Ru , the isotope of greatest interest, are in the range of 10^5 dis/min/L , even though the isotope has aged through seven half-lives. Condensate activity, measured in one sample, indicates a preliminary decontamination factor from HLW feed to condensate of $\sim 10^5$ for ruthenium. Of the ruthenium in the off-gas system, 80% is volatile material and 20% carried as nonvolatile in solids penetrating the filters.

Technetium-99, a potentially volatile product, may not be a problem during spray calcination/in-can melting or during HLW

concentration in preparation for solidification. Following HLW feed concentration and prior to calcination, the content of ^{99}Tc in the HLW was 3000 $\mu\text{Ci/L}$. The condensate from the evaporation contained 1.62 $\mu\text{Ci/L}$ and the scrub solution 1.00 $\mu\text{Ci/L}$. Based on these numbers, a decontamination factor of ~1150

was obtained from ^{99}Tc during waste concentration. The condensate sample taken during waste solidification showed ^{99}Tc activity below detectable limits of 0.18 $\mu\text{Ci/L}$. Based on the lowest detectable limit, the decontamination factor for ^{99}Tc during spray calcination/in-can melting was 16,500.

11. 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

Several changes have been made in the instrumentation located at the Buried Waste Test Facility (BWTF). An additional net radiometer and two additional anemometers have been installed to allow a more complete characterization of meteorological conditions affecting evaporation. A new, more stable relative humidity probe has been added to increase the reliability of that measurement.

The first phase has been completed in a cooperative project between PNL and Washington State University to characterize soil transport coefficients. Soil samples were taken at the BWTF for laboratory analysis of basic hydrologic and thermal properties. The soil-particle size distribution and soil water characteristic function were characterized, and the thermal conductivity and saturated hydraulic conductivity were measured.

FIELD MEASUREMENTS - R. R. Kirkham

Several instrumentation changes have been made at the BWTF. An additional net radiometer has been installed and both radiometers have been placed lower to the soil surface. One radiometer now faces the irrigated lysimeters and one the ambient lysimeters. This arrangement should reveal

any differences in net radiation that are due to different soil water contents. Two cup anemometers have been added to characterize the wind profile with height. This will allow the calculation of surface roughness parameters necessary for evaporation calculations. A new relative humidity sensor has replaced the polystyrene impedance sensor used previously. The polystyrene sensor was not very durable and also showed long-term changes in calibration. The new sensor, a thin-film capacitance probe, is expected to show improved performance. Preliminary calibration with standard Assman psychrometer readings shows the new sensor to be comparable over the range of 15 to 90% humidity.

LABORATORY ANALYSIS - A. Cass,
G. S. Campbell, and T. L. Jones

The first phase has been completed in a cooperative effort between PNL and Washington State University to measure soil transport coefficients needed to model soil water evaporation. Soil samples from the BWTF have been analyzed for their basic hydrologic and thermal properties (Cass et al. 1981). The soil particle size distribution and soil characteristic function were characterized, and the thermal conductivity function and saturated hydraulic conductivity were measured.

The soil material used to fill the BWTF lysimeters was a mixture of the material excavated during construction to a depth of 8.5 m. The excavated material was mixed, passed through a 1/2-in. screen and then packed into the lysimeter caissons (Phillips et al. 1979). The original profile consisted of surface eolian deposits of medium sands, while the deeper sediments were coarse sands and gravels that had resulted from catastrophic flooding of the area. The surface soil, belonging to the Quincy soil series, is identified in previous reports as B-Soil (Gee et al. 1980, 1981; Jones 1979).

A comparison of the BWTF soil, identified as L-Soil, with the B-Soil is shown in Figures 11.1 and 11.2. The soil-particle size distribution depicted in Figure 11.1 shows that the L-Soil contains more coarse sands than does B-Soil. This is due to the mixing with the coarser flood deposits during construction. The soil water characteristic curve is shown in Figure 11.2. The B-Soil and L-Soil curves are very close except near saturation. The reason for the high saturated water content of the L-Soil

(0.26 kg kg^{-1}) is the lower bulk density found in the lysimeters (1.6 kg kg^{-1}). Figure 11.3 shows that the mid-range of the soil characteristic function can be described very well by the traditional power function approach where:

$$\Psi = \Psi_e \left(\frac{\theta - \theta_d}{\theta_s - \theta_d} \right)^b \quad (1)$$

where Ψ = soil water potential (J kg^{-1})
 Ψ_e = air entry potential (J kg^{-1})
 θ = soil water content (kg kg^{-1})
 θ_d = residual water content (kg kg^{-1})
 θ_s = saturated water content (kg kg^{-1})
 b = curve-fitting parameter.

The parameter values used in Equation 1 to draw Figure 11.3 are:

$\Psi_e = 0.7 \text{ J kg}^{-1}$
 $\theta_d = 0.03 \text{ kg kg}^{-1}$
 $\theta_s = 0.25 \text{ kg kg}^{-1}$
 $b = 1.3.$

The results of the saturated hydraulic conductivity measurements compare well with previous measurements made with L-Soil. The value measured was $1.4 \times 10^{-4} \text{ m sec}^{-1}$.

FIGURE 11.1. Particle Size Distribution for L-Soil and B-Soil

FIGURE 11.2. Soil Water Characteristic Curve for L-Soil and B-Soil

as compared with $1.7 \times 10^{-4} \text{ m sec}^{-1}$ measured by Jones et al. (1979). This value may be used with the formulas of Bressler et al. (1978) or Campbell (1974) to estimate the entire conductivity function.

Figure 11.4 shows the relationship of thermal conductivity to soil water content. The equation used to generate the solid-line curve in Figure 11.4 is of the form proposed by McInnis et al. (1981). The general equation is:

FIGURE 11.3. L-Soil Characteristic Function Modeled with Power Function

$$K_T = A + B\theta - (A-D) \exp [-(C\theta)^X] \quad (2)$$

where K_T = soil thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)

θ = soil water content (kg kg^{-1})

A, B, C, D = curve-fitting parameters.

The values of the curve-fitting parameters used in Figure 11.4 are:

$$A = 0.64 \text{ W m}^{-1} \text{K}^{-1}$$

$$B = 1.63 \text{ W m}^{-1} \text{K}^{-1}$$

$$C = 17$$

$$X = 2$$

$$D = 0.135 \text{ W m}^{-1} \text{K}^{-1}.$$

This analytical expression is useful in relating thermal conductivity to thermal diffusivity.

FIGURE 11.4. Thermal Conductivity for L-Soil Measured at 21 to 26°C

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12. 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

The Natural Activities Calibration Facility has been sampled, and the concentrations and distribution of the primordial activities present are being determined. Three field portable spectrometer systems have been completely calibrated in this facility.

Mathematical modeling of gamma-ray spectra has been initiated to assist in spectral stripping for ^{90}Sr bremsstrahlung analyses.

The reaction of $^{90}\text{Sr}(n,\gamma)^{91}\text{Sr}$ was investigated as a potential method for in situ analysis of ^{90}Sr . The details and results of these experiments are described.

Bench testing of the proportional counter tritium logging system is under way.

The feasibility of applying mass spectrometric and laser excitation techniques to the in situ analysis of tritium has been investigated, and the potential for these methods is discussed.

A computer code has been developed to generate calibration factors for the passive neutron transuranic measurement technique.

Tungsten collimators have been obtained for improving spatial resolution with the actinide photon well-logging spectrometer.

DEVELOPMENT OF LOGGING SYSTEMS CAPABLE OF MEASURING ^{90}Sr

- R. L. Brodzinski,
W. K. Hensley, R. M. Campbell, L. A. McVey,
and J. H. Reeves

The surface of the Natural Activities Calibration Facility has been sampled, and analysis of these samples has demonstrated the site to be spatially homogeneous. Drilling and sampling as a function of depth have also been completed, and the soil samples have been sealed in aluminum cans to allow the radon daughter activities to reach equilibrium prior to determination of the primordial radionuclide concentrations. A calibration well has been installed, and three different field portable spectrometer systems have been completely calibrated.

Development of a mathematical model that can describe the shape of a gamma-ray spectrum has begun. It now looks as though the best way to proceed is to construct the spectrum in pieces using strict boundary conditions. In this manner, it is hoped that the limitation confining a library of standard spectra to one set of parameters can be overcome, and that individual components of a gamma-ray spectrum can be accurately stripped to leave only the bremsstrahlung radiation spectrum from ^{90}Sr . The

general shape of the broad Compton plateau and the region between the Compton edge and the beginning of the full energy peak are currently receiving the most attention since mathematical models of these areas have not been well defined. Monte Carlo simulations of these regions are also being investigated.

The reaction $^{90}\text{Sr}(n,\gamma)^{91}\text{Sr}$ was investigated as a potential method for in situ analysis of ^{90}Sr based on suitable decay characteristics of the product, ^{91}Sr , and the favorable thermal-neutron capture cross section of 800 mb reported in the literature (Zeisel 1966).

Although the neutron activation product, ^{91}Sr , emits several relatively intense gamma-rays at energies of 556, 750, and 1024 keV, the target material, ^{90}Sr , is itself radioactive, and generates large quantities of bremsstrahlung radiation which interfere with the spectroscopic analysis.

Initial experiments were performed in the laboratory utilizing a solution containing ^{90}Sr . Interferences from the bremsstrahlung radiation produced by deceleration of ^{90}Sr beta particles was minimized by using lucite and lead absorbers around the sample and the high-resolution germanium diode gamma-ray spectrometer in the configuration shown in Figure 12.1. The 6.4-mm-thick lucite attenuates the beta particles emitted by ^{90}Sr and ^{90}Y , while the low Z matrix minimizes the generation of bremsstrahlung radiation. The 2.54-cm-thick lead disc prevents a large fraction of the bremsstrahlung photons generated in the lucite from reaching the germanium diode, allowing only those in a direct line from the sample to be incident on the detector. The 3.2-mm lead plug in the bottom of the conical hole in the lead disc attenuates low-energy bremsstrahlung photons preferentially to the higher energy activation product pho-

tons, which maximizes the signal-to-noise ratio. This counting configuration was chosen after several experiments were performed to determine the optimum geometry for counting the photon peaks while maintaining satisfactory detector dead-time levels. Nevertheless, because of the bremsstrahlung radiation, the maximum amount of ^{90}Sr which could be counted was limited to about 4 mCi.

Standards were prepared from NH_4Br and National Bureau of Standards (NBS) Orchard Leaves. Bromine was selected as a primary standard because of its well-known cross section and because the neutron activation product, ^{82}Br , emits relatively intense gamma-rays at energies of 554 keV, 776 keV, and 1044 keV—very nearly the same as ^{91}Sr . The Orchard Leaves provided a matrix which would contain some of the anticipated interferences (^{76}As , ^{140}La , and ^{42}K), yet still be a calibrated source of several isotopes for calculating the neutron flux. In addition, empty irradiation containers and double-distilled water samples were prepared to be irradiated as blanks.

Care was taken during the preparation and handling of the samples, standards and blanks to eliminate potential interferences from activation of impurities. Each sample, standard, or blank was heat-sealed in a small primary polyethylene vial which had been cleaned in boiling nitric acid. These small vials were then heat-sealed in larger, cleaned, secondary polyethylene vials. Finally, the secondary vials were sealed in plastic bags. The samples were rotated during irradiation in a 1 MW TRIGA reactor at a measured thermal neutron flux of $9.36 \pm 0.35 \times 10^{11} \text{ n/cm}^2\text{sec}$ for 5 hr. Following the irradiation the small primary polyethylene vials were transferred into larger unirradiated sample containers. This

FIGURE 12.1. Counting System Configuration and Shielding

step eliminated the radioactive impurities associated with the large secondary polyethylene vials, leaving only those from the primary containers.

All samples were counted on a Ge(Li) diode gamma-ray spectrometer having a relative efficiency of 16.2% and an FWHM resolution of 1.84 keV at the 1332 keV line of ^{60}Co . Data were stored in a 2048 channel analyzer and transferred to both a floppy

disc for computer data reduction and a hard-copy channel-by-channel printout for manual data evaluation.

The absolute efficiency of the detector and counting geometry was determined as a function of gamma-ray energy by counting an NBS traceable $^{152,154}\text{Eu}$ standard prepared in the same geometry as the samples. The weighted efficiency curve is shown in Figure 12.2.

FIGURE 12.2. Weighted Counting Efficiency Curve

A plot of the gamma-ray energy spectrum from the irradiated ^{90}Sr sample is shown in Figure 12.3. The magnitude of the ^{91}Sr and impurity photopeaks relative to the ^{90}Sr bremsstrahlung continuum clearly demonstrates the difficulty of the measurement.

The half-lives, major gamma-ray energies, and branching fractions for the activation products of interest in this study are given in Table 12.1. Standard equations of radioactive growth and decay were used to determine the reactor neutron flux from the known cross sections and the measured activities induced in the NH_4Br and Orchard Leaves standards. These data are presented in Table 12.2. The average flux and the measured ^{91}Sr activity level were then used to calculate the $^{90}\text{Sr}(n,\gamma)^{91}\text{Sr}$ cross section.

All sources of error have been propagated by standard mathematical methods throughout the computations to determine reasonable and conservative uncertainties. Where several peaks were measured for a given isotope, the production rate was taken to be the average of the values calculated from each photopeak, and the uncertainty was taken to be

the standard deviation of these values. For individual photopeaks the error was propagated based on the uncertainties in the basic nuclear data, i.e., half-life branching fraction, cross section, etc., taken from the literature (Lederer 1978; IAEA 1974). All reported uncertainties represent one standard deviation.

The thermal neutron capture cross section for the reaction $^{90}\text{Sr}(n,\gamma)^{91}\text{Sr}$ is determined to be 14.0 ± 2.4 mb.

The thermal neutron capture cross section for ^{90}Sr may be slightly in error due to a contribution from resonance capture. However, no corrections were made for the resonance integral capture reactions in any of the standards. Therefore, unless the epithermal capture reactions in ^{90}Sr contribute substantially differently than the average of the monitor reactions, no significant error is expected.

When more than one isotope contributed to a photopeak of interest due to similar gamma-ray energies, the interfering activity was determined from other independent and resolvable peaks, corrected for branching

FIGURE 12.3. Gamma-Ray Spectrum of a Thermal Neutron Activated ^{90}Sr Source

TABLE 12.1. Nuclear Data for Activation Products of Interest

Isotope	$t_{1/2}$, hr	E_γ , keV	Branching Fraction
^{91}Sr	9.48 ± 0.01	556	0.607 ± 0.049
^{91}Sr	9.48 ± 0.01	750	0.228 ± 0.017
^{91}Sr	9.48 ± 0.01	1024	0.33 ± 0.02
^{24}Na	14.964 ± 0.015	1369	1.00
^{24}Na	14.964 ± 0.015	2754	0.9985
^{42}K	12.361 ± 0.003	1023	$(2.09 \pm 0.16) \cdot 10^{-4}$
^{42}K	12.361 ± 0.003	1525	0.188 ± 0.006
^{82}Br	35.344 ± 0.013	554	0.707 ± 0.008
^{82}Br	35.344 ± 0.013	698	0.286 ± 0.008
^{82}Br	35.344 ± 0.013	776	0.834 ± 0.009
^{82}Br	35.344 ± 0.013	828	0.239 ± 0.008
^{82}Br	35.344 ± 0.013	1044	0.274 ± 0.005
^{82}Br	35.344 ± 0.013	1317	0.269 ± 0.006
^{82}Br	35.344 ± 0.013	1475	0.166 ± 0.002
^{140}La	40.27 ± 0.05	1596	0.955 ± 0.003

TABLE 12.2. Reactor Neutron Fluxes from Measured Activities

Standard	Reaction	Cross Section, mb	Flux
NH_4Br	$^{81}\text{Br}(n, \gamma)^{82}\text{Br}$	5.7 ± 0.2	$(8.98 \pm 0.44) \times 10^{11}$
Orchard Leaves 1	$^{23}\text{Na}(n, \gamma)^{24}\text{Na}$	0.528 ± 0.005	$(9.06 \pm 0.37) \times 10^{11}$
Orchard Leaves 2	$^{23}\text{Na}(n, \gamma)^{24}\text{Na}$	0.528 ± 0.005	$(9.67 \pm 0.40) \times 10^{11}$
Orchard Leaves 1	$^{41}\text{K}(n, \gamma)^{42}\text{K}$	1.46 ± 0.03	$(9.84 \pm 0.28) \times 10^{11}$
Orchard Leaves 2	$^{41}\text{K}(n, \gamma)^{42}\text{K}$	1.46 ± 0.03	$(9.60 \pm 0.24) \times 10^{11}$
Orchard Leaves 1	$^{139}\text{La}(n, \gamma)^{140}\text{La}$	8.63 ± 0.34	$(9.39 \pm 0.78) \times 10^{11}$
Orchard Leaves 2	$^{139}\text{La}(n, \gamma)^{140}\text{La}$	8.63 ± 0.34	$(8.99 \pm 0.75) \times 10^{11}$
Average			$(9.36 \pm 0.35) \times 10^{11}$

fractions and efficiencies, and subtracted from the peak of interest. Generally, the identifiable interferences were from ^{76}As , ^{140}La , and ^{42}K .

Interferences from the 559 keV photopeak of ^{76}As and the 752 keV photopeak of ^{140}La could not be adequately resolved from the 556 and 750 keV peaks of ^{91}Sr in the strontium sample. In addition, a correction to

the 556 keV peak would need to have been made due to the contribution from thermal neutron capture reactions on ^{90}Y , the equilibrium daughter-product of ^{90}Sr , leading to the same gamma-ray cascade via the $^{90}\text{Y}(n,\gamma)^{91\text{m}}\text{Y}$ reaction. Hence the ^{91}Sr activity was obtained based on only the 1024 keV peak, which, although lower in intensity than the 556 or 750 keV peaks, had virtually no interference. Other peak interferences were less of a problem. Corrections for the activities in the blanks were less than 1% in all cases, except for ^{24}Na .

Based on this measured cross section for the $^{90}\text{Sr}(n,\gamma)^{91}\text{Sr}$ reaction, an average thermal neutron flux of $5 \times 10^4 \text{ n/cm}^2\text{sec}$ throughout the matrix, and empirical sensitivities for a subterranean high-resolution germanium diode gamma-ray spectrometer, the detection limit for in situ measurement of ^{90}Sr in sediments by neutron activation analysis is calculated to be 366 mCi/cm^3 for a 10,000-sec irradiation and count period. This lack of sensitivity is largely due to the intense bremsstrahlung radiation from the $^{90}\text{Sr}(^{90}\text{Y})$ beta activity and leaves the technique unsuitable for practical applications.

A review of the reactions $^{90}\text{Sr}(n,p)^{90}\text{Rb}$ and $^{90}\text{Sr}(n,\alpha)^{87}\text{Kr}$ was made with consideration given to experimentally measuring the cross sections. However, there is no reason to believe that these fast neutron reaction cross sections should differ markedly from comparable reactions on other elements of similar mass and Q value. Hence, cross sections on the order of 5 mb are expected for these reactions with 14 MeV neutrons. If such a value is assumed, the detection of the ^{90}Rb and ^{87}Kr products would not be possible with a fast neutron flux of less than about $10^{12} \text{ n/cm}^2\text{sec}$. At the present

time such a flux is unobtainable; consequently no attempt was made to measure these cross sections. Similarly, the low anticipated reaction cross sections and the even lower fast neutron fluxes obtainable in a subterranean environment make these transmutation reactions even more impractical than the thermal capture reaction as a method for determining the ^{90}Sr concentration in soil.

The measurement of ^{90}Sr in soil, then, is probably best accomplished by the bremsstrahlung measurement technique (Brodzinski and Nielson 1980), for which a far superior detection limit is anticipated.

DEVELOPMENT OF LOGGING SYSTEMS CAPABLE OF MEASURING TRITIUM – R. L. Brodzinski, B. A. Bushaw, J. R. Morrey and C. Menninga

The control wiring has been completed on the tritium logging system under development that employs a Nafion sampler and a gas proportional counter. The system is currently undergoing bench tests in the form of six subassemblies temporarily connected with flexible tubing.

A change in the design of the system has been tested which would eliminate the need for a high-temperature furnace in the probe. The magnesium reduction furnace was replaced by a calcium carbide converter and hydrogen/palladium reducer to generate tritium-tagged ethane counting gas. Problems were encountered with the efficiency of the calcium carbide conversion step, and the original magnesium reduction furnace was reinstalled. Problems involving proper operation of the cold trap also resulted in several modifications to that portion of the system. The magnesium reduction furnace controller has been tested and calibrated. Sufficient heat is provided by the system to maintain

the furnace at 600°C even while the casing is submerged in water. Procedures are being investigated for transferring the sample from the cold trap into the furnace. The design manual for the tritium logging system has been completed and will be issued soon.

A preliminary study has been completed that demonstrates the potential for real-time in situ tritium analysis by mass spectrometry. This study indicates mass spectrometric techniques could be as much as a factor of two more sensitive than predicted gas proportional counting techniques. As soon as the actual sensitivity limits of the sophisticated gas proportional counting system currently under development are determined, the results from the preliminary mass spectrometric analysis study will be reexamined with a view toward the potential cost/benefits obtainable.

A basic investigation into the potential application of laser excitation analysis to well-logging tritium measurements has been completed, and the results and findings are being evaluated. Preliminary indications are that a pure laser excitation technique will not provide satisfactory sensitivity by itself, but that when laser excitation is used as the ion source for a mass spectrometer, extremely sensitive measurements may be possible. Comparisons between the sensitivities and cost effectiveness of the proportional counting technique, static mass spectrometric analysis, and laser/mass spectrometer hybrid techniques will continue to be examined.

A tritium enrichment procedure involving cryogenic/magnetic techniques is also being considered as an input stage to any of the potential analytical systems.

DEVELOPMENT OF LOGGING SYSTEMS CAPABLE OF MEASURING ACTINIDES – R. L. Brodzinski and L. A. McVey

A computer code has been developed to generate calibration factors for the passive neutron transuranic measurement technique developed earlier in this program. A five-dimensional empirical data field has been programmed such that inputting the relative transuranic isotopic composition, the fluorine to oxygen ratio, the moisture content, the monitoring well size, and the matrix material generates a calibration coefficient for converting the experimentally measured thermal neutron flux to the absolute concentration of all actinides in the matrix. The effect of the fluorine to oxygen ratio on the neutron yield from (α, n) reactions on light isotopes in the matrix material has been accurately measured. A linear increase has been observed in this portion of the neutron flux with increasing F/O ratio corresponding to the factor $4.509 \cdot 10^{-3} (F/O)$
 $n \text{ cm}^{-2} \text{ sec}^{-1} / n\text{Ci} \propto \text{cm}^{-3}$.

The tungsten collimators for improved spatial resolution with the actinide photon well-logging spectrometer have been received. Field tests are currently under way at the Natural Activities Calibration Facility to provide calibration factors for each new configuration and to compare the effectiveness with the new system to that with the old lead collimators.

Glenn Popper from Argonne National Laboratory visited PNL to gather information on the instrumentation developed in this and other programs for inclusion in an instrumentation capabilities manual he is preparing for the TRU program.

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13. 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

Optimization of the passive TRU package assayer has been completed, and sensitivity/selectivity tests will be initiated soon.

Relevant waste package parameters are identified and discussed.

Waste package measurement requirements and capabilities are prioritized and evaluated.

Technology transfers are described.

WASTE RECEIPT INSTRUMENTATION DEVELOPMENT -

R. L. Brodzinski and L. A. McVey

Optimization of the individual amplifier/discriminators, used to isolate $^{10}\text{BF}_3$ proportional neutron counters from one another, has been completed. These modules have been connected to the detectors and wired into "octets" (four inner annular quadrants and four outer annular quadrants) in the passive TRU package assayer being assembled. Tests will begin soon on the sensitivity of this system for quantitatively determining the concentration and distribution of TRU materials in a waste package as well as the general nature of the matrix material. If the concentration of TRU activities in a waste package can be rapidly assayed at the 10 nCi/g level, the package can be properly

directed to low-level waste disposal or to TRU waste storage, thus making the most cost-effective operation possible. If a single "hot spot" of TRU activity can be located within the waste package, retrieval may permit the rest of the package to be disposed of as low-level waste rather than transuranic waste. Finally, the relative degree of thermalization of neutrons generated and moderated within the waste package will provide information concerning the hydrogenous composition of the matrix material, particularly when coupled with information on the bulk density of the package. A method is being examined that will allow a simple, rapid conversion of the TRU assayer data acquisition system from this octant counter for spatial and distribution measurements to a coincidence counter for isotopic and concentration measurements.

Discussions were held with Jack Dowell and Jim Weber of UNC Nuclear Industries regarding application of the package TRU assay system to the characterization of waste packages containing solidified sludge from N-Reactor spent fuel storage basins. It is hoped that quantitative assay of packages at the 10 nCi/g level will allow some of the packages to be disposed of as low-level waste rather than costlier storage as TRU wastes.

IDENTIFICATION OF RELEVANT WASTE PACKAGE
PARAMETERS - R. L. Brodzinski

Unquestionably, the most important aspect of radioactive waste disposal by land burial is the ability to confine the wastes until they have decayed to innocuous levels. Just as unquestionably, the greatest mobilizing factor for buried wastes is water intrusion.

Proper operation of a land disposal site with respect to long-term management can be generally defined as the efficient interment of radioactive wastes in a manner such that hazardous quantities of radionuclides never enter the biosphere under normal climatic conditions or from predictable catastrophic events. This means that the combination of engineered barriers and geologic containment should be adequate to confine the wastes for periods of time far beyond the anticipated operation and maintenance period of a disposal site. Through proper choice of waste form, matrix material, waste package, trench construction, and terrestrial geology, such confinement can probably be ensured in arid western environments, but will be exceedingly more difficult to accomplish in a humid eastern environment. Consequently, disposal at an eastern site can be considered a worst possible case, and acceptable methodology at a humid site will be more than adequate for use at arid western sites.

Ideally, all waste package parameters that could have any bearing on confinement or mobilization of the radioactivity should be measured at the disposal site just prior to interment, and these measurements should be made quickly on each package and should provide extreme accuracy. A realistic approach, however, can at best hope to measure the radionuclide content of a representative number of waste packages from each shipment. The choice of acceptable

waste forms, matrix materials, and packages will have to be made legislatively, and after that has been done, a decision can be made regarding implementation of a nondestructive assay technique to test for compliance. Obviously, visual inspection can be used to determine if the package itself is acceptable.

To make reasonable predictions of management potentials, it will be necessary to know the concentrations and total activities of the radionuclides present in the waste package. Again, however, it is expedient to consider only those radionuclides that present a long-term potential hazard. Relatively short-lived nuclides or those that represent minimal biological hazard can realistically be presumed to be containable for periods of time sufficient to render them innocuous. The radionuclides ^3H , ^{14}C , ^{90}Sr , ^{99}Tc , ^{129}I , ^{237}Np and the transuranics have been determined to be the most important activities in terms of radiological health, due to their high mobility potential, high hazard-to-man index, and/or long half-life. The concentration and total activity of these radioisotopes are the important waste package parameters to be determined. The volume and weight of the waste packages are also of interest and are easily measurable by conventional techniques. The concentrations of other radioactivities present, such as gamma-ray emitting fission products, are also of interest but of less importance from the standpoint of long-term management. These types of isotopes can probably be determined to sufficient accuracy levels with state-of-the-art high-resolution gamma-ray spectrometric techniques.

Of the important radionuclides listed above, only ^{237}Np and the transuranics are likely to be measurable with nondestructive

assay techniques. Such measurements are extremely important, however, since waste packages containing transuranic concentrations above prescribed levels are not allowed to be disposed of in low-level land burial sites. Therefore, the capability to segregate waste packages containing enough transuranic activities to be considered TRU waste is extremely important. The exact definition of which isotopes at what concentrations constitute TRU wastes differs depending on the government agency and is likely to be changed or modified in the future.

Tritium and ^{14}C concentrations will probably have to be estimated or measured prior to encapsulation in a waste package. The ability to measure ^{90}Sr , ^{99}Tc , and ^{129}I non-destructively in a sealed package will depend largely on the success of measurement technology currently under development.

EVALUATION AND PRIORITIZATION OF WASTE PACKAGE MEASUREMENT REQUIREMENTS AND CAPABILITIES - R. L. Brodzinski

With due consideration of the preceding discussion, prioritization of waste package measurement requirements will be treated in descending order of importance in the following paragraphs. Evaluation and discussion of existing measurement capabilities will correspond to the prioritized requirements.

1. Probably the most important requirement in measuring low-level waste receipts is the transuranic activity concentration. Certainly, if the TRU concentration exceeds the prescribed limit for low-level wastes, then the offending package does not qualify as low-level waste and cannot legally be disposed of in a low-level land burial site regardless of its other attributes or shortcomings. The current

generally accepted definition of TRU wastes is those that contain greater than 10 nCi of alpha activity per gram of matrix material and variously include or exclude ^{235}U , ^{238}U , ^{237}Np , and ^{238}Pu . No single measurement technique currently in existence or under development is capable of measuring all TRU activities at the prescribed level of sensitivity in all packages. In fact, it will require a combination of techniques to make TRU measurements at 10 nCi/g, and even then not all determinations will be possible.

The most informative TRU assay technique available is the measurement of the distinctive gamma-ray lines emitted by specific isotopes utilizing high-resolution germanium diode gamma-ray spectroscopy. With this technique, ^{235}U , ^{238}U , ^{237}Np , ^{239}Pu , ^{241}Pu , and ^{241}Am can all be measured simultaneously at 10 nCi/g but only in the absence of large quantities of other gamma-ray emitting radionuclides. This latter condition is not likely to be found in most low-level waste packages. Another shortcoming of the gamma-ray measurement technique is the inability to measure ^{238}Pu , ^{240}Pu , or the curium isotopes.

Active neutron interrogation techniques are less sensitive to gamma-ray interferences but only measure the fissile species present. A technique that measures the increase in a steady-state neutron flux caused by multiplication due to fission is not likely to be sensitive enough and is very dependent on matrix material. This technique, e.g., a steady-state neutron flux produced by $^{241}\text{AmBe}$ sources and measured with ^3He proportional counters, again cannot measure ^{238}U , ^{237}Np , ^{238}Pu , ^{240}Pu , or the

curium isotopes and cannot tell the difference between ^{235}U , ^{239}Pu , and ^{241}Pu , the fissile species. A shuffler system, ^{252}Cf cyclic-induced fission with delayed neutron detection, is more sensitive than the steady-state increase technique, but is subject to all the other limitations.

A passive neutron detection technique, such as in use at the Kernforschungszen-trum, Karlsruhe, or that being developed in this program, measures the neutrons emitted by spontaneous fission of trans-uranic elements or alpha-induced neutron emissions from light isotopes in the matrix. These techniques can be made sufficiently insensitive to gamma radiation, are adequately sensitive for measuring TRU levels, and can measure the total quantities of both spontaneous fission activity and alpha particle activity. These measurements are also very matrix-dependent, however, and re-inforce the necessity for standardized packages and matrix materials.

Other more exotic TRU measurement techniques under consideration, such as accelerator-induced interrogation, are not sufficiently practical for application to real disposal operations.

2. The next most important measurement requirements are for the radionuclides ^3H , ^{14}C , ^{90}Sr , ^{99}Tc , and ^{129}I . Unfortunately, as if to confirm Murphy's law, these are also the most difficult to measure nondestructively in a sealed package. In fact, no existing techniques appear at all suitable for ^3H and ^{14}C . It may be possible to measure the bremsstrahlung radiation emitted by ^{90}Sr (^{90}Y) in the waste package, but the interferences caused by gamma-ray emitting radioactivities, which are likely to be pres-

ent in many instances, and the variations introduced by the waste form and matrix material create substantial accuracy problems for this technique. The potential of this method will be better defined as soon as current research developments in this field are completed. The ability to measure ^{99}Tc and ^{129}I non-destructively does not now exist, but research is ongoing or proposed for investigating such technologies.

3. As has been implied in the two preceding requirements, a knowledge of the waste form and/or matrix material is extremely important in order to obtain meaningful information from other package assay methods. However, even more important than being able to measure the waste form or matrix material is the need for standard specified acceptable forms/materials. Since both the waste form and the matrix material are important, and since the distinction between them is not necessarily apparent, no attempt to separate them will be made here. Once the acceptable forms/materials have been specified, ordinary measurement techniques, such as densitometry, magnetometry, radiography, etc., will be available for testing compliance.
4. The easiest requirement to measure is the package itself. Again, a standard should specify a number of acceptable waste packages. This requirement is necessary to make all other measurement requirements practical. Obviously, a single piece of survey equipment cannot make quantitative measurements on an infinite variety of package shapes and sizes. Visual inspection should suffice for determination of compliance with this requirement.

5. Measurement of radionuclide concentrations other than those specifically referenced in the preceding paragraphs is necessary from an inventory and control standpoint even if of little importance from a long-term management position. Most radionuclides in this category emit distinctive and copious gamma radiations which can be quantitatively measured with a segmented gamma scanner or other similar high-resolution gamma-ray spectrometric equipment.
6. Of least importance are the total volume and weight of the waste. The volume is important only from the standpoint of record keeping and cost distribution and is most easily determined by utilizing standard packages of known volume. The weight is important only for normalizing the radioactivity concentration, such as for TRU activities, or for determining compliance with waste form/matrix material requirements. Standard scales or load cells will perform adequately for these measurements.

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14. 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 how and to what extent organic complexants affect the mobility of low-level waste radionuclides in soils.

SUMMARY

The status of the work on this project as of July was summarized in a formal report, Effect of Organic Complexants on the Mobility of Low-Level Waste Radionuclides in Soils: Status Report (PNL-3927). The report was issued in September.

Experimental work during the quarter was curtailed by a shortage of funding. The work that was done further illustrates that the approach to equilibrium in the systems involving the EDTA and DTPA complexes of cobalt and nickel is very slow.

RESULTS

Experiments are in progress in which metal ion/complexant stock solutions were diluted after different time periods for long-term exposure to Hanford soil. The concentrations in the stock solutions were made relatively high (1×10^{-5} M metal ion and 2×10^{-5} M complexant) in an effort to ensure that complex formation would be complete before the soil contactings were begun. Such experiments are in progress in the Ni/EDTA, Ni/DTPA, Co/EDTA, and Co/DTPA systems.

Typical results obtained when the 2-day-old stock solutions were diluted and contacted with soil are presented in Figure 14.1. These experiments (each of

which contains 1.0×10^{-8} M complexant and 5.0×10^{-9} M metal ion) provide a varied pattern of results. In the Ni/EDTA case, 100% of the nickel has remained in solution (none has been sorbed by the soil) for 69 days. In the Co/DTPA case, only about 5% of the cobalt remained in solution after 15 days, and slow changes with time have continued. The Ni/DTPA and the Co/EDTA cases show an intermediate behavior; that is, more regular changes occurred with time over the entire 102-day period examined. In each of these four experiments the pH was 8.4 to 8.5 after 104 days of soil contact.

These results provide good examples of the overriding importance of kinetic factors in these systems. Thermodynamically the DTPA complexes of nickel and cobalt are stronger than the EDTA complexes; thus, at equilibrium at a given pH and a given free complexant concentration, a greater fraction of nickel or cobalt should remain in solution in the DTPA cases than in the EDTA cases. Since the reverse behavior has been observed (so far) in these experiments at the same pH and total complexant concentrations (thus presumably at comparable free complexant concentrations), it is concluded that the attainment of equilibrium in some of the systems is extremely slow.

Essentially identical results (fraction of nickel or cobalt in solution versus time)

FIGURE 14.1. Rates of Sorption of Nickel and Cobalt from EDTA and DTPA Solutions

are being obtained at soil-to-solution ratios of 0.010 g/mL as at 0.033 g/mL. This suggests that the slow changes are being caused by the slow dissociation of the complexes rather than by slow soil-sorption reactions.

When experiments similar to those shown in Figure 14.1 were done in the cobalt systems with dilutions of 35-day-old (rather than 2-day-old) stock solutions, the additional aging was found to have little or no effect in the Co/EDTA system but a large effect in the Co/DTPA system. With dilutions of the 35-day-old stock solutions, the fraction of the cobalt remaining in solution was slightly higher in the DTPA case than in the EDTA case, instead of being markedly lower as was the case with the 2-day-old stock solutions (Figure 14.1).

This result demonstrates the existence of another kinetic problem in the Co/DTPA system; that is, slow attainment of an equilibrium complex position in the absence of soil even at the 10^{-5} M concentration level. It is thought that slow attainment of this equilibrium position may involve oxidation of Co(II) to Co(III).

In other cobalt experiments, the 35-day-old stock solutions were diluted in the presence of 10^{-5} M complexant and then contacted with soil (0.033 g soil/mL solution). Some sorption of cobalt was observed, demonstrating that the free complexant concentration that results from this combination of total complexant concentration and soil-to-solution ratio is not high enough to prevent (partial) dissociation of the Co/EDTA and Co/DTPA complexes from occurring.

15. HANDBOOK OF METHODS TO DECREASE THE GENERATION OF LOW-LEVEL WASTE

M. J. Schliebe - Project Manager

The objective of this project is to produce a handbook on minimizing the generation of low-level waste, providing waste generators the technology necessary to assist in the reduction of low-level waste generation.

A working draft of methods to decrease the generation of low-level waste (LLW) was completed and released for review and comment, fulfilling FY 1981 project milestone commitments. The handbook was prepared in support of the National Low-Level Waste Management Program (NLLWMP); Oak Ridge National Laboratory has responsibility for administrating the technology development efforts associated with this program.

SUMMARY OF HANDBOOK

The amount of LLW that requires disposal can be reduced both by decreasing the rate of generation and by reducing the volume of the waste after generation. The handbook, intended to assist generators of LLW in decreasing waste generation, focuses on techniques for decreasing the rate of LLW generation. Reducing the volume of LLW after generation, although important, is generally accepted and relatively well documented, and thus is not specifically addressed.

The handbook is divided into four chapters: Design and Engineering, Operation and Maintenance, Decontamination, and Administrative Methods. Each chapter includes an approach to reduce waste generation and a description of waste-reduction methods. Cost/benefit relationships and

examples are discussed at the end of each chapter.

The approach and methods in each chapter are presented in terms of contamination-control considerations, recycle or reuse potential, materials and equipment selection, and process characteristics. This organization is intended to allow convenient identification of pertinent methods to help reduce waste generation. For example, if a new facility or process is being considered, methods for decreasing waste generation related to the design and engineering should be used. However, a pertinent concern, such as contamination control, may require a review of all four chapters.

The handbook is designed for the following generators of LLW:

- commercial nuclear fuel-cycle facilities related to generation of electricity
- installations engaged in government-related activities that involve nuclear materials
- institutions such as hospitals, universities, and research foundations that use nuclear materials for research
- industrial processors and users of radioactive materials.

Examples and cost/benefit tradeoffs are included to illustrate the application of methods to reduce waste generation.

STUDY RESULTS

The handbook is based on information obtained from generators of radioactive waste. Pertinent data were collected through interviews and site visits. Approximately 80 persons were contacted, representing 35 to 40 organizations. Available literature on the reduction of waste generation was also studied. Few unique developments or technological breakthroughs were identified, and common-sense practices prevail. The increasing costs of transportation and disposal provide growing economic incentives to develop new methods. However, these incentives are not totally effective since waste generators can often pass on the additional waste disposal costs by increasing customer charges such as medical costs or utility rates.

Results of the study indicate that the generation of waste can be controlled and ultimately reduced by following a systematic

plan. Although it would be beneficial to reduce wastes in the areas of the greatest generation, the most significant reduction results from the systematic evaluation of waste-generation factors throughout the facility. Thus the handbook presents methods to decrease waste generation in terms of facility and equipment design, operation and maintenance, decontamination, and administrative controls. Although proper training and the modification of equipment and facilities can contribute, a significant reduction requires the continuous, conscious effort of all involved personnel.

Of the many potential advantages for decreasing the generation of LLW, the major advantages are the prolonged life of existing LLW disposal sites and the reduced overall costs of waste management. These factors provide real incentives for pursuing methods to decrease the generation of LLW.

16. WASTE MANAGEMENT SYSTEM STUDIES

J. V. Robinson - Project Manager

The objectives of this program are to focus technical analysis on the independent assessment of the information base upon which to make decisions to implement waste management systems and technologies of interest and to develop information required to ensure effective communications with the public.

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

Work on this part of the program continued at a high level of effort in order to complete the remaining research tasks. The major work on Task 1 was the completion of the third revision of the social science research plan for nuclear waste management. The report was sent to DOE-RL and DOE Headquarters for comment. A second report, regarding the preservation of information at nuclear waste repositories, remained in the clearance process during the fourth quarter. Final work on this task, which was sent to DOE Headquarters, was completed on Task 2 in July, through an analysis of the public comments on the public participation and the NEPA procedures aspects of Working Draft 4 of the National Plan for Nuclear Waste Management.

Task 3 was completed last quarter with the finalizing, printing and distributing of the final three of four reports regarding public perceptions of risk associated with nuclear waste repositories and other hazardous industrial facilities. The three reports that were distributed include: Public Perceptions of Industrial Risks; The Context of Public Attitudes Toward Radioactive Waste (PNL-3799); Risk Per-

ception, Risk Evaluation, and Human Values, Cognitive Bases of Acceptability of a Radioactive Waste Repository (PNL-3798); and Comparative Analysis of Risk Characteristics of Nuclear Waste Repositories and Other Industrial Facilities (PNL-3796).

Tasks 4 and 8 were combined for the preparation of a summary report of existing survey data on nuclear power and nuclear waste management. Most of the work on this report was completed during the fourth quarter. Existing nuclear power surveys were located, collected, and analyzed. A data tape of one of the surveys was acquired, and relevant data were subjected to additional statistical analysis for inclusion in the report. Finally, a draft report was prepared and sent to PNL/RL for clearance.

Task 5 was the analysis of the waste management hearings process. Two more drafts of the report were completed after initial review. The report was then finalized and sent to PNL/RL for clearance in September.

Task 6 was the analysis of regionalization concepts in the U.S. that could have some bearing on state compacts regarding nuclear waste repositories. The draft report was completed and sent to PNL/RL for clearance.

Task 7 was the analysis of the styles used to make decisions about nuclear waste

management by the different Federal agencies involved with waste management. The report went through two drafts this quarter. Because this task was to result in a letter report, it was sent to PNL for review without clearance forms. The decision regarding how to publish the information will be made the first quarter of the next fiscal year in conjunction with PNL and RL.

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

Work continued on the task to provide support to DOE regarding waste management EISs. The EIS Support members continued their involvement in the Uranium Mill Tailings Remedial Action (UMTRA) environmental impact statement (EIS) processes. Our involvement included providing to DOE a summary of the issues raised at the Durango scoping meeting. This was also provided to UMTRA personnel at Sandia National Laboratory for their use. EIS Support members and R. Scott, DOE-HQ, met on September 29 to discuss project progress, problems and possible solutions. Changes were discussed that should be made for DOE and EIS contractors to get the most benefit from this project.

The two reports prepared for this project were completed. NEPA: A Brief Overview for Program Managers discusses the purpose of NEPA, examines the means of fulfilling this purpose, and describes the role of the courts in enforcing NEPA's requirements. EIS Scoping covers the objectives of scoping, information on scoping policies, issues raised concerning mill tailings environmental impact statements, and PNL's recommendations for improving future scoping meetings.

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

The Radiological Condition Chapter of the Standardized Input for Hanford Environmental Impact Statements, Part II: Site Description (PNL-3509, pt. 2) was completed and reviewed by the Hanford contractors. Final publication of the report has been delayed until FY 1982 to allow more time for Rockwell Hanford Operations to review the report in detail. Comments were received in September from the Basalt Waste Isolation Project. Comments from other Rockwell personnel are expected in early November.

WASTE MANAGEMENT FACT BOOK - O. F. Hill

As a first step in this task, we developed a list of references from which to compile information for the fact book. These were transmitted to DOE-RL and DOE-HQ for comment and approval to proceed.

NUCLIDE TRANSPORT EXPERIMENTS - J. C. Laul

A seminar on the methodological approach used to develop the report Radionuclide Disequilibria Studies for Investigating the Integrity of Potential Nuclear Waste Disposal Sites: Subseabed Studies (PNL-3698) was conducted by J. C. Laul and R. W. Perkins for BWIP Office and DOE-RL in July. This initial technical exchange was viewed as beneficial and was followed by further meetings between BWIP staff and the PNL researchers. Dr. Laul made final revisions to the draft PNL-3698 report, and the report was published in September.

(a) For background information see PNL-3000-9 and -10, prior reports in this series.

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

The draft report Understanding Radioactive Waste (PNL-3570), was cleared for

(a) For background information see PNL-3000-9 and -10, prior reports in this series.

publication. The intent of the report is to acquaint the quasi-lay person about radioactive waste management. Also, a paper by Dr. Murray and J. V. Robinson entitled "Developing Public Information on Radioactive Waste Management" was accepted for presentation at the American Nuclear Society Meeting in San Francisco in December. This paper is based on the task which led to PNL-3570.

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17. 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 as various alternative fuel cycles become viable and to develop assessment methods and identify portions of waste management systems that could benefit by safety design emphasis.

SUMMARY

The safety methods survey report was completed and submitted for publication clearance. A draft report of the spent fuel storage preliminary safety analysis was completed.

SAFETY METHODS SURVEY

The safety methods survey report was completed and submitted for publication clearance. The safety analysis methods examined include expert opinion, maximum credible accident approach, design basis accident approach, hazards indices, preliminary hazards analysis, failure modes and effects analysis, fault trees, event trees, cause-consequence diagrams, GO methodology, Markov modeling, and a general category of consequence analysis models. Previous and ongoing studies on the safety of waste management systems are discussed along with their limitations and potential improvements. The major safety methods and waste management safety-related studies are surveyed. This survey provides information on what safety methods are available, what waste management safety areas have been analyzed, and what are potential areas for future study. The information developed should assist the

process of implementing the use of consistent and cost-effective safety methods throughout the DOE Waste Management Programs.

SPENT FUEL STORAGE PRELIMINARY SAFETY ANALYSIS

A draft report was prepared of a preliminary safety assessment of an independent spent fuel storage facility (ISFSF). This study develops and demonstrates an analytical approach for performing a safety evaluation of a generic ISFSF. Radioactive material inventories and process operations are evaluated on a safety basis to identify potentially critical and hazardous subsystems at the ISFSF. Once these critical subsystems have been identified, sophisticated safety analysis techniques can be applied to determine the overall safety of the facility. Through choice of this analytical approach a cost-effective method to demonstrate the safety of an ISFSF is developed that can be applied to many other nuclear and non-nuclear facilities. The analytical techniques applied to the reference ISFSF include safety indices, checklists, preliminary hazards analysis, failure modes and effects analysis, fault trees, and event trees.

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18. ASSESSMENT OF EFFECTIVENESS OF GEOLOGIC ISOLATION SYSTEMS (AEGIS)

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.*

TECHNICAL PROGRESS

The theoretical description using boundary-element methods for flow in a fractured permeable medium was essentially completed in September. The utility of this fracture-flow theory and associated research analysis code to ONWI is in four areas:

1. to evaluate the equivalent permeable porous medium concepts for describing saturated flow in fractured rock
2. to reduce statistical data on aperture, length, and orientation to tensorial values of equivalent permeability
3. to study transport of contaminants through fractured materials when sorptive properties differ in the fissures and in the surrounding rock
4. to study the effects of thermomechanically induced changes in fracture apertures and lengths upon the equivalent permeability tensor.

The fracture-flow analysis code is a research and evaluation tool that provides understanding of fracture flow and makes possible the generation of equivalent permeabilities representing fractured systems for

subsequent input to dual-porosity models that actually provide hydrologic-flow solutions. Accordingly, this fracture-flow model does not solve actual repository-related flow problems, but rather provides the much-needed equivalent permeability input data used by dual-porosity or similar models in ONWI (Office of Nuclear Waste Isolation) performance assessments.

During the quarter, progress in the development, testing and verification of a research computational package analyzing ground-water flow as a stochastic process was documented. The stochastic analysis of ground-water flow is a promising new methodology that can provide the user community with access not only to the mean-flow solution, but also a measure of the sensitivity of the solution to uncertainties in the aquifer's parameters and boundary conditions.

The FY 1981 analytical effort provided experience in the methodology with single-layer aquifers of horizontal extent while producing a research stochastic analysis capability. Kriging was employed to describe the uncertainty in field data; the

resulting stochastic parameters entered the problem physics through boundary conditions and Darcy's equation. Both the mean and variance of the piezometric head were produced directly by the stochastic analysis. Results showed that statistical dependence of physical parameters and boundary conditions can have a dramatic effect on the stochastic response. This implies that Monte Carlo simulations, where independence is assumed, may not be a satisfactory tool.

Results from 500 simulations using the Geologic Simulation Model for the Columbia Plateau were analyzed, and preparation of the final report was begun. The GSM performed well and produced plausible results; however, verification of the code and input data is necessary before it can be used as a licensing tool. The principal findings from completion and running of the GSM were as follows:

1. The GSM is greater than the sum of its parts. Synergistic interactions between processes did occur, and some processes had results quite different from those predicted by expert consultants. This clearly indicates that some model like the GSM is necessary in the performance assessment of complex geologic/hydrologic systems. Delphi or similar processes are inadequate to the task of forming a gestalt of such a system and testing its limits.
2. The GSM is a unique tool for organizing geologic and hydrologic data, showing which data appear to have a controlling influence on knowledge of the behavior of the system, and showing where data or understanding of phenomena are lacking. This process allows problem areas to be identified early enough in the investigation to allow time for their solution and helps detect errors in data.

3. Documentation of the GSM and its input data provides an organized "audit trail," showing assumptions and decisions made during a continuously-refined analysis spanning several years.
 4. A working GSM allows rapid incorporation of new data or scientific developments into the analyses and facilitates exploration of the implications of both sides of any relevant scientific controversies.
- Further work to calibrate and verify the GSM for the Columbia Plateau is outside the scope of the AEGIS Project.

Geostatistical evaluation of all potentiometric surfaces defined in the scope of work for the data analysis task was completed. Flow analysis for the Paradox Basin was about 75% complete by the end of September and will be completed early in October. Potentiometric surfaces for the Paradox Basin and Gulf Coast Salt Dome areas were well received by the site contractors. Large geostatistical estimation errors for data from the Paradox Basin pointed out the need to consider the possibility that some spring measurements may be for perched water. Geostatistical evaluation of the Permian Basin data showed a need for better screening of data by the site contractor. A revised data set was in preparation at the end of September.

FUTURE ACTIVITIES

The draft Technology Project Plan (TPP) was completed. In FY 1982 the documentation of Dr. Strack's fracture-flow analysis, the salt dome RSIA, the basalt RSIA, results of the basalt Geologic Simulation Model, and the data analysis task will be completed and published. Major new or continuing work in the AEGIS Project will be in the following areas:

1. technical adaptation of waste-package codes in the waste package branch
2. technical applications and technical adaptation of rock-mechanics, fracture-flow, and near-field codes in the repository branch
3. technical applications, technical adaptation, and development of the Geologic Simulation Model, far-field hydrologic and transport, flow analysis under uncertainty, and inverse problem codes in the site branch
4. technical adaptation of a Systems Approximate Simulator for the Columbia Plateau in the system branch.

19. WASTE/ROCK INTERACTIONS TECHNOLOGY PROGRAM (WRIT)

R. J. Serne - Project Manager
D. J. Bradley - Associate Manager

The objectives of the Waste/Rock Interactions Technology (WRIT) Program are:

- 1. identify and quantitatively characterize mechanisms of waste-form radionuclide release and subsequent geochemical interactions with engineered barriers and natural geologic media, e.g., leaching, solubility, and sorption*
- 2. develop and evaluate the effectiveness of models to 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 repository site characterization licensing.*

Within the overall NWTS Program Plan the WRIT Program supports efforts in Waste Package and Site Selection by performing specific tasks on waste-form leaching, waste package performance testing and nuclide retardation evaluations and geochemical modeling, respectively. For both areas, Waste Package and Site Selection, WRIT contributes to performance assessment activities used in licensing pursuits.

TECHNICAL PROGRESS

Surface roughness increases the corrosion rate of PNL 76-68 glass, but the effect is short term. After several days of leaching at 90°C, the corrosion rates of glasses with widely varying surface preparations are identical. Surface roughness is thus a minor consideration in predicting elemental release rates.

PNL 76-68 glass corroded less at high than at low surface area-to-volume ratios, implying that corrosion of the glass in cracks when exposed to water is much less important than has been found previously for simple glasses. Cracking of a waste glass monolith in a repository thus should not adversely affect the durability of the glass.

Some of the pH behavior during static leach tests of waste glass has been ex-

plained in terms of a silicic acid/boric acid buffer. Analysis of LLNL flowing leach test data was begun in order to develop a common static/flowing leach model. At least some of the actinides appear to release according to an apparent solubility.

In an initial series of tests on glass/mineral buffer systems at 250°C, the variable in the experiments was the sample surface area-to-solution volume ratio. The tests indicate that glass dissolution has a dominant influence on solution composition. The need for longer term tests is indicated by the presence of a buffering reaction beginning at 8 wk for the tests of systems containing the smallest amount of glass.

A preliminary series of tests on glass-tuff interactions was begun using welded tuff samples for G tunnel at the Nevada Test Site. Calcium from the tuff appears to react with the waste glass, causing a

decrease in calcium solution concentration. In general, this welded tuff does not inhibit glass degradation.

The validation of uranium in the WATEQ geochemical model is being carried out by comparing model-calculated equilibrium solid phases with laboratory studies of uranium-mineral solubilities. This has led to improvements in the code data base and a firm basis upon which to guide the model validation of uranium for field studies. The addition of plutonium to the code data base has been initiated by compiling available data and references. WRIT-supported development of EQ3/EQ6 at LLNL is continuing. It is aimed at improving the temperature extrapolation code (MCRT) and adding a mineral dissolution kinetics capability to EQ6. Additional modeling work with the basalt ground waters has shown that wairakite is in apparent equilibrium with the solution. This emphasizes the need for adding a wider assemblage of zeolites to the code data base. Two of the samples for the salt dome site characterization study have been radiochemically analyzed, and a disequilibrium has been measured between ^{238}U and ^{234}U . The presence of a disequilibrium is being confirmed by additional measurements.

Tracer runs were made at LLNL with three intact Climax Granite cores containing natural fractures using ^{137}Cs , ^{85}Sr , ^{95m}Tc and ^3H . Retardation of strontium and technetium was slight, but cesium was tightly held by material in the fracture. Fracture-flow studies at Los Alamos National Labora-

tory (LANL) were conducted, and they compared well with the kind of behavior predicted by a fracture-flow, matrix-diffusion, adsorption model. Computer simulation of laboratory columns at PNL yielded an equation that gives a lower limit to water velocities that should be used for column studies. The basalt radionuclide screening test was completed at Rockwell Hanford Operations. Parameters that significantly affect adsorption of americium, radium, selenium and technetium were determined. A Freundlich isotherm was found to describe the relationship between the K_d and concentration of most radionuclides in basalt systems. Uranium adsorption studies at Lawrence Berkeley Laboratory showed that sorption of U(VI) on silica is much greater than expected when carbonate is present in solution.

Research on osmium redox buffers done for the WRIT program by T. W. Newton (LANL) has shown that the Os(2,2'-bipyridine) (II/III) couple can be used to convert plutonium from one oxidation state to another. The effect on the Pu(VI)/Pu(V) couple is dependent on the pH of the solution in the low pH range, while the effect on the Pu(IV)/Pu(III) was independent of the pH, indicating that Pu^{4+} and PuOH^{3+} react at essentially the same rates. Some of the Os(II)(2,2' bipyridine) $_3$ perchlorate and Os(II)(diphenyl-bipyridene) $_3$ was sent to PNL for further testing. Results from plutonium and neptunium experiments were discussed in several publications that are currently under review.

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ONWI

20. HIGH-LEVEL WASTE FORM PREPARATION (HLWFP)

D. H. Siemens - Project Manager

The objective of this program is to characterize, prepare and ship the NWVP-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.

Work during this report period was basically limited to assisting with efforts to amend the license for the NLI 1/2 cask. From information received during discus-

sions with the NRC, it appears that drop tests with cold canister will be required before the high-level waste log is accepted as a shippable waste form.

31275
AP-05-15-15
ONWI

21. DEVELOPMENT OF BACKFILL MATERIALS

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 were:

- radionuclide sorption (K_d) measurements on candidate backfill materials
- continuation of experiments designed to clarify the kinetics of backfill saturation
- irradiation of bentonite samples to check for structural damage
- initiation of dry heating tests to set upper limits on bentonite stability.

TECHNICAL PROGRESS

Measurements of batch distribution coefficients (k_d) for 20 candidate backfill materials in Grande Ronde (basalt) ground water (pH = 9.9) were completed. Representative results for seven elements are presented in Table 21.1.

Bentonite and zeolites will retard all the radionuclides studied except technetium and iodine. If it is determined that enhanced retardation for technetium, iodine, and possibly neptunium is required, addition of a material similar to coconut charcoal should be considered.

Tests to clarify the mechanism of clay hydration have continued through this quarter. The breakthrough test for a 2-cm sodium-bentonite compact has been under way

for 113 days without breakthrough. Extrapolation of breakthrough data from the 0.5-cm and 1-cm test indicates that breakthrough should occur between 80 and 120 days. The 3-cm sodium-bentonite compact (pressed density $\sim 2.2 \text{ g/cm}^3$) was carefully extruded from the permeability cell after being pumped at 15 MPa for 29 days. The first third of the compact was uniformly darkened by the adsorption of water; the rest of the compact was uniformly light in color. The compact was sectioned into three equal parts and the water content of each was determined as follows:

Initial clay	7.5 wt% H_2O
First cm of clay	14.3 wt% H_2O
Second cm of clay	10.8 wt% H_2O
Third cm of clay	10.5 wt% H_2O .

These initial data seem to imply that water is moving into the clay by two distinct mechanisms. One is darcian flow, the other possibly diffusion or vapor transport.

The first set of bentonite samples, heated at 100, 200, and 300°C, at 1 atm, were removed from laboratory ovens after 60 days at temperature. Initial testing of these samples indicates that they readily rehydrate when exposed to moisture at room temperature. These results are significant because they suggest that the backfill will remain functional after the initial thermal pulse, during which it will probably dehydrate.

TABLE 21.1. Representative Batch Distribution (K_d) Values for Backfill Candidates

Material	Distribution Coefficient, K_d							Final pH
	^{85}Sr	^{137}Cs	^{241}Am	^{237}Np	^{125}I	^{233}U	^{99}Tc	
Coconut charcoal	979	8	1.2E5	583	8.3E3	290	1.5E4	8.9
Iron (powder)	320	9	1.2E5	710	2.4	9.2E3	2.2E3	8.7
13-X, [®] powder (faujasite)	6.8E4	1.8E3	35	18	1.2	194	0.8	9.4
4A, [®] powder (Type A)	2.0E4	1.0E3	--	11	0.4	--	0.8	10.1
Calcium bentonite	865	1.1E5	9.2E3	78	1.5E-3	76	0.9	8.2
Sodium bentonite	6.8E3	1.0E3	1.4E4	29	1.4E-3	8	--	8.6
AW-400 [®] (erionite)	2.3E4	6.7E4	92	13	0.8	7	1.2	8.5
AW-500 [®] (chabazite)	2.3E3	7.8E4	1.3E3	18	1.5	17	0.9	8.4
Zeolon-900 [®] (mordenite)	1.5E4	8.3E4	24	12	1.8	35	1.6	8.6

[®] 13X, 4A, AW-400, and AW-500 are registered trademarks of the Linde Molecular Sieves Division of the Union Carbide Company.

[®] Zeolon-900 is a registered trademark of the Norton Chemical Process Products Division of Norton Company.

A series of bentonite samples were irradiated in a ^{60}Co gamma source to total doses up to 10^{10} R. These samples will be characterized to check for structural damage in the clays.

Work during the next quarter will concentrate on sorption K_d s in tuff ground

water, determination of hydraulic conductivities and swelling pressures for a range of densities and temperatures, and mechanisms of clay hydration. The samples for the irradiation and heating tests will be characterized, and autoclave tests will be initiated to determine backfill stability.

22. DEVELOPMENT OF STRUCTURAL ENGINEERED BARRIERS

R. E. Westerman - Project Manager

The objective of this project 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 radioisotope release rates to near-zero values for the time periods of approximately 1000 years.

TECHNICAL PROGRESS

A Westinghouse AESD conceptual waste package design, designated the "self-shielded" design, utilizes a cast-iron overpack 13 in. thick to provide both radiation shielding and corrosion resistance. In response to this design approach, the corrosion screening of cast ferrous materials in simulated Hanford basaltic ground water at 250°C and 150°C is currently under way. Three materials are in test: cast 2-1/4 Cr - 1 Mo steel; cast 1-1/4 Cr - 1/2 Mo steel; and a ductile (nodular) iron. The oxygen level of the water at the autoclave inlet is maintained at 6 to 8 ppm by an inert gas/oxygen sparge. The outlet oxygen is ~1 ppm. (These conditions are considered conservative.) Data from these tests are shown in Table 22.1.

As expected, the 150° exposure resulted in significantly less corrosion than the 250°C exposure, and there is a substantial diminution in corrosion rate with time.

Since all data were obtained on specimens descaled for the first time, the 250°C data show that the corrosion product film and/or the calcium/magnesium-rich deposit left by the ground water is exerting a significant rate-limiting effect.

The 250°C data in the table indicate that <1 in. of cast iron would be consumed in 1000 yr if the rates were linear and invariant over this time period. This is consistent with results obtained in past corrosion tests of various cast irons in simulated Hanford basalt ground water at 250°C (PNL-3484) and suggests that the self-shielded package concept meets the corrosion requirements of a basalt repository.

As the autoclave heating elements for the irradiation-corrosion test facility have finally arrived, the milestone for facility startup, moved incrementally from July to October 1981, now seems fairly well assured.

TABLE 22.1. Corrosion Rate, mil/yr

Material	1-Month Exposure			3-Month Exposure		
	2-1/4 Cr - 1 Mo	1-1/4 Cr - 1/2 Mo	Ductile Iron	2-1/4 Cr - 1 Mo	1-1/4 Cr - 1/2 Mo	Ductile Iron
150°C	0.08	0.13	0.31			
250°C	0.76	0.57	0.97	0.17	0.16	0.31

Simulated oxic Hanford basalt ground water is being irradiated, in the ^{60}Co facility, in the presence of crushed basalt, at 8×10^5 R/hr and 42°C . Monitoring the inlet and outlet water has revealed no change in ground water chemistry.

Fatigue-crack-growth-rate tests of titanium Grade 12 are being conducted at a low cyclic rate, 0.01 Hz, in fluoride-ion-enhanced Hanford ground water. These low-cyclic-rate tests are expected to be the most severe in the current corrosion-fatigue test matrix. The data have not yet been analyzed.

A high-temperature, high-pressure corrosion fatigue system is being designed to test materials for their environmental cracking susceptibility under repository-relevant conditions. The design of the facility and selection of ancillary equipment will be essentially completed within the next reporting period.

A paper, "Development of Engineered Structural Barriers for Nuclear Waste Packages," describing the status of the Structural Engineered Barriers project, has been prepared for presentation at the November 1981 meeting of the Materials Research Society in Boston.

Two milestones were successfully achieved in August: a letter by R. E. Westerman recommending materials for use in basalt waste package conceptual designs was sent to D. T. Moak, ONWI; and a document on the susceptibility of titanium alloys to stress-corrosion cracking in basalt ground water, PNL-3915, by S. G. Pitman, is in clearance/publication.

FUTURE ACTIVITIES

Future activities are planned as follows:

- Fatigue-crack-growth-rate tests of titanium alloys at low cyclic frequencies will continue.
- Screening tests of selected cast ferrous materials in Hanford basalt ground water at 150°C and 250°C will continue.
- Startup of the irradiation/corrosion test facility will be initiated.
- Design and construction will continue on a high-temperature corrosion-fatigue device for determining threshold stress intensities in materials in repository-relevant environments.

23. 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.

TECHNICAL PROGRESS

During this quarter, the repository cost model, RECON, was used to develop sensitivity analyses for the reference case costs reported last quarter. The reference cases assume that fuel rods from 3 PWR or 8 BWR assemblies are disassembled in facilities at the repository and packaged in 0.4-m-dia steel canisters clad with 0.64 cm of tita-

nium. These are emplaced in holes with a carbon steel liner surrounded by a 0.3-m annulus of bentonite.

The effect of packaging intact elements (1 PWR or 2 BWR assemblies per canister) in either plain carbon steel or titanium-clad steel canisters on unit costs is shown in Figure 23.1. The figure indicates that using the very expensive titanium package would result in overall repository costs

FIGURE 23.1. Effect of Packaging Concept on Unit Repository Costs in Various Media

almost double those calculated using simple carbon steel packages. However, if the fuel is disassembled as in the reference case, the reduction in the number of packages and associated emplacement requirements results in cost savings that almost make up for the more expensive packages.

Other variables that have noticeable effects on overall repository costs are waste emplacement criteria, package dimensions, hole barriers, cost-of-money, and repository size. The minimum-cost combinations of waste emplacement criteria result in 5 to 10% cost reductions from the reference case. Increasing the repository size

50% also results in cost reductions of about 10%, while using a 3% uninflated cost-of-money (instead of the reference case value of zero) increases costs by 11 to 12%.

Future activities are planned as follows:

- The results reported here will be published early next quarter.
- Improvements will be made in the RECON model to refine the algorithms and increase the level of detail in some of the input data.
- Instructions and training in the use of the model will be given to ONWI personnel.

24. ANALYSIS OF SPENT FUEL POLICY IMPLEMENTATION

R. L. Engel - 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.

A draft of the Spent Fuel Management Fee Methodology and User's Manual was prepared during this period and is currently undergoing revision. This report includes a detailed discussion of the fee methodology,

detailed instructions for preparing input to the model, and several benchmark fee alternative cases. The final draft will be issued during October.

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25. 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.

SUMMARY

Four formal reports and two papers were prepared during this quarterly period. Also, a publication in German dealing with a spent fuel storage subject was translated into English.

The Zircaloy-clad Shippingport fuel was shipped from the Battelle-Columbus hot cell to the Receiving Basin for Offsite Fuel (RBOF) at the Savannah River Plant. Examination of stainless-steel-clad Connecticut Yankee Assembly S004 has been completed. Rods from S004 have been traded with Assemblies H07 and G11 to provide a range of burnups and storage times in S004, which will continue to serve as a surveillance assembly.

Examination was completed on several specimens from spent fuel components, including stainless steel and aluminum with pool residences of 15 and 16 years, respectively.

PROGRAM MANAGEMENT

The following publications were prepared during the quarter:

1. A. B. Johnson, Jr., "Technical Bases for Interim Storage of Spent Nuclear Fuel," PNL-SA-9537, presented at the American

Nuclear Society topical meeting Technical Bases for Nuclear Fuel Cycle Policy, Newport, Rhode Island, September 20-23, 1981; published in Proceedings.

2. A. B. Johnson, Jr., et al., Annual Report - FY 1980 - Spent Fuel and Fuel Pool Component Integrity, PNL-3868, September 1981.
3. E. R. Bradey et al., Examination of Zircaloy-Clad Spent Fuel After Extended Pool Storage, PNL-3921, September 1981.
4. Russell H. Jones et al., "An Evaluation of Stress Corrosion Cracking of Sensitized 304 SS in Low-Temperature Borated Water," presented at the Second International Conference on Environmental Degradation of Engineering Materials, Virginia Polytech Institute, September 21-23, 1981, published in Proceedings.
5. F. M. Kustas et al., Investigation of the Condition of Spent Fuel Pool Components, PNL-3513, August 1981.
6. D. C. Langstaff et al., Examination of a Stainless Steel Clad Fuel Assembly - Significance to Spent Fuel Storage in PWR Pools, PNL-3828, October 1981.

An article published in German was translated and published: N. Eickelpasch et al., Radioactivity Releases from Fuel Elements Stored in the KRB-A Storage Pool Over

Prolonged Periods of Time, PNL-TR-414, June 25, 1981.

INTERNATIONAL

The draft of the International Survey of Spent Fuel Storage Experience is proceeding through IAEA (Vienna) publication channels. No publication date has been indicated.

SPENT FUEL EXAMINATION

Shippingport Fuel Examination

A letter from L. C. Sjostrom of SRO indicated that the Zircaloy-clad Shippingport fuel would be accepted at the Receiving Basin for Offsite Fuel (RBOF) at the Savannah River Plant. The Shippingport fuel (124 fuel rods from two bundles) was shipped to the RBOF facility in September.

The formal report (PNL-3921) that describes the results of the hot-cell examination of the Shippingport fuel was completed and approved and is being prepared for distribution.

Connecticut Yankee Fuel Examination

Connecticut Yankee fuel assembly S004 was reconstituted in September 1981. Mutual agreement was reached by PNL and Northeast Utilities Service Company (NUSCO) on the interchange of fuel rods from Connecticut Yankee fuel assemblies S004, H07, and G11. PNL received five rods from NUSCO: one (595A01) from G11 and four rods (010E03, 1007E01, 065E11, and 075E05) from H07. NUSCO received five rods (AEK, AEI, ADU, ALF, and AJ0) from S004. In reconstituting S004, the one rod from G11, the four rods from H07 and the three rods (AHL, AGR, and AAP) from S004 that were nonde-

structively examined were all reinserted into peripheral positions in S004.

The draft of the formal report (PNL-3828) that describes the results of the hot-cell examination of S004 (DOE Control Milestone 5) was cleared for publication in September. Copies of the draft were sent to the technical contact as the Savannah River Plant and to the Northeast Utilities Service Company, British Nuclear Fuels Limited, Combustion Engineering, Babcock and Wilcox, Battelle Columbus Laboratories, and Electric Power Research Institute for review and comment. A number of comments have been received; however, approval from the Savannah River review is pending.

SPENT FUEL COMPONENT EXAMINATIONS

Examinations have been completed on spent fuel pool components, outlined in the most recent quarterly progress report (Chikalla and Powell 1981). In addition, an aluminum spacer was examined that had been in the deionized water RBOF pool ~16 yr. The spacer was adjacent to an irradiated Zircaloy-clad fuel assembly. The oxide films were too thin to resolve by optical metallography on stainless steel specimens with up to 15 yr in deionized storage pool water and 6-2/3 yr in borated storage pool water. Maximum oxide thickness on an aluminum spacer was ~20 μm after 16 yr in deionized water, under irradiation from an adjacent fuel assembly.

REFERENCE

- Chikalla, T. D. and J. A. Powell. 1981. Nuclear Waste Management Quarterly Progress Report April Through June 1981. PNL-3000-10, Pacific Northwest Laboratory, Richland, Washington.

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26. 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.

Analyses of the hypothesized accidents have been completed. The postulated accidents involve the separation of a 3 x 3 array of depleted fuel from a borated rack

and the compaction of a nonborated fuel rack. A draft report was completed that describes the analyses performed.

27. ASPHALT EMULSION SEALING OF URANIUM MILL 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

The 1981 joint field test conducted at the Grand Junction tailings pile was completed. Technologies to reduce radon released from uranium mill tailings were tested in plots that covered about 1.2 ha (3 acres). The technologies tested included: 1) earthen covers; 2) multilayer earthen covers; and 3) asphalt emulsion radon barrier system. In addition to the larger test plots, 1.8-m-dia-column tests are being carried out with cover systems similar to those in the larger field test plots. This is to allow a direct comparison of the two types of test procedures as well as provide detailed information on radon transport.

Before the field test, the site was characterized. Measurements included density, moisture, radium, emanation, radon flux and chemical composition.

A radon barrier was applied consisting of an asphalt emulsion seal 8 cm thick and a 0.5-m protective overburden. A cold-mix paver was used to apply the cationic asphalt emulsion/sand mixture. After the seal cured for ~6 wk, it was compacted to form the final seal. Preliminary results indicate a radon flux reduction of greater than 99.9% to near background levels.

Four earthen cover systems were applied to a depth of 3 m using Mancos shale, bentonite clay, and adobe clay in various configurations. No results are yet available on the effectiveness of these earthen covers.

The column cover systems were applied and are being instrumented for continuous monitoring. A data logger will accumulate data on moisture, temperature, and radon concentration.

In addition to the field studies, stability testing in the laboratory continued, including aqueous leaching and oxidation studies. Structural stability tests were completed on samples of the FY 1980 field test admix seal, including triaxial shear tests and modulus of rupture tests at three different temperatures.

LABORATORY STUDIES

Asphalt Emulsion Seal Chemical Stability - D. A. Nelson

The samples of leachate from the aqueous extraction of asphalt (6.5 months exposure) were examined by capillary gas chromatography. Samples were quite complex, each containing more than 30 major components. The patterns appear somewhat typical of those

in asphalt itself. Since the material has shown such a complex nature, gel permeation chromatography will be used to gain information concerning the molecular weights of the components.

A quantitative infrared procedure was applied to the asphalt emulsion and a known oxidized pavement asphalt. This differential technique determined the oxidation products (ketones, dicarboxylic anhydrides, carboxylic acids and 2-quinolones) present in small samples of asphalt. The results are presented in Table 27.1.

Laser-Raman spectroscopy was applied to the air components present over asphalt emulsion samples in sealed glass cylinders. These results are shown in Table 27.2.

These two analytical procedures have been undertaken to determine the effects of oxidation on the aging of asphalt emulsion. The differential infrared procedure is a direct measurement of oxidation and must be

performed at specific intervals over an extended time. From it the rate of asphalt oxidation can be determined. The results in Table 27.1 indicate that little oxidation occurred from the time of manufacture until the barrier was applied. This now serves as the baseline for our future analyses. The 1946 sample indicates the extent of oxidation that can be expected under harsh conditions for 35 years.

The results from the laser-Raman procedure (Table 27.2) indicate that oxygen uptake does occur in asphalt emulsion. The oxygen absorption is more rapid with the newer sample than with the asphalt applied July 1980. This appears consistent with previous research conducted by Shell-Holland on road asphalt, i.e., a rapid initial uptake followed by a long-term decrease in absorption. That work also correlated increased viscosity in asphalt with oxygen absorption. Since both effects are related to oxidation

TABLE 27.1. Differential Infrared Spectroscopy of Asphalt

Asphalt Type	Oxidation Products, moles L ⁻¹			
	Ketones	Anhydrides	Free Acids	2-Quinolone
Emulsion of 7/9/81 ^(a)	0	<0.004	<0.02	0
Camp Hanford 1946 ^(b)	1.2	0.12	0.11	0

(a) Sample recovered 1 day after barrier application and analyzed 14 days later.

(b) Sample recovered from 4% asphalt aggregate sidewalk that had been laid in 1946 at Hanford, Washington.

TABLE 27.2. Laser-Raman Spectroscopy of Air Components over Asphalt

Asphalt Type	No. Days in Sealed Cell	Ratio of $\frac{O_2}{N_2}$	O_2 Absorption
			$\frac{cm^3 (O_2)}{g \text{ asphalt}}$
Emulsion of 7/9/81	19	0.270	0.77
	37	0.249	1.62
Emulsion of 7/80 ^(a)	21	0.256	0.34
	39	0.208	0.75

(a) Sample collected from Grand Junction Site on 4/81.

and its products, the correlation of oxygen absorption with oxidation products should allow an indirect measurement of viscosity. Several viscosity measurements will be made to confirm whether the correlations are valid. If indeed the correlations can be achieved, the laser-Raman procedure will provide a rapid and simple measurement of asphalt aging.

Structural Stability - C. F. Voss

Material characterization tests were conducted by the New Mexico Research Institute in Albuquerque using the 1980 asphalt emulsion admix seal material. Specimens were taken from the 1980 test seal at the Grand Junction Site in April 1981. Triaxial shear tests and modulus of rupture tests were performed at three temperatures (24.4, 50, and 75°F). Results show significant property changes with variations in temperature. The material behaves in a visco-elastic manner as shown by the triaxial shear test results in Figures 27.1 - 27.3. The shear strength increases significantly with lower temperatures; it ranges from 1 to 4 psi at 75°F up to 245 to 170 psi at 25°F. Changes in the shear strength by two orders of magnitude were observed over a 50°F temperature span and can be approximated by the exponential relationship:

$$\text{Shear strength (psi)} = A e^{B(\text{temperature})}. \quad (1)$$

Values for A and B vary with the confining pressure present (Figure 27.4).

The modulus of rupture was determined from the beam tests according to the American Society for Testing and Materials "Third Point Loading" Test Method. Regression analysis of the results gave the

following relationship for the modulus of rupture R:

$$R(\text{psi}) = -4.98 T (^{\circ}\text{F}) + 373.6. \quad (2)$$

One additional series of laboratory tests is necessary before an accurate stability analysis is possible. Beam tests using the asphalt-admix seal are needed that simulate actual loading conditions (uniform) at predicted settlement rates. Strain rates and relative strain over the beam span will be monitored using a strain circle technique. Once this information is obtained over the temperature range, the New Mexico Engineering Research Institute data can be incorporated to predict failure. The strain circle data will provide estimates of the relative strain taking place at various locations along the seal during settlement (Figure 27.5). The stresses at these points will be estimated using the stress-strain relationships determined at Albuquerque. This information can be compared with estimates of the modulus of rupture to locate possible failures. Long-term beam tests could monitor post-failure healing of the seal.

FIELD TEST - J. N. Hartley

The 1981 joint field test was completed at the Grand Junction, Colorado, tailings pile. The objective of this field test was to investigate the relative effectiveness of the most promising radon barrier systems, including 1) earthen covers, 2) multilayer covers, and 3) asphalt emulsion radon barriers. The specific activities carried out were 1) site characterization, 2) site preparation, 3) cover/seal application, 4) reclamation, and 5) site monitoring. The data obtained from the field test will be used

SPECIMEN NO.	9	10	11	12
CONFINING PRESSURE, psi	0	10	20	30
AVERAGE TEST TEMPERATURE, °F	21.4	22.1	26.2	28.0

FIGURE 27.1. Triaxial Shear Test Results at 24.4°F

SPECIMEN NO.	5	6	7	8
CONFINING PRESSURE, psi	0	10	20	30
AVERAGE TEST TEMPERATURE, °F	49.4	50.0	48.8	49.0

FIGURE 27.2. Triaxial Shear Test Results at 50°F

SPECIMEN NO.	1	2	3	4
CONFINING PRESSURE, psi	0	10	20	30
AVERAGE TEST TEMPERATURE, °F	74.3	75.5	71.7	74.6

FIGURE 27.3. Triaxial Shear Test Results at 75°F

FIGURE 27.4. Shear Strength Versus Temperature at Various Confining Pressures

FIGURE 27.5. Strain Across Beam During Bending

to evaluate the effectiveness of the systems and develop engineering specifications for input to an architectural engineering firm.

Site Characterization - M. R. Elmore and H. D. Freeman

In April 1981, prior to the field test, an area of 1.2 ha (3 acres) in the south-east corner of the Grand Junction tailings pile was selected for the 1981 field test site. Core samples were taken using Shelby tubes at 15 locations as shown in Figure 27.6, to a depth of 2.7 m. These samples were used to characterize the test site. Elemental analyses were performed using x-ray fluorescence, and the results are shown in Tables 27.3 and 27.4.

Table 27.5 summarizes measurements of radium

content, emanation coefficients, and moisture for each hole. Rogers and Associates Engineering Corporation, Salt Lake City, Utah, performed these analyses. Densities of the tailings, determined from the core samples, are listed in Table 27.6.

Radon fluxes were also determined for the overall field test area as shown in Figure 27.7. The fluxes ranged from 7.8 to $1198 \text{ pCi m}^{-2}\text{sec}^{-1}$, with an average flux of $400 \text{ pCi m}^{-2}\text{sec}^{-1}$ and standard deviation of 276.

Application of Asphalt Emulsion Radon Barrier at the Grand Junction Test Site - E. G. Baker

Based on the 1980 Grand Junction field test and a review of asphalt emulsion application methods, a cold-mix paver (CMP) was selected as the most promising technique for applying an asphalt emulsion radon seal. The CMP was field-tested in July 1981 at Grand Junction to obtain sufficient operating data to evaluate the technical and economic feasibility of the stabilization/sealing procedure. Some items investigated in the 1981 field test were:

FIGURE 27.6. Core Hole Locations on 1981 Field Test Site at Grand Junction, Colorado

TABLE 27.3. Elemental Composition of Surface Tailings Samples from Grand Junction Site.
Results shown are for the top 1 ft of tailings.

Element	Conc.	Core Hole Number												
		1	2	3	4	5	6	7	8	9	10	12	14	15
Al	%	4.3	5.51	--	5.9	5.3	7.6	4.4	5.29	3.16	6.5	2.18	5.0	--
As	ppm	376	422	165	412	466	626	420	414	193	412	161	297	165
Br	ppm	2.51	--	--	--	--	2.30	--	--	--	--	--	2.04	--
Ca	%	4.26	4.32	2.27	4.74	4.80	4.66	4.53	4.23	2.60	4.63	2.23	4.10	1.36
Cl	%	--	0.123	--	--	0.107	--	0.122	0.152	--	0.203	--	0.135	--
Cr	ppm	105	106	105	100	96	134	98	76	132	119	79	97	71
Cu	ppm	38.6	37.5	19.1	42.9	41.9	64.7	39.6	40.5	22.0	39.8	20.9	43.2	17.4
Fe	%	2.30	2.33	1.02	2.80	2.76	2.85	2.51	2.24	1.24	2.59	0.941	2.31	0.884
Ga	ppm	13.7	12.6	4.6	16.6	16.9	15.9	15.0	14.0	6.82	14.3	5.39	11.6	5.5
K	%	0.936	0.781	0.741	0.983	0.863	0.869	0.894	0.809	0.722	0.840	0.793	0.991	0.424
Mn	ppm	33.6	44.8	26.6	60	58	29	67	48.8	26.5	42	36.6	70	24.9
Mo	ppm	16.8	15.7	19.5	18.7	16.9	18.8	17.8	17.0	21.5	16.9	18.5	17.7	21.6
Nb	ppm	8.12	5.77	3.01	7.80	8.60	7.43	5.94	6.16	3.36	6.49	3.35	5.93	3.14
Ni	ppm	201	324	133	200	387	429	284	268	231	260	155	226	307
Pb	ppm	148.3	194	89.6	155	198	322	182	186	113	172	89.1	111	104
Rb	ppm	13.25	13.6	13.8	12.4	14.0	15.3	13.5	14.3	14.8	13.9	14.0	18.9	15.4
S	%	3.16	3.19	1.90	2.92	3.56	3.07	3.13	3.00	2.29	3.23	2.15	2.78	1.59
Se	ppm	4.08	8.44	41.9	2.77	2.43	--	8.43	4.85	44.5	11.5	46.4	16.9	64.2
Si	%	26.2	26.7	29.2	24.9	24.8	27.6	26.5	25.7	25.6	26.9	28.7	26.8	20.6
Sr	ppm	265	290	104	317	335	327	289	310	122	269	98.1	247	91.7
Ti	%	0.241	0.246	0.142	0.264	0.271	0.291	0.251	0.239	0.165	0.251	0.178	0.252	0.104
U	ppm	247	161	90.4	369	227	146	252	2114	141	189	134	231	96.7
V	ppm	1920	1950	2170	1840	1990	3300	1930	1820	2080	2030	2150	1860	1290
Y	ppm	19.2	20.0	4.99	24.6	28.2	340	27.0	25.4	8.97	14.5	6.09	21.6	5.37
Zn	ppm	96.4	117.5	95.6	102	121	167	107	105	91.0	125	66.2	109	81.0
Zr	ppm	161	143	139	162	159	156	169	168	126	163	130	158	187

TABLE 27.4. Elemental Compositions from Three Core Holes at Grand Junction Site.
Results show composition of tailings from top to bottom of the core hole.

Element	Conc.	Core Hole Number and Depth, ft								
		Hole No. 2			Hole No. 8			Hole No. 14		
		0-3	3-6	6-9	0-3	3-6	6-9	0-3	3-6	6-9
Al	%	6.04	4.73	3.33	4.14	4.76	4.0	3.10	2.77	6.00
As	ppm	463	420	297	315	878	315	206	201	515
Ca	%	4.81	5.05	3.23	3.33	3.77	3.06	2.66	2.37	4.61
Cr	ppm	107	128	105	89.3	111	132	102	142	140
Cu	ppm	38.4	44.9	27.9	37.3	93.3	24.1	30.0	24.1	41.4
Fe	%	2.44	2.86	1.79	1.70	2.73	1.68	1.43	1.29	3.91
Ga	ppm	14.8	16.7	9.90	9.66	13.5	9.81	7.54	7.71	17.8
K	%	0.823	0.884	0.960	0.833	0.866	0.717	0.889	0.899	0.737
Mn	ppm	43.9	64.0	48.1	34.7	73.7	40.6	50.3	39.2	65.0
Mo	ppm	14.8	19.6	15.2	18.9	12.1	18.0	17.8	18.3	11.1
Nb	ppm	6.57	6.88	5.60	4.95	8.17	5.03	4.53	4.15	8.58
Ni	ppm	388	210	51.9	247	226	193	219	387	534
Pb	ppm	213	175	116	145	302	104	97.4	105	174
Rb	ppm	15.7	15.2	16.1	14.7	15.7	12.2	16.8	18.2	7.34
S	%	3.68	3.71	2.65	2.55	2.91	2.33	2.31	2.17	2.42
Se	ppm	4.02		20.5	26.8	5.00	31.4	36.0	38.9	6.78
Si	%	25.5	25.5	27.3	27.2	27.3	28.2	29.2	29.4	23.7
Sr	ppm	291	207	196	208	286	167	143	132	364
Ti	%	0.254	0.270	0.216	0.206	0.244	0.183	0.186	0.176	0.287
U	ppm	146	218	226	177	181	108	134	109	173
V	ppm	1980	1820	1593	2247	2091	1869	2193	2337	1855
Y	ppm	18.3	14.4	16.0	15.3	17.1	6.34	10.8	10.2	23.5
Zn	ppm	126	97.0	111	91.1	133	80.0	94.0	95.3	111
Zr	ppm	167	176	181	153	191	141	160	156	129

TABLE 27.5. Radium Activity, Emanation Coefficients and Moisture Content of Core Samples from the Grand Junction Field Test Site(a)

Hole Number	Sample Depth, ft	Radium Activity, pCi/g dry tails	Emanation Coefficient	Moisture Content, g water/g dry tails
1	0-3	1522	0.38	0.209
	3-6	1658	0.44	0.257
	6-9	760	0.37	0.160
2	0-3	1579	0.36	0.252
	3-6	1915	0.43	0.258
	6-9	1236	0.37	0.205
3	0-3	1862	0.41	0.286
	3-6	1780	0.39	0.279
	6-9	1074	0.39	0.093
4	0-3	1507	0.38	0.211
	3-6	1520	0.41	0.191
	6-9	564	0.43	0.080
5	0-3	1424	0.38	0.271
	3-6	1709	0.41	0.347
	6-9	599	0.33	0.081
6	0-3	1799	0.38	0.317
	3-6	1869	0.39	0.265
	6-9	1446	0.36	0.187
7	0-3	1297	0.38	0.185
	3-6	874	0.37	0.099
	6-9	456	0.32	0.057
8	0-3	1192	0.38	0.161
	3-6	1278	0.40	0.206
	6-9	748	0.36	0.156
9	0-3	1233	0.37	0.190
	3-6	1526	0.42	0.241
	6-9	746	0.37	0.102
10	0-3	949	0.36	0.112
	3-6	450	0.38	0.055
	6-9	490	0.36	0.067
11	0-3	872	0.38	0.106
	3-6	805	0.43	0.104
	6-9	1243	0.46	0.353
12	0-3	513	0.35	0.057
	3-6	1105	0.38	0.166
	3-9	637	0.38	0.077
13	0-3	337	0.31	0.038
	3-6	454	0.32	0.066
	6-9	439	0.33	0.158
14	0-3	825	0.34	0.103
	3-6	821	0.37	0.106
	6-9	1426	0.42	0.359
15	0-3	489	0.33	0.054
	3-6	498	0.36	0.065
	6-9	500	0.36	0.064

(a) Analysis performed by Rogers and Associates Engineering Corporation, Salt Lake City, Utah.

TABLE 27.6. Density of Grand Junction Tailings Taken from Sample Locations Shown in Figure 27.6

Hole Number	ft	lb/ft ³
1	0-3	80.0
	3-6	73.3
	6-9	78.7
2	0-3	72.5
	3-6	61.4
	6-9	69.5
3	0-3	67.0
	3-6	67.0
	6-9	6-9
4	0-3	78.7
	3-6	64.7
	6-9	79.7
5	0-3	66.5
	3-6	75.1
	6-9	78.8
6	0-3	76.6
	3-6	67.2
	6-9	67.8
7	0-3	75.8
	3-6	81.0
	6-9	84.9
8	0-3	81.2
	3-6	67.6
	6-9	85.2
9	0-3	77.2
	3-6	68.7
	6-9	71.8
10	0-3	83.7
	3-6	85.5
	6-9	83.0
12	0-3	92.8
	3-6	71.0
	6-9	82.6
13	0-3	73.3
	3-6	86.4
	6-9	72.3
14	0-3	76.3
	3-6	90.1
	6-9	94.7
15	0-3	85.0
	3-6	86.4
	6-9	84.3

FIGURE 27.7. Radon Flux Values, $\text{pCi m}^{-2}\text{sec}^{-1}$, for 1981 Joint Field Test Area in Grand Junction, Colorado

1. site preparation requirements
2. quantity of asphalt emulsion required
3. effect of modifications to the CMP designed to allow faster, smoother operation.

Other items that will be investigated as part of the continuing evaluation of the seal are:

1. reduction in radon flux
2. seal integrity (compaction requirements, root penetration, weathering)
3. overburden requirements (including herbicides and revegetation).

Description of Cold-Mix Paver

A cold-mix paver (CMP), as illustrated in Figure 27.8, was used to apply the admix seal. Dump trucks load aggregate into the hopper on the paver. The aggregate is moved to the pugmill on a constant speed conveyor. The aggregate flow rate is controlled by adjusting the gate height on the opening between the hopper and the conveyor. Asphalt is transferred from trucks to a

tank on the paver (capacity ~2700 gal). The asphalt emulsion is pumped to the pugmill, where it is mixed with the aggregate. Admix from the pugmill is distributed on the surface to be paved by two augers and a screed.

The cold-mix paver was modified prior to the application to allow smoother operation with the high residual content of asphalt in the admix. We reduced the aggregate feed belt speed and increased the asphalt emulsion pumping capacity.

Site Preparation

A plot, 150 ft (45.7 m) x 250 ft (76.2 m), at the Grand Junction tailings pile was selected for the field test. To prepare the site for seal application, the top 4 to 10 in. (10 to 25 cm) of cover material were removed and the site was surveyed and contoured. About 4 in. (10 cm) of 3/4-in. gravel road base was laid down to provide a stable base for seal application. The site was then watered and compacted with a vibratory roller.

FIGURE 27.8. Cold-Mix Paver

Asphalt Emulsion Properties and Selected Operating Conditions

The asphalt used for the Grand Junction field test was a cationic medium-set (CMS-2) asphalt emulsion containing 63 wt% asphalt. The emulsion had a zeta potential of +76 to +80 mV and a specific gravity of 1.01 at 60°F. It was mixed in the CMP with concrete sand to produce an admix containing 22 wt% asphalt (22 lb asphalt/100 lb dry aggregate).

Approximately 5100 lb/min (2 to 3 metric tons/min) of concrete sand and 200 gpm (760 L/min) of emulsion were mixed in the CMP to produce the desired admix. At these rates $\sim 230 \text{ ft}^2$ of the admix seal was applied per minute.

Seal Application

The main test plot was paved over a 2-day period, July 8 and 9. Ten passes 15-ft (4.6 m) wide by 250 ft (76 m) long were required to cover the test plot. We used just over 32,000 gal of asphalt emulsion, or 0.85 gal/ft^2 (35 L/m^2). Based on our experience during the field test and assuming no delays other than those required to refill the CMP and turn around, about 1.2 acres could be paved in an 8-hr day.

In general, operation of the cold-mix paver went smoothly, with only minor mechanical difficulties. However, there were some problems with seal quality, including:

- contamination of the aggregate with clay
- severe sloughing of the admix, resulting in a thin seal of the seams
- variations in the asphalt content of the seal resulting from variations in the paver speed.

Recommendations are being developed to correct these problems.

On the third day, we paved a test area $\sim 50 \text{ ft}$ (15.2 m) by 150 ft (45.7 m) that had a slope of about 7%. No unusual problems were encountered paving up the slope. Sloughing was reduced and the seam quality appeared to be better than on the main test plot.

Approximately 6 wk after application, the seal was compacted with a vibratory roller. Compacted depth and density of the seal will be measured at a later date.

Post-Seal Measurements

After the seal was applied, 16 samples were taken from various locations on the test plot to determine the asphalt content, thickness, and moisture content of the seal. The results of these analyses are shown in Table 27.7.

Radon flux measurements were also made to get a preliminary idea of the seal effectiveness. The radon fluxes ranged from 0.1 to $3.5 \text{ pCi/m}^2 \text{ sec}$, with an average of $0.7 \text{ pCi/m}^2 \text{ sec}$. This shows that no major leaks occurred in the areas of the seal that were measured. A complete set of radon flux measurements will be taken in late October 1981.

Preliminary Economic Comparison

Based on the asphalt emulsion requirements defined by the 1981 field test, we have developed a preliminary cost estimate for a full-scale seal application. The cost is broken down in Table 27.8. Asphalt emulsion usage during the field test was 9.2 gal/m^2 . Although this breakdown is preliminary, it shows the economic incentives favor the asphalt emulsion.

TABLE 27.7. Properties of the Asphalt Emulsion Admix Radon Barrier Seal

	Average	Range
Asphalt content, lb/100 lb dry aggregate	22	17-27
Thickness as applied, in.	4.6	2-7
cm	11.7	5-18
Water content, wt% initial	10	
24 hr	4	
2 wk	<1	

TABLE 27.8. Cost of Asphalt Emulsion Radon Barrier, \$/m²

Tailings stabilization	2.0
Cold-mix paver operation	0.3
Asphalt emulsion, \$1.25/gal, \$0.33/L	11.5
Aggregate	1.0
Cover material, 0.6 m	2.1
Miscellaneous	0.5
Total	17.4

To compare asphalt emulsion covers with earthen covers, we estimated the cost of applying earthen covers at two potential sites for the Durango pile. The cost for the earthen cover ranged from \$10 to \$26/m², depending on the site and the amount of earthen cover required. The cost of an asphalt emulsion cover is equal to the cost of applying 4 to 5 m of earthen cover. Costs for removing, transporting, and placing the tailings are not included in these costs but should be similar for both asphalt emulsion and earthen covers. Additional estimates will be made for other tailings piles.

Earthen Covers - J. N. Hartley and M. R. Elmore

The objective of the earthen cover portion of the joint field test is to investigate the effectiveness of earthen cover systems as radon diffusion barriers. The earthen materials were to be native to

the Grand Junction area in order to be cost-effective. The four earthen cover systems are illustrated in Figure 27.9.

Before the field test, samples of the materials to be used for the earthen covers were collected and evaluated. Table 27.9 summarizes the standard material characteristics for the three selected cover materials. The relationship between dry densities and moisture contents is shown. In addition, Figures 27.10 and 27.11 show the water retention characteristic curves for adobe clay and Mancos shale. Comparing these data with those on density-moisture relationships in Table 27.9 indicates that, with time, drainage will take place from these materials. Therefore, early radon flux measurements from compacted materials will be erroneous when compared with long-term equilibrium flux values. It may take several years before drainage will take place and equilibrium water contents are developed in these compacted materials.

FIGURE 27.9. Profile for Earthen Cover Test Plot

TABLE 27.9. Earthen Cover Material Characteristics(a)

Material	Maximum Dry Density, ^(b) g/cm ³	Optimum Moisture, ^(b) wt%	Specific Gravity	Sieve Analysis, % Passing 200 mesh
Adobe clay	1.87	13.9	2.63	85.0
Mancos shale	1.89	12.8	--	18.7
Bentonite clay	1.58	22.3	2.41	87.6

(a) Data from field samples taken during cover application.

(b) This proctor was completed in accordance with ASTM D-698, Moisture-Density Relationship of Soil.

*ASTM D-698 STANDARD PROCTOR

FIGURE 27.10. Water Retention Characteristics for Adobe Clay at Maximum and 95% of Maximum Proctor Densities

*ASTM D-698 STANDARD PROCTOR

FIGURE 27.11. Water Retention Characteristics for Mancos Shale at Maximum and 95% of Maximum Proctor Densities

Effective diffusion coefficients were also determined for materials to be used for the earthen covers (Table 27.10). The bentonite clay had the lowest D_e ($0.011 \text{ cm}^2/\text{sec}$) at an ambient moisture content of 11 wt%.

The earthen covers were applied to the tailings in the following steps:

1. dumping the overburden and spreading it out with a tractor, forming a 15- to 20-cm (6 to 8 in.) lift
2. watering the cover, using a distribution water truck
3. compacting the lift with a vibratory sheep's foot compactor
4. measuring the density and water content of the compacted lift, using a nuclear density-moisture meter.

Table 27.11 summarizes the characteristics of the 1.2 m (4 ft) of compacted

earthen covers as applied. Based on the proctors, we were able to achieve only 80 to 93% of proctor using 10 to 15 cm lifts and 6 to 8 passes of compaction and close to optimum moisture. To improve upon this compaction would significantly increase the cost because smaller lifts would have to be applied and more compaction would be needed.

The top 1.8 m (6 ft) of the earthen cover systems were applied by dumping and spreading the overburden in 15- to 20-cm lifts. The only compaction was provided by the 30-yd³ trucks driving over the lifts, which had ambient moistures of 4 to 8 wt%. However, relatively good compaction was achieved with these trucks.

To verify our density and moisture measurements, Table 27.12 compares density and water content measurements as determined by

TABLE 27.10. Earthen Cover Materials Effective Diffusion Coefficients

Material	Dry Density, g/cm^3	Moisture ^(a) Content, wt%	Effective Diffusion Coefficient, D_e , ^(b) cm^2/sec
Adobe clay	1.51	5.3	$0.021 \pm 5\%$
Bentonite clay	1.68	11.0	$0.011 \pm 5\%$
Mancos shale	1.51	3.3	$0.014 \pm 5\%$

(a) Moisture content of as-collected materials.

(b) Diffusion coefficients were determined by Rogers and Associates Engineering Corp., Salt Lake City, Utah.

TABLE 27.11. Characteristics of Compacted Earthen Covers

Material	Maximum Dry Density, ^(b) g/cm^3	Average Dry Density, ^(a) g/cm^3	Optimum Moisture, ^(b) wt%	Moisture, wt%	Average % Maximum Proctor ^(a)
Adobe clay	1.87	1.50	13.9	11.9	80
Bentonite clay	1.58	1.38	22.3	20.2	87
Mancos shale	1.89	1.75	12.8	15.8	93

(a) These values were obtained with a nuclear density meter during cover application.

(b) These proctors were completed in accordance with ASTM D-698.

TABLE 27.12. Comparison of Density and Water Content Determinations on Mancos Shale, Adobe, and Tailings from Grand Junction Test Site

Material	Method	Water Content, % dry wt	Dry Density, g/cm ³
Mancos shale	Sand cone	10.1	1.84
	Nuclear		
	Direct transmission	11.6	1.88
	Backscatter	13.6	1.78
Adobe	Direct transmission	11.7	1.53
	Backscatter	12.5	1.52
Tailings	Direct transmission	9.0	1.49
	Backscatter	8.5	1.42

sand cone, and direct-transmission and backscatter nuclear probes. The backscatter (Seaman Model C-200®) probe was used in the density measurements, and, although it appeared to give slightly lower readings than the direct-transmission nuclear probe, it is assumed that the calibration of the instrument was satisfactory for estimating the density within $\pm 0.05 \text{ g/cm}^3$. Care had to be taken to smooth the surfaces so that repeatable readings could be taken, particularly with the compacted Mancos shale material.

Final characterization is not completed. The earthen covers will be cored to determine the uniformity and characteristics of the systems. Monitor pipes will be installed for downhole logging of the covers using neutron and gamma probes. The effectiveness of the cover systems has not yet been determined since at least 2 months are needed for the radon to equilibrate within the earthen cover system. Radon flux measurements will be made at the end of October to determine the initial effectiveness of the systems. It will, however, be at least 12 months and a complete climatic cycle

before the real effectiveness of the system can be determined. Along with radon flux measurement, we will be continuously monitoring moisture and temperature of the systems.

Column Tests - J. N. Hartley, M. R. Elmore and H. D. Freeman

The objective of the column tests is to more closely monitor and evaluate the behavior of radon transport in the various radon barrier systems and to compare this to the results obtained from the larger field tests.

Radon barrier systems, similar to those used in the larger field test, were installed in seven test columns (Figure 27.12). For example, moisture and compaction of the earthen covers was maintained at conditions similar to those of the larger field test. The physical characteristics of the tailings and radon barriers in the columns are presented in Table 27.13.

Experimental monitoring of the columns will include continuous monitoring of moisture profiles, temperature profiles, radon concentration profiles and periodic flux measurements (Figure 27.13). The

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radon flux measurements will be used to characterize the overall effectiveness of the radon barrier system.

No results have yet been obtained since the systems have not had time to equilibrate. Initial data should be available after November 1981.

FIGURE 27.12. Profile of Cover Materials in Column Tests

TABLE 27.13. Characteristics of Cover Materials in Column Tests

Column	Material	Thickness, m	Dry Density, g/cm ³	Moisture, % (g/g)
1	Tailings	1.8	1.12	--
	Mancos shale	1.2	1.77	16.2
	Adobe clay	1.8	1.69	5.6
2	Tailings	1.8	1.12	--
	Bentonite clay	1.2	1.35	29.4
	Adobe clay	1.8	1.57	5.5
3	Tailings	1.8	1.12	--
	Adobe clay	1.2	1.69	11.9
	Adobe clay	1.8	1.45	6.4
4	Tailings	1.8	1.12	--
	Adobe clay	3.0	1.35	3.75
5	Tailings	1.8	1.12	--
	Asphalt seal	0.8	2.08	0.5
	Adobe clay	0.6	1.6	5.0
6	Tailings	1.8	1.12	--
	Multilayer	0.3	1.67	15.0
	Adobe clay	1.2	1.56	5.4
7	Tailings	1.8	1.12	--
	Multilayer	0.3	1.94	16.8
	Adobe clay	1.2	1.45	5.2

FIGURE 27.13. Column Instrumentation

28. 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

The catalytic airblown asphalt membrane and bentonite liner, identified from the accelerated laboratory tests as the two most suitable liner materials for field testing, were installed in an excavated pit at the Grand Junction, Colorado, tailings pile. Over the next 2 to 3 years, the liners will be independently monitored for leachate and radionuclide migration through the liners.

LINER SELECTION

Following the accelerated aging tests described in the last quarterly report, the catalytic airblown asphalt membrane and soil amended with natural sodium bentonite were selected for field testing from eight materials. The bases for selection were the liner stability as a function of time, the relative permeability effectiveness (the ratio of permeability to liner thickness), and the relative cost. The asphalt membrane and bentonite were the only liners of low final permeabilities to exhibit a stable permeability versus time of exposure curve. They are also among the least expensive materials to install.

FIELD TESTING

The liners were installed in a specially excavated pit 30 by 20 by 1.8 m deep in the Grand Junction, Colorado, tailings pile. Extra precautions were observed to prevent extraneous moisture from migrating into the supporting soil beneath the liners. This will ensure that any moisture detected in the supporting soil has passed from the tailings through the liner and not from other sources. As part of these precautions, a moisture barrier consisting of clear rock 25 to 35 cm thick was placed beneath the sub-base to prevent upward migration of moisture. The edges of the pit were designed to prevent runoff from contacting the sub-base. Also the supporting soil for the bentonite liner was separated from that of the asphalt membrane so that detected moisture can be traced to its origin.

The asphalt membrane was installed by spraying 2600 kg of catalytic airblown asphalt at 200°C onto a 30-cm layer of soil in the western half of the pit. Approximately 6800 kg of Wyoming quality sodium bentonite was spread at a concentration of 20 kg/m² over the eastern half of the 30-cm

layer of soil. The bentonite was then roto-tilled into the soil to a depth of 10 cm, moistened to 12 to 18% moisture along the walls of the pit, and compacted. Sixteen moisture blocks, eight lysimeters, eight piezometers, and various thermocouples were placed at strategic locations to monitor

moisture migration, radionuclide movement, temperature, hydrostatic pressure, and exposure conditions. This information will provide real-time performance characteristics which can be related to the accelerated laboratory tests.

29. 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.

FIELD TESTS

During the last quarter of FY 1981, efforts focused on site characterization, instrumentation, and cover application at the field site in Grand Junction, Colorado. To characterize the site, the surface radon flux was measured and samples taken. Radon fluxes were measured at 70 locations on the test plot, at 10 locations along the perimeter, and at 40 locations on the FY 1980 test plot. Sample-time-comparison measurements were also taken to determine whether sample duration could be reduced from 4 to 2 hr. A new control box was installed on the FY 1980 test plot to monitor radon diffusion into the overburden as well as flux originating from the overburden. Measurements were taken to compare fluxes before and after cover application. The majority of the samples were counted using the NaI detector; the remaining samples require longer decay periods and will be counted later.

Tailings materials were collected for moisture, density, and radium content on the 1981 test plot. Core samples were collected using a split-tube coring method. After the overburden thickness was measured, the top 0.3 m of tailings was placed in a sealed container for later analysis. The samples were sent to Bendix Field Engineering Corporation for counting and determination of the radium content.

Permanent monitoring sites were established on the 1981 test plot. Instrumentation installed at the test plot included neutron access tubes, gypsum blocks, and thermocouples. The 12 neutron access tubes are 5 cm ID and extend about 1.5 m into the tailings and about 15 cm above the multilayer cover surface. Neutron probe count data and grab samples were collected at several depths to aid in calibration of the neutron probe. An additional tube installed adjacent to the plot was surrounded by an earthen dike. The areas enclosed by the dike remained flooded until September to provide data on saturated soil for the neutron probe calibration. Gypsum blocks and thermocouples were installed at several locations within the cover and their leads routed to a central location that houses logging equipment. Neutron probes, salinity monitors, moisture blocks, and other devices were installed and calibrated for use in the caisson (large column) test. These devices will be monitored periodically during the duration of the test. The meteorological station was moved from the FY 1980 test plot to the FY 1981 test plot. A new data logger with greater monitoring capabilities was also installed. Meteorological data collected at the FY 1980 test plot have been tabulated. These data include soil and air temperature, wind velocity at direction, humidity, and solar

radiation. Moisture content calibration was also begun for the neutron tubes installed in the FY 1981 multilayer test plot.

Cover application involved the mixing, spreading and compaction of about 2700 t of roadbase material, alum, bentonite, lime, and topsoil, and the spreading of about 10,000 t of washed rock and overburden. The materials, constituting the three types of multilayer earthen covers, were mixed by a portable pug mill and spread in uniform lifts by a paddle-wheel scraper. Smooth-drum and tamping-foot vibratory compactors and heavily loaded trucks were used for compaction.

The four cover systems applied included compacted layers containing 1860 m² of alum gel mix with thicknesses of 15 and 30 cm, 930 m² of bentonite/lime mix 40 cm thick and 464 m² of bentonite mix 30 cm thick. Preliminary data indicate an average compacted density of 1.95 g/cm³ and a minimum average moisture content of 11.3%.

Application of the multilayer earthen cover was completed and received final inspection and approval. To prepare the cover for radon flux measurements, the overburden surface was bladed smooth and the sampling grid reestablished. Completion of the cover lagged somewhat behind the anticipated schedule because of the contractor's involvement with other research work being done at Grand Junction. Radon flux measurements of the completed cover system will be undertaken in October.

Installation of the caisson cover test was completed. The 1.8-m-dia aluminum culverts contain 1.8 m of tailings and a radon seal composed of one of the following: adobe clay, bentonite clay, Mancos shale, gel, bentonite/lime mix, or asphalt. Each column was fully instrumented and the density and moisture content of the radon

seal closely monitored during placement. Numerous characterization samples were also collected. Because of soil heave in the instrumentation caisson the concrete floor was fractured, causing the radon concentration to be much higher than expected. As a result it was necessary to install a new reinforced concrete floor. Monitoring will continue to determine whether additional radon sealing of the caisson is needed. Future field data collection will be aided by modifications to the automatic data logging system.

MODELING

In radon gas diffusion modeling, one-dimensional, partially saturated flow analysis was completed using the water characteristics for two distinctly different layer materials. This resulted in the generation of moisture content profiles and moisture storage for the top 100 cm of a multilayer earthen cover system. One-dimensional radon diffusion analysis was completed using the moisture content predicted by the partially saturated flow analysis, and radon gas surface flux plots were generated. The multidimensional transient heat transfer code, TRUMP, was modified to solve the radon diffusion equation by including a sink term to account for decay and by adding an air-filled porosity term, P-0. Work began using TRUMP to solve the one-dimensional steady-state radon diffusion equation for the bare tailings flux.

The difficulty experienced with the modified version of TRUMP has been resolved. In the future this code will be referred to as RADMD for Radioactive Diffusion in Multidimensions. RADMD has been successfully applied to one-dimensional steady-state

problems involving bare tailings and covered tailings piles. The agreement with the analytic solutions for concentrations and fluxes is within 3%. A two-dimensional problem has also been successfully simulated with RADMD. The problem involves a tailings pile with a discontinuous cover. A two-dimensional analytic solution is not available for the problem of the discontinuous cover; however, at some distance from the discontinuity the numerical results match the analytic one-dimensional solution within 3%. Furthermore, the predicted surface flux values are qualitatively correct and agree with field observations made for a similar geometry. The draft report entitled Radon Diffusion Through Multilayer Earth Covers: Models and Simulations is essentially complete and has been submitted for clearance. A final report was completed on this study in September.

COVER OPTIMIZATION - Rogers and Associates (RAE)

Revision of the Task 2 report was completed. It reports radon measurements on test columns with composite earth covers in various configurations. Revision was required on the moisture model to account for the water content in covers on a dry weight basis and to more realistically assess the moisture effect in wet soils.

The report Laboratory Measurements of Radon Diffusion Through Multilayered Cover Systems for Uranium Tailings, resulting from the Task 2 effort, has been reviewed and will be published by PNL in early October. Results from the study on the correlation between the climate and soil water content

are being finalized, and a status report will be submitted early in October. Samples from the 1981 field test site were analyzed for radium content and emanation coefficients by RAE. This work was completed for over 100 samples taken from 15 sites at depths to 3 m in the tailings. Emanation coefficients of as high as 0.4 were observed. The data are being rechecked to confirm these high emanation coefficients.

Moisture correlation studies relating radon flux to cover water contents continue. The cover material used in a hanging water column experiment was compacted and the water column attached following leak testing. The column is presently equilibrating, and radon flux, and moisture measurements are being conducted. Preliminary work indicates that water control can be successfully achieved with a hanging water system. Flux reductions were achieved by adjusting the hanging water column and allowing for increased additions of water to the controlled soil layer. This work will continue through next quarter.

REPORTS

The following reports were issued:

Zellmer, J. T. August 1981. Stability of Multilayer Earthen Barriers Used to Isolate Mill Tailings: Geologic and Geotechnological Considerations. UMT/0202; PNL-3902.

Simmons, C. S. and G. W. Gee. September 1981. Simulation of Water Flow and Retention in Earthen Cover Materials Overlying Uranium Mill Tailings. UMT/0203; PNL-3877.

Mayer, D. W., C. A. Oster, R. W. Nelson and G. W. Gee. September 1981. Radon Diffusion Through Multilayer Earthen Covers: Models and Simulations. UMT/0204; PNL-3989.

The following papers were prepared for presentation at the Fourth Symposium on Uranium Mill Tailings Management, Fort Collins, Colorado, October 26-27, 1981:

Mayer, D. W., R. W. Nelson and G. W. Gee.
"Multidimensional analysis of Radon Diffusion Through Uranium Mill Tailings and Cover Systems."

Hartley, J. N. and G. W. Gee. "Uranium Mill Tailings Remedial Action (UMTRA) Joint Field Test."

Gee, G. W. et al. "Radon Control by Multi-layer Earth Barriers: Two Field Tests."

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30. 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 that are designed to prevent plant and animal breachment of uranium tailings containment systems.

SUMMARY

A pelletized polymeric carrier/delivery (PCD) system as a plant root barrier was produced and installed over the asphalt emulsion seal and multilayer earthen cover located at the Grand Junction uranium tailings site. The molded pellets were added in a soil layer ~2 in. above the seals at 1- and 2-in. centers over the multilayer earthen cover and at 2-in. centers over the asphalt emulsion seal. About 2 ft of cover soil was placed over the pellets. The pellets contain 23.4% trifluralin and release 28 µg/day at 13°C ambient temperature in laboratory tests. The cost for the manufacture was estimated at 12 cents/ft² when placed on 2-in. centers and 47 cents on 1-in. centers.

DEVELOPMENT OF PCD SYSTEMS - W. E. Skiens
and F. G. Burton

The slow-release pellets (PCD system) that were installed at Grand Junction were manufactured using a 24-cavity mold. New blending techniques and formulations were developed for preparing the pellets. It was found that merely mixing the components thoroughly at room temperature produced a mixture that would not feed into the screws of either an injection molding machine or an extruder. Suitable blends

were prepared by premixing the polyethylene powder and carbon black and then slowly adding the molten trifluralin at 100 to 110°C while constantly mixing. This procedure produced a friable powder that fed well into the screws of either machine, producing well-fabricated pellets. The final blend contained 24% trifluralin, 17% carbon black, and, as the binder, 59% polyethylene. The actual trifluralin content in the manufactured pellets was 23.4%. Each pellet contained 156.5 mg ± 4.6 SD of trifluralin and weighed 0.67 g ± 0.003 SD. A small portion of the trifluralin (1.3%) was washed from the pellet surface with isopropyl alcohol. The remaining 22.1% is considered incorporated in the pellet matrix to be released slowly.

The effect of different ambient temperatures on the release rate of trifluralin from the pellets was determined in the laboratory. The release rates are shown in Table 30.1. These laboratory studies are

TABLE 30.1. Effect of Temperatures on Release Rates of Trifluralin from Manufactured Pellets

Solution Temperature, °C	Release Rate, µg/day ± SD
13	28 ± 1
22	135 ± 15
37	855 ± 70

considered the extreme conditions; release rates will be slower in soils, thus increasing the effective lifetime of the pellets under field conditions.

To further increase the efficiency of the PCD system, blends were pelletized containing up to 40% trifluralin and 40% carbon black and only 20% polyethylene as a binder. This versatility of blending allows additional control of reservoir capacity and the release rate of herbicide from the PCD system.

FIELD APPLICATION STUDIES - J. F. Cline

Manufactured pellets (PCD system) were placed over the asphalt emulsion seal and multilayer earthen cover installed at the Grand Junction test site. The pellets were placed in a layer in soil cover ~2 in. above the seals at densities of 144 pellets/ft² (on 1-in. centers) over the multilayer earthen cover and 36 pellets/ft² (on 2-in. centers) over the asphalt emulsion and multilayer clay seals. Each of the three test plots contained 200 ft². Greenhouse and laboratory data indicate that the pellets placed on the 2-in. centers will be sufficient to maintain adequate concentration of trifluralin in the soil near the pellets to prevent root elongation beyond the pellets. As trifluralin diffusion is

in the range of ~4 cm, this spacing allowed some overlap (1 to 2 cm) in the soil.

The estimated cost to produce the pellets at the two application rates is shown in Table 30.2.

A pit was dug through the soil cover of the asphalt emulsion seal installed in FY 1980. Soil samples were taken from a soil layer located 10 cm above the seal, the depth at which liquid trifluralin had been sprayed in August 1980. Chemical analysis of these samples showed maximum trifluralin concentrations of 20 ppm in the soil nearest to the application zone. No plant roots were observed near the treated soil. These data show that trifluralin can remain effective as a root barrier for at least 1 year, even applied as a liquid (not in PCD system form). It may remain effective several more years, because the 20-ppm concentration after 1-year exposure is higher than the 6 ppm considered effective against root intrusion.

PRESENTATIONS

A paper entitled "The Use of Controlled Release of Herbicides in Waste Burial Sites" was presented on July 29, 1981, at the Eighth International Controlled Release Symposium held at Ft. Lauderdale, Florida.

TABLE 30.2. Estimate of Production Cost of the Pellets Used at the Grand Junction Test Site

	Material, \$/lb	Pellets on 1-in. Centers		Pellets on 2-in. Centers	
		lb/ft ²	cents/ft ²	lb/ft ²	cents/ft ²
Trifluralin	6	0.05	30.	0.0125	7.5
Carbon black	0.34	0.04	1.4	0.01	0.4
Polyethylene	0.65	0.10	6.5	0.025	1.6
Manufacture costs ^(a)	0.50		9.5		2.4
Totals	7.49	0.19	47.4	0.0475	11.9

(a) This is an estimated cost for automated manufacturing of large quantities of pellets.

31. REVEGETATION OF INACTIVE URANIUM TAILINGS SITES

L. L. Cadwell - Project Manager

The objective of this program is to establish guidelines for surface stabilization that provides for compatibility with sealant/barrier systems and is suited to soils and climates at inactive uranium tailings sites.

SUMMARY

Monthly sampling of soil moisture and vegetation cover continued at the Grand Junction test plot. Soil density was also measured. The irrigation system was dismantled and stored for the winter. Construction of the San Juan test site was completed.

Regional soil and vegetation sampling continued. Sampling was completed in southwestern Colorado, northwestern New Mexico, central Idaho, southwestern North Dakota, central Wyoming, and east-central Ohio/west-central Pennsylvania.

Results from computer simulations of soil-water dynamics and field lysimeter studies indicate that surface stabilization methods must be selected carefully. The moisture-content response of the tailings pile and cover system can be radically altered by different surface treatments.

TEST PLOTS - P. A. Beedlow, L. L. Cadwell, B. K. DeWaard, J. L. Downs-Berg, J. R. Skalski, and C. M. McKell (Native Plants, Inc., Salt Lake City, Utah)

Interactions between vegetation and sealant/barrier systems are being studied at the Grand Junction Test Site in conjunction with UMTRA projects testing sealants, and biological barriers. Monthly measure-

ments of water potential were continued using gypsum blocks. In addition, soil water content was measured with a neutron probe on September 23. A densimeter was used to obtain soil density measurements at 20 locations on September 22. On July 25 and September 21, vegetative cover was sampled and transpiration of annual and perennial species was measured with an autoporometer. The irrigation system on the test plot was dismantled during the September visit and stored at the Grand Junction DOE-Bendix site for winter.

The effects of irrigation and rock covers on soil moisture and plant establishment are being evaluated at a second test plot. This test plot was constructed in late August on the Juniper reclamation area at the San Juan Mine, Waterflow, New Mexico. The site occupies an area 174 by 162 ft plus a border. Three major surface treatments are being considered: 1) topsoil only, 2) topsoil plus sorted cobble, and 3) unsorted mixture of rocks up to a foot in diameter.

To test combinations of plant materials, each of the three surface treatments was divided into six subplots 24 by 18 ft. The planting treatments were as follows:

1. seeded with forb/shrub-dominant mix (90% shrub/forb seeds)
2. seeded with grass-dominant mix (90% grass seeds)

3. seeded with forb/shrub-dominant mix plus shrub transplants
4. seeded with grass-dominant mix plus shrub transplants
5. planted with shrub transplants only
6. control, no planting/seeding.

The six planting treatments, with three replicates each, were further divided into four irrigation subplots 6 by 18 ft, representing 18 replications per surface treatment and a total of 216 irrigation subplots [3(3 x 6 x 4)].

The test plot was constructed on recently graded and topsoiled mine spoils. The topsoiled surface was smoothed with a grader to fill furrows. On August 21, 1981, 78 yd³ of 3- to 4-in.-dia cobbles were delivered. A front-end loader provided by the San Juan Mine was used to spread and level the cobbles to an approximate 3-in. depth. Although care was taken to provide a uniform cobble depth, any lack of uniformity was considered to represent actual field conditions. On the same day, 96 yd³ of mixed rock was delivered to the site and spread to an approximate 6 in. depth.

Neutron probe ports were located in the middle of each irrigation subplot. A soil core sampler, attached to a pickup truck provided by San Juan Mine, was used to drill holes 36 in. deep, where a capped 42-in.-long, 2-in.-dia piece of PVC pipe was placed. Placement of the 216 pipes began on August 21 and was completed on August 23.

Planting began on August 23 and was completed on August 26. Within each irrigation subplot, four shrub species were planted on 3-ft centers. The resulting density was 12 plants per plot. The shrub species were:

- rubber rabbitbrush (*Chrysothamnus nauseosus*)

Source-Provo, Utah

- squawbush (*Rhus trilobata*)

Source-Washington Co., Utah

- Rocky Mountain juniper (*Juniperus scopulorum*)

Source-Broadwater Co., Montana

- fourwing saltbush (*Atriplex canescens*)

Source-NW New Mexico

Each plant received 1/2 gal of water after it was planted. Until irrigation began on August 27, plants were watered manually each evening.

A cyclone seeder was used to broadcast seed on the topsoil surface treatment. The soil was then hand-raked to cover the seeds. On the cobble and mixed rock surface treatments, seed was hand broadcast. The seed mixture is listed in Table 31.1.

The irrigation system installed at the Farmington test plot was based on a line-source design developed by Dr. R. J. Hanks at Utah State University. This system applies a high rate of water (20 in. annually) in the middle of the plot and decreases to zero at the sides. The value of this system is that it is possible to determine the minimum amount of water necessary for plant establishment. To construct this variable system on the test plot, a 6-in.-dia main pipe was placed at right angles to the existing irrigation line. Three 3-in.-dia pipes were placed lateral to the main pipe at 30-ft intervals and oriented parallel to the prevailing westerly winds. Each lateral was 200 ft long, extending 20 ft beyond each end of the plot area. Eleven impact-head sprinklers were spaced 20 ft apart on each lateral. The area covered by the sprinklers is ~25 to 30 ft in diameter when the water is delivered at a pressure of 65 psi.

The test plot was irrigated on the same schedule (but with shorter durations) as the reclaimed areas at the mine. Irrigation

TABLE 31.1. Plant Species Seeded at the San Juan Test Plot.
Seeding rate was 30 pure live seeds (PLS)/ft². Species proportions varied with treatment.

Species	Purity	Germination	Dormant	Pure Live Seeds (PLS) ^(a)
Forbs				
<i>Sphaeralcea grossulariaefolia</i>	98	90	-	88
<i>Aster tanacetifolia</i>	98	61	3	63
<i>Ratibida columnaris</i>	97	87	-	84
<i>Hedysarum boreale</i>	97	95	-	92
<i>Oenothera pallida</i>	99	74	12	85
<i>Penstemon palmeri</i>	98	90	-	88
Grasses				
<i>Oryzopsis hymenoides</i>	97	72	-	70
<i>Sporobolus airoides</i>	98	77	5	80
<i>Sporobolus cryptandrus</i>	91	82	15	88
<i>Sitanion hystrix</i> ^(b)	65	60	-	39
<i>Hilaria jamesii</i>	36	42	13	20
<i>Bouteloua gracilis</i>	57	86	-	49
Shrubs				
<i>Chrysothamnus nauseosus</i>	27	86	-	23
<i>Atriplex canescens</i> ^(b)	97	50	-	49
<i>Atriplex confertifolia</i>	95	50	-	48
<i>Cercocarpus ledifolius</i> ^(c)	92	50	-	46
<i>Kochia prostrata</i>	71	58	-	41

(a) Purity x germination = PLS

(b) Cut (fill) test

(c) Tetrazolium test

water was applied immediately after seeding and repeated after 2, 4 and 6 wk in the fall. Irrigation will stop on October 5 and will resume in the spring (possibly April) and continue through July 1982 at 3-wk intervals.

DATA ACQUISITION AND REGIONAL SAMPLING -

M. C. McShane, P. A. Beedlow and D. S. Daly

To examine the range of environmental conditions expected at the inactive tailings sites and their effects on vegetation, a regional sampling effort is being conducted. Specific objectives of this task

are to 1) determine climatic and edaphic influences on plant community structure, 2) provide necessary data to develop a predictive model for estimating revegetation potential, and 3) provide data necessary for erosion modeling. Regional groupings and sampling methods were described in the previous quarterly progress report, PNL-3000-10.

During the fourth quarter of FY 1981 the following regions were sampled:

- July - Southwestern Colorado and northwestern New Mexico; seven soil types were sampled (two near Gunnison, Colorado;

three near Durango, Colorado; and two near Grants, New Mexico).

- August - Central Idaho, southwestern North Dakota, central Wyoming, northwestern New Mexico; eleven soil types were sampled (one near Loman, Idaho; three in Converse County, Wyoming; three near Riverton, Wyoming; three between Bowman and Belfield, North Dakota, and one near Farmington, New Mexico).
- September - East-central Ohio/west-central Pennsylvania; a widely distributed soil type, representative of soils that might be used as topsoil for the Canonsburg site, was sampled.

ROCK COVERS - P. A. Beedlow, T. J. Bander, J. W. Batey (Indiana Central University), L. L. Cadwell, D. W. Mayer, R. L. Skaggs and W. Walters

The objective of this task is to model erosion and soil water on tailings as affected by vegetation, rock cover and climate. This quarter, work continued on the erosion models. Simulations of varying soil moisture content in covered tailings were completed. A summary of the soil water modeling and field verification efforts follows.

Rock and vegetation covers have been proposed for surface stabilization of inactive uranium mill tailings piles. To the extent that rock covers impede runoff and restrict plant growth and evaporation from the soil surface, they may result in increased soil/tailings moisture. Elevated moisture content can be beneficial by reducing pore space and thereby suppressing radon release. Excess moisture, however, may be detrimental if it promotes leaching and drainage of contaminants through the tailings to ground water or affects the

stability of cover materials. Differences in local climates and soil properties at the tailings disposal sites, as well as engineering design criteria, require an integrated approach to any proposed remedial action. Long-term functional stability can be ensured only if all the elements impacting the success of a remedial action design are jointly considered.

A partially saturated flow model (UNSATV) was used to analyze the Grand Junction uranium mill tailings pile with different cover treatments. The modeling effort provided a qualitative assessment of the effects of vegetation and rock covers on soil moisture. Also, field studies are being conducted to evaluate actual evaporation rates from soils having a variety of rock and vegetative covers.

Model simulations of unsaturated water flow indicate that care must be taken when selecting a cover system for a tailings pile. The moisture-content response of the tailings pile and cover system can be radically altered by different cover treatments. The two cases considered in this study indicate that evapotranspiration from a vegetated cover resulted in a relatively stable moisture content. A rock cover, however, increased moisture storage by significantly reducing evaporation. In fact, the moisture storage increased to the point that drainage occurred.

To investigate evaporation from rock covers experimentally, a series of weighing lysimeters filled with Ritzville silt loam were constructed on the Arid Lands Ecology Reserve at Hanford. Covers of sand, pea gravel and coarse gravel were applied to different lysimeters at a rate of 22.4 kg/m^2 (1.9 cm thick). Following an initial watering equivalent of 5 cm of precipitation, evaporative water losses from the various

aggregate covers were compared with that from bare soil. As the surfaces of the sand treatments dried, evaporation effectively ceased; the gravel treatments permitted evaporation, albeit at a lower rate than bare soil. Comparisons of coarse gravel applied at rates of 22.4 (1.9), 44.8 (3.8), 67.3 (5.7), and 89.7 kg/m² (7.6 cm deep), showed that bare soil lost water much more rapidly than the rock cover treatments during the first 7 days following watering. Beyond 7 days, however, a decline occurred in the rate of evaporation from bare soil relative to the rates of evaporation from the rock cover treatments. A dry surface layer was formed during this period as well. At 14 days and beyond, little difference was observed in the cumulative water losses from bare soil compared to the rock cover treatments.

Results from the lysimeter study indicate that, for the coarse aggregate size and treatment rates employed, the effect of rock cover on evaporation is most pronounced shortly after precipitation; thus, when rock covers were employed, the frequency of precipitation may be the major factor determining water accumulation. In addition, since the application rates of aggregates used in this study permit the establishment of vegetation, it may be possible to combine rock cover with vegetative covers to provide ef-

fective surface stabilization. Transpiration by vegetation would remove water from the sealant/barrier system, thus reducing possible problems associated with water accumulation.

During September a new experiment was initiated using the lysimeters at ALE to examine soil moisture and rock cover relationships when vegetation is introduced. Four treatments were used, with six replicates of each treatment:

Treatment A - Bare Soil

Treatment B - Rock Cover

Treatment C - Soil/Vegetation

Treatment D - Rock Cover/Vegetation

Lysimeters to contain vegetation were planted with cheatgrass (*Bromus tectorum*) at ~80 seeds per lysimeter, or roughly 1 seed/in.², allowing for germination variability. Rock cover was applied to the appropriate lysimeters after planting, and the lysimeters were watered to achieve 20% soil moisture. Irrigation of the lysimeters continued until the cheatgrass was established. Soil moisture block readings and relative humidity measurements are taken three times each week, weather permitting. Lysimeters are weighed twice a week to monitor water losses. This study will continue through the life cycle of the cheatgrass plants (i.e., summer 1982).

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