Nuclear Waste Management Quarterly Progress Report April Through June 1981

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

September 1981

**Prepared for the U.S. Department of Energy
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NUCLEAR WASTE MANAGEMENT
QUARTERLY PROGRESS REPORT
APRIL THROUGH JUNE 1981

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

September 1981

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RL0 1830

Pacific Northwest Laboratory
Richland, Washington 99352

FOREWORD

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

These reports are issued quarterly. The prior one in this series is Nuclear Waste Management Quarterly Progress Report January Through March 1981, PNL-3000-9.

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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

An occurrence has been investigated, corrective action begun, and permission to restart requested. Analytical equipment has been procured and/or installed, and sample analyses are under way.

Examination of the liquid-fed ceramic melter (LFCM) was completed. Investigations determined that the materials selected for melter construction generally exhibited good corrosion resistance. It was concluded that the design of the melter must consider the differences in thermal expansion, temperature gradients, and temperature transients encountered by the ceramic materials in melter operation. The melter demonstrated that it could operate satisfactorily over an extended time with moderate refractory cracking.

The commercial waste definition report was completed and submitted for review. This report describes, in detail, a commercial waste, a reference glass, and a reference canister. The design studies on alternative waste forms (AWF) canisters and barrier canisters were finished and the final reports

nearly completed. A series of full-scale canister impact tests was conducted. The Savannah River Laboratory (SRL) reference top was successfully dropped 9 m.

RADIOACTIVE PROCESS DEVELOPMENT - C. A. Knox

After the conclusion of the West Valley run, radioactive solution was found in piping in the operating gallery on two different occasions. This necessitated the shutdown of all radioactive operations while an investigation was under way. It was concluded that the incidents were the result of operator and procedural errors. Corrective action has been initiated.

A multichannel gamma energy analyzer and a liquid scintillation counter have been procured and are being installed for continuous on-line sample analyses.

The NO_x destructor has been installed, and operational safety tests are being completed.

The sample analyses for the SRL and West Valley runs are complete and are being analyzed.

DISMANTLED LFCM EXAMINATION - D. E. Larson,
S. M. Barnes and G. B. Long

Examination of the original LFCM glass contact refractories revealed that a protective layer of spinel crystals and relatively viscous glass is formed on the Monofrax K-3[®] surface. The thickness of the protective layer was minimal near the wall centers and greatest in the corners. The crystals in this layer were not attached to the refractory wall nor to each other, but were suspended in the glassy phase. These observations combined with generally increased refractory corrosion with distance from the corners indicate that K-3 corrosion varied with spinel layer thickness and that the protective layer stability is temperature-sensitive. The latter conclusion is based on the temperature-versus-viscosity behavior of the glasses. At the wall center the temperature is higher and glass viscosity is lower. Therefore the spinel crystals suspended in the glassy phase are more likely to be swept away by convection-driven glass contacting the refractory face.

The refractory stress analysis portion of the LFCM destructive examination indicates that stress levels present in the K-3 refractory is highly dependent on the degree to which the K-3 is restrained from vertical expansion. A calculation performed with the riser block totally restrained from vertical growth produced stress levels 40 times greater than did a simulation with no vertical restraints. The expansion restriction in the other two dimensions were held constant for this calculation. The result may be a large factor in the cracking disparity noted between the calcine-fed ceramic melter

(CFCM) and the LFCM. The CFCM Monofrax K-3 was free to expand vertically, whereas the LFCM K-3 was restrained by a refractory layer in the melter lid. Designing future melters with the freedom to expand vertically should prove a good method to relieve thermal stresses in the K-3.

The stress analysis calculations also explain the tears that developed in each of the melter lid corners. In each of the corners there is an intersection of two stainless steel strengtheners welded to the lid exterior. A tear in the Inconel[®] 601 lid developed where these structural members crossed. These tears probably developed during the melter lid temperature cycling due to the differential thermal expansion between the Inconel and stainless steel.

Examination of an off-gas line removed from the melter and a section off the flexible metal bellows used to seal the ionic booster electrodes revealed attack by sodium chloride and sulfur compounds. This type of corrosion, commonly called sulfidation, can occur under both oxidizing and reducing conditions. Nickel alloys are particularly sensitive to this corrosion mechanism as low-melting nickel-sulfur compounds are formed. Sulfidation is characterized by the breakdown of the passivating chromium oxide layer by molten salt fluxing or reduction to chromium sulfide. This exposes the chromium-depleted base alloy to corrosion by sulfur and chlorine compounds. Temperature conditions encountered by metallic melter components during thermally boosted liquid feeding operations are likely to increase the attack by sulfidation.

Three documents were issued during this quarter. Design and Performance of Atomizing

[®]Monofrax K-3 is a registered trademark of the Carborundum Company.

[®]Inconel is a registered trademark of Huntington Alloys, Inc.

Nozzles for Spray Calcination of High-Level Wastes, PNL-3702, and Connecting Section and Associated Systems Concept for the Spray Calciner/In-Can Melter Process, PNL-3170, were issued in May. Design and Performance of a Full-Scale Spray Calciner for Nonradioactive High-Level Waste Vitrification Studies, PNL-3742, was issued in June.

CANISTER DESIGN STUDIES - S. C. Slate

Work was completed on the document defining a reference commercial high-level waste glass and canister this quarter. A first draft was issued to the SRL lead office in April and a final draft at the end of June. In September 1981 the report will be released as a PNL topical report. This document is important because it identifies, for the first time, a reference commercial waste and canister. It comprises the most recent information on the high-level liquid waste stream, the HLW glass, and the canister. Table 1.1 summarizes the information contained in the document. With the data are included discussions on the reasons for selection of items such as the waste stream, glass composition, and canister diameter.

Two design efforts were completed this quarter. The first was a study to develop conceptual canister designs for selected alternative waste forms. A document was completed that discusses canister criteria, process requirements, and a canister design for each waste form. The forms studied were SYNROC, tailored ceramic, coated pellets in a particulate matrix, concrete, porous glass, and marbles in a lead matrix. Most of the new canister designs were much like existing glass canister designs because of the requirements other than processing that are placed on the canister.

The second design study was on the new concept of a barrier canister. The purpose was to develop designs for, and to evaluate the feasibility of, canisters that could serve as a long-lived engineered barrier in disposal. The major benefit of a barrier canister is that packaging costs would be much lower for a given volume of waste. Titanium grades 2 and 12 and Inconel 625 were selected as candidate materials. Test specimens of these materials were subjected to thermal treatments that simulated glass-filling cycles. Then we conducted tensile tests, Charpy V-notch impact tests, and hydrothermal corrosion tests. The results on the tensile and impact tests indicate little detrimental effect from the heat treatments. The corrosion tests, in 150°C brine, are in progress and will be completed by December 1981. A report will be issued that documents the test data and describes a conceptual barrier canister design. So far the results of the study indicate that a barrier canister can serve as an effective barrier in a repository.

CANISTER TESTING

Under study are new filling and cooling techniques to reduce cracking in cast HLW glass. A series of bench-scale tests and one full-scale test were completed this quarter. These tests were used to discover the reasons for cracking and to test crack-reducing techniques. A draft of a topical report on this study was completed; it contains a large amount of data on cracking levels in canister, a discussion of causes of cracking, and recommendations for methods to reduce cracks.

At the end of the quarter, a series of full-scale canister impact tests was conducted. A total of six canisters were

1.4

dropped from a height of 9 m onto a large steel plate, backed by concrete. Two of them, which had SRL-reference-design tops, were dropped on their tops without a failure. Another canister, filled with marbles in a lead matrix, was dropped onto a bottom cor-

ner. This canister will be sectioned to evaluate the effect of the drop on the matrix waste form. The other canisters were dropped to test the PNL twist-lock closure and to practice the drop-testing procedure.

TABLE 1.1. Summary of Reference Waste, Glass, and Canister

<u>High-Level Liquid Waste</u>		
Composition	HLLW and intermediate-level liquid wastes (ILLW) are combined. The reference concentration is 620 ℓ /MTU.	
Activity	4.476×10^5 Ci/MTU; 722 Ci/ ℓ (5 yr after reactor discharge)	
Decay heat	1624 W/MTU; 2.62 W/ ℓ (5 yr after reactor discharge)	
	<u>Constituents</u>	<u>Oxide Form, kg/MTU</u>
Calcine (some vitrification processes have a separate calcination stage)	Fission products	34.7
	Actinide plus daughters	12.36
	Nonradioactive chemicals	<u>39.81</u>
Total		86.87
<u>High-Level Waste Glass</u>		
PNL identification	Reference glass is much like HLW glass 77-260 developed for AGNS FRP flowsheet.	
Composition	<u>Constituent</u>	<u>wt%</u>
	SiO ₂	36
	B ₂ O ₃	9
	P ₂ O ₅	2
	Alkali metal oxides	13
	Alkaline earth oxides	1
	Fe ₂ O ₃ , Cr ₂ O ₃ , NiO	1
	Al ₂ O ₃	2
	TiO ₂	6
	CuO	3
	Gd ₂ O ₃	10
	Fission product oxides	12
	Actinide oxides	5
Waste loading	The oxides from the HLLW constitute 31 wt% of the glass	
Quantity	277 kg/MTU; 89 ℓ /MTU	
Activity	1616 Ci/kg; 5029 Ci/ ℓ (5 yr after reactor discharge)	
Decay heat	5.9 W/kg; 18.3 W/ ℓ (5 yr after reactor discharge)	

TABLE 1.1 (contd)

Density	3.1 g/cc
Process melting temperature	1050 to 1150°C
Softening temperature	575 to 650°C (viscosity = 4×10^7 poise)
Transition temperature	500 to 550°C (viscosity = 10^{13} poise)
Temperature limit to prevent devitrification	475°C
Leach rate	$1.0\text{--}2.0 \times 10^{-6}$ g/cm ² -day (25°C water)
Thermal conductivity	0.8-1.3 W/m-°K from 0 to 500°C
Heat capacity	700 to 800 J/kg-°C (estimated)
Thermal expansion	$1 \times 10^{-5}/^\circ\text{C}$
Tensile strength (compression-loaded specimen)	4×10^7 Pa
Young's modulus	7×10^{10} Pa (estimated)
<hr/> HLW Canister <hr/>	
Material	Stainless steel 304L
Dimensions	10 ft ht x 12.25 in. ID cylinder; 1/4 in. wall thickness
Bottom	Slightly reversed dished flanged tank end
Top	Flanged-only tank head
Closure	PNL "twist-lock"
Fins (internal)	Required for ICM process but not for JHGM process. Capacities given below assume no fins.
Empty wt	160 kg
Fill ht	90%
Glass content	200 g; 630 kg; 2.28 MTU HLW
Activity	1.02×10^6 Ci (5 yr from reactor discharge) 6.58×10^5 Ci (10 yr from reactor discharge)
Decay heat	3.71 kW (5 yr from reactor discharge) 2.2 kW (10 yr from reactor discharge)
Maximum centerline temperature in repository	620°C (5 yr from reactor discharge) 480°C (10 yr from reactor discharge)

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

Titanium and aluminosilicate glass matrix waste forms containing SPC-4E pellets were scaled up to 8 cm dia. Both waste forms had a waste-free outer envelope 1 cm thick of pure matrix material and a random separation of pellets such that individual pellets would be separated, on the average, by 2 mm of matrix material.

Chemical-setting cements have been obtained and samples fabricated for leaching tests for comparison with hydraulic-setting cements.

Alumina, titania, and zirconia were evaluated as matrices for encapsulating disc pelletized and sintered SPC-4E supercalcine by hot-pressing at temperatures of 1200°C or lower. TiO_2 matrices had very little to moderate cracking, while ZrO_2 matrices were extensively cracked. The matrix density attainable with Al_2O_3 at 1200°C was too low to achieve a nonporous matrix.

NiS-bonded graphite matrix samples containing simulated waste forms were fabricated. The quality of these compacts was not as good as the NUKEM-produced samples--possibly because of unreacted nickel.

A series of rods made with different fillers and organic binders has been produced

at General Atomic Company (GAC) and shipped to PNL for evaluation.

Lead matrix-encapsulated borosilicate waste glass has been identified by chemical durability testing as the more promising option of the possible matrix/glass combinations. Initial examinations have indicated a good waste form/matrix bond, with the presence of lead in the glass at the interfacial region, possibly aiding in a chemical protection process.

Water permeability testing at 1000 to 1500 psi has shown that some types of graphite matrix rods are impermeable even after heat treatment to 400°C. Thus they have potential for use as a matrix material.

Gamma radiation doses up to 5.4×10^7 roentgens caused no measurable reaction of graphite with either water or oxygen at 30°C. The graphite did catalyze the radiolysis of the water, however.

Data from leach tests conducted on 76-68 glass with deionized water solutions in metal matrix containers indicate that the presence of lead can decrease leaching by two orders of magnitude as compared to 76-68 glass in Teflon® containers.

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Thermal spray coatings of aluminum, lead, and tin alloy on simulated TDS-211 glass marbles all present an effective barrier to leaching.

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-year 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, and essentially no changes in the above properties were found.

The hot-cell occurrence investigation for D-cell, 324 Building, is complete. Permission to restart hot-cell activities has been requested from DOE-RL. The hot-press and accessory equipment is ready to be installed in the hot cell.

Low-temperature pyrolytic carbon (PyC) coating runs were made at reduced pressures at Battelle Columbus Laboratories (BCL). No significant improvement in coating rate or quality was observed. However, it was possible to fluidize larger diameter SPC-4E particles by this method.

Savannah River Laboratory (SRL) composition calcine/frit particles were coated in a fluidized bed coater with carbon and with silicon using conventional chemical vapor deposition (CVD) techniques. The latter coating is intended as a seal so that higher temperatures can be employed in carbon coating.

Simulated Savannah River Plant (SRP) waste marbles were coated with aluminum using the wire gun process for the lead

matrix encapsulation demonstration. Two batches of waste marbles were also coated for the SRL comparative leach test—one with lead by the wire process, the other with aluminum by the plasma process. An 80-kW plasma spray unit has been installed and tested along with a newly designed marble agitator.

Twenty-five kilograms of aluminum-coated SRP simulated waste glass marbles, 1 cm dia, were encapsulated in pure lead using a vacuum casting technique. The lead matrix infiltrated the porous aluminum coating, forming a tight mechanical bond between the aluminum coating and the lead matrix.

A document covering metal matrix process demonstrations conducted at PNL has been issued as PNL-3750, Nuclear Waste Encapsulation by Metal-Matrix Casting.

WASTE FORM DEVELOPMENT AND CHARACTERIZATION

Matrix Development

Titanium/Glass Matrix Development - W. E. Gurwell

Two of the more promising matrix-waste core combinations were scaled up from the exploratory size (2.2 cm dia) to 7.6 cm dia by 7.6 cm high. They consisted of a supercalcine (SPC-4E) bead (~0.5 to 1 cm dia) in a matrix of either titanium - 6% aluminum - 4% vanadium or aluminosilicate glass (Corning code 1720®). Both matrices were hot-pressed to full density using the same time-temperature-pressure conditions used with the smaller size. The titanium matrix waste form was pressed at 960°C and 30 MPa for 60 min. The aluminosilicate glass waste form was pressed at 825°C and 10 MPa for

®Corning Glass Works, Corning, New York.

80 min. Both finished waste forms had a waste-free outer envelope of pure matrix material about 1 cm thick. Inside the envelope there was 35 vol% SPC-4E in the matrix. This waste loading allows the SPC-4E pellets to be separated, that is, individually encapsulated. On the average, the pellets will be separated by about 2 mm of matrix material. This was achieved by incremental loading of properly proportioned mixtures of pellets and matrix powder.

Ceramic Matrix - H. T. Blair

Samples of four different chemical-setting cements were obtained from two different suppliers. Chemical-setting cements differ from hydraulic-setting cements in their composition and the bonding mechanisms. Hydraulic-setting cements contain calcium silicates or aluminates that form hydrates to bond the material together when water is added. Chemical-setting cements contain sodium or potassium silicates and a setting agent that reacts with the silicates when water is added to form silicate chains that bond the material. The samples were mixed with water, cast, and cured according to the manufacturer's instructions. The samples were cast without any waste loading.

A third supplier of chemical-setting cements also furnished cast samples of four different cements and several other types of cements or mortars to be cast that will be prepared for inclusion in scoping leach tests. The objective of the tests will be to determine the leach resistance of the chemical-setting cements as compared to other castable ceramic matrix candidates such as Portland cements and castable refractories.

Hot-Pressed Ceramic Matrices - D. W. Brite

Alumina, titania, and zirconia were evaluated as hot-pressed matrices for encapsulating disc-pelletized and sintered SPC-4E supercalcine. Initial experiments were performed using 7/8-in.-dia graphite dies, vacuum atmosphere, heating and cooling rates of 600°C per hr, hot-pressing temperatures of 1100 and 1200°C, pressures of 3000 and 5000 psi, and pressing times of 1 hr or less at the maximum temperature. Three specimens were hot-pressed in a 3-in.-dia die at 4000 psi and 1100°C. Processing parameter details and density data for the 24 hot-pressing runs completed are shown in Table 2.1.

The hot-pressing experiments showed very little to moderate cracking of TiO_2 matrices and extensive cracking of ZrO_2 matrices. The matrix density attainable with Al_2O_3 at 1200°C was too low to achieve a nonporous matrix. Consequently, no Al_2O_3 samples containing SPC-4E pellets were prepared.

TiO_2 matrix samples were produced with a nearly crack-free, nonporous, 97% TD matrix in the 7/8-in. die. However, moderate to extensive cracking of the TiO_2 matrix occurred in the 3-in. die. Density of the SPC-4E pellets in the samples after hot-pressing averaged 4.41 g/cm³ for 3000 psi, 1200°C pressing; 4.28 g/cm³ for 3000 psi, 1100°C pressing; and 4.43 g/cm³ for 5000 psi, 1100°C pressing. SPC-4E loadings were in the range 23 to 28 vol% after hot-pressing. In run No. HP-10, a TiO_2 sample was hot-pressed at a heating rate of 120°C per hour to determine the temperatures where densification starts and ends. These temperatures were 810°C and 1115°C. In run No. HP-26, it was determined that SPC-4E by itself begins to densify at 950°C and densification is complete by 1100°C when heated at 120°C/hr.

TABLE 2.1. Ceramic Matrix Hot-Pressing Parameters

Run No.	Material	Pressure, psi	Temp., °C	Time, minutes	Density		Vol. % Open Porosity	Comments
					g/cm ³	% TD		
HP-1	TiO ₂	3000	1200	30	4.12	96.7	0.0	No cracks
HP-2	SPC-4E Pellets in TiO ₂	"	"	"	4.26		0.0	No cracks
HP-3	" " " "	"	"	"	4.21		1.1	Few cracks
HP-4	" " " "	"	"	"	4.21		0.1	Submitted for leach testing
HP-5	8% Y ₂ O ₃ stabilized ZrO ₂	"	"	115	4.79	79.4	7.0	No cracks
HP-6	SPC-4E pellets in ZrO ₂	"	"	60	5.24		1.2	Extensive cracking
HP-7	" " " "	"	"	"	5.20		1.8	Submitted for leach testing
HP-8	" " " "	"	"	"	5.11		2.3	Cracks
HP-9	Al ₂ O ₃	"	"	"	2.14	53.7		
HP-10	TiO ₂	"	"	12	4.14	97.2	0.0	120°C/hr heating rate. Densification started at 810°C and was complete at 1115°C
HP-11	SPC-4E pellets in TiO ₂	"	1100	30	4.15		0.1	Few cracks
HP-12	SPC-4E pellets in ZrO ₂	"	1200	60	5.25		2.0	Extensive cracking
HP-13	" " " "	"	"	"	5.22		1.2	Extensive cracking
HP-14	SPC-4E pellets in TiO ₂	"	1100	30	4.17		0.1	Few cracks
HP-15	" " " "	"	"	"	4.17		0.1	Few cracks
HP-16	A. 8% Y ₂ O ₃ stabilized ZrO ₂ (0.1 μm particle diameter) B. CaO stabilized ZrO ₂ (plasmadyne spray powder)	5000	1200	60	5.37 3.17	89.0 57.7	1.4 42.4	No cracks No cracks. Particles can be scraped off.
HP-17	SPC-4E pellets in ZrO ₂	"	"	30	5.21		0.6	Cracks
HP-18	SPC-4E pellets in TiO ₂	"	1100	18	4.23			No cracks
HP-21	Al ₂ O ₃ (Linde A)	5000	1200	60	2.87	72.1	25.3	No external cracks visible
	12Y ₂ O ₃ -ZrO ₂	5000	1200	60	4.03	66.9	29.2	No external cracks visible
	TiO ₂ (Technical grade)	5000	1200	60	4.16	97.6	0	No external cracks visible
HP-22	SPC-4E pellets in 12% Y ₂ O ₃ -ZrO ₂	5000	1200	60	5.17		2.8	Extensive cracking
HP-26	SPC-4E (pellets crushed to -14 mesh)	3000 5000	1100	15 15	4.25 ^(a) 4.43		 0.4	120°C/hr heating rate. Densification started at 950°C and was complete at 1100°C. No external cracks visible.
HP-27	TiO ₂ (in 3" dia. die)	4000	1100	30	4.17	98.0		No cracks
HP-30	SPC-4E pellets in TiO ₂ (in 3" dia. die)	4000	1100	30	4.09			600°C/hr cooling rate Extensive cracking
HP-33	" " " "	4000	1100	40	4.13			120°C/hr cooling rate Moderate cracking

(a) Calculated from ram movement upon increasing pressure from 3000 to 5000 psi.

An extensive reaction between the SPC-4E pellets and the TiO_2 occurred at 1200°C in 30 min, as revealed by ceramography. Components of the supercalcine apparently diffused into the TiO_2 and reacted, causing extensive grain growth and the formation of several different crystalline phases. The extent of reaction appeared to be significantly less in samples heated to 1100°C for 18 min. Because densification of both the SPC-4E and the TiO_2 is complete at $\sim 1100^\circ\text{C}$, the hot-pressing temperature for TiO_2 matrix samples was limited to 1100°C after the initial experiments in order to minimize the reaction between the two materials.

Cracking in the first 3-in.-dia TiO_2 matrix sample (HP-30) was revealed to be extensive upon sectioning of the specimen. The cracks appear to have formed upon cooling. In run No. HP-33, the cooling rate was reduced to 120°C/hr to reduce thermal shock. However, moderate cracking, significantly greater than observed in the 7/8-in.-dia samples, still occurred. In run No. HP-27, no cracks were present in the TiO_2 hot-pressed by itself and cooled at 600°C/hr .

The difference in thermal expansion/contraction of the two materials is in the direction to minimize cracking of TiO_2 . The thermal expansion coefficient for SPC-4E is $9.35 \times 10^{-6} \text{ cm/cm}^\circ\text{C}$, while that for TiO_2 is $7.6 \times 10^{-6} \text{ cm/cm}^\circ\text{C}$. The SPC-4E pellets should shrink more than the TiO_2 during cooling, thus minimizing residual stresses in the TiO_2 . A possible contributing factor to the greater severity of cracking in the 3-in. samples is the use of larger SPC-4E pellets (1.35 versus 0.62 g per pellet).

Still another factor that could affect the properties of the TiO_2 is the apparent difference in oxidation state of the TiO_2 in the central portion of the larger samples. The 7/8-in.-dia TiO_2 matrix samples were

blue-gray, believed to indicate a reducing condition caused by the graphite die. The 3-in.-dia samples have the same blue-gray color to a depth of about 1/2 in., but the TiO_2 in the central portion is very light gray to white. However, the central portion of HP-27, the 3-in. TiO_2 sample containing no SPC-4E pellets, is blue-gray, indicating that the SPC-4E provides an oxidizing environment for the TiO_2 .

Severe cracking was present in each of the seven hot-pressed Y_2O_3 stabilized ZrO_2 matrix samples containing SPC-4E pellets. However, there appears to have been no reaction between the pellets and the matrix. Cracking may be partially due to differential thermal contraction of the matrix and pellets during cooling from 1200°C . The coefficients of thermal expansion for 8% Y_2O_3 and stabilized ZrO_2 and for SPC-4E supercalcine are 10.2×10^{-6} and $9.35 \times 10^{-6} \text{ cm/cm}^\circ\text{C}$, respectively. The difference in these values is in the direction, causing stresses to form in the ZrO_2 because it shrinks more than do the SPC-4E pellets. However, the difference is quite small. Cracks appear to radiate from the pellet/matrix interface, and in some cases supercalcine had extruded into the crack, indicating that the cracks were present when the supercalcine was still hot enough to behave plastically.

The possibility that the presence of supercalcine negates the stabilization effect of Y_2O_3 on the zirconia was suggested by the density of the hot-pressed composite samples, $\sim 5.2 \text{ g/cm}^3$, which is greater than that of both the ZrO_2 alone, $\sim 4.8 \text{ g/cm}^3$, and the SPC-4E alone, $\sim 4.3 \text{ g/cm}^3$. This effect could be due to a change in the relative amounts of cubic and tetragonal phases present in the ZrO_2 . X-ray diffraction analysis, however, showed essentially the same crystalline phases present in uncracked

hot-pressed ZrO_2 matrix samples and in cracked hot-pressed samples of ZrO_2 containing SPC-4E pellets. Thus cracking cannot be attributed to a phase change in the ZrO_2 matrix.

The most probable cause of cracking in the ZrO_2 is believed to be the difference in densification rates of the SPC-4E pre-sintered pellets and the matrix during hot-pressing. The SPC-4E starts to densify at $\sim 950^\circ\text{C}$ and reaches final density at $\sim 1100^\circ\text{C}$. The ZrO_2 also starts to densify at $\sim 950^\circ\text{C}$, but the rate is much slower and the densification continues slowly even after 1 hr at 1200°C . Cracks in the ZrO_2 matrix appear to have occurred during hot-pressing, rather than upon cooling, as evidenced by the extrusion of supercalcine into the cracks and the presence of areas of matrix offset into the supercalcine pellets. In these experiments, the pellets were loaded in the central portion of the sample surrounded by an annular layer of ZrO_2 containing no pellets. This loading arrangement is believed to amplify the problems caused by nonuniform densification rates of the two materials.

Some of the more significant observations made as a result of this work are as follows:

- Presintered disc-pelletized SPC-4E supercalcine can be hot-pressed in vacuum in graphite dies at 1100°C to 4.25 g/cm^3 at 3000 psi and 4.43 g/cm^3 at 5000 psi.
- 8% $\text{Y}_2\text{O}_3\text{-ZrO}_2$ has better hot-pressing characteristics than 12% $\text{Y}_2\text{O}_3\text{-ZrO}_2$ with similar characteristics. (Crystallite size, $0.02\text{--}0.3 \mu$; agglomerate size, 0.1μ). Twelve percent $\text{Y}_2\text{O}_3\text{-ZrO}_2$ was hot-pressed at 1200°C and 5000 psi to 4.03 g/cm^3 (66.9% TD). Eight percent $\text{Y}_2\text{O}_3\text{-ZrO}_2$ attained a density of 5.37 g/cm^3 (89.0% TD) under the same conditions.

- The presence of supercalcine pellets in a ZrO_2 matrix increases the density attainable by hot-pressing at 1200°C . The 8% $\text{Y}_2\text{O}_3\text{-ZrO}_2$ alone was hot-pressed at 1200°C to 4.79 g/cm^3 (79.4% TD) at 3000 psi and to 5.37 g/cm^3 (89.0% TD) at 5000 psi. As a matrix for supercalcine pellets, it was hot-pressed to 5.59 g/cm^3 (92.7% TD) and 5.57 g/cm^3 (92.4% TD) at 3000 and 5000 psi, respectively. Density of the 12% $\text{Y}_2\text{O}_3\text{-ZrO}_2$ hot-pressed at 1200°C and 5000 psi was 4.03 g/cm^3 alone and 5.52 g/cm^3 (91.5% TD) as a matrix for supercalcine pellets.
- Technical grade TiO_2 was hot-pressed to the same density attained using reagent grade TiO_2 (4.16 g/cm^3 ; 97.6% TD).
- Linde A alumina was hot-pressed to 2.87 g/cm^3 (72.3% TD) at 1200°C and 3000 psi for 1 hr.

Graphite Matrix (Inorganic Binders) - L. R. Bunnell

Specimens of NiS-bonded graphite were prepared by a warm-pressing process approximating that used by NUKEM. A similar time-temperature cycle was used, the only difference being the use of a peak pressure of 4000 psi instead of the 7000 psi used at NUKEM. In addition to waste-free matrix, compacts were made containing sintered SPC-4P supercalcine and simulated waste glass marbles. These materials were both arranged in the die to preclude particle-to-particle contact and to provide a skin of waste-free matrix on external surfaces. The compacts look very good metallographically except for unreacted nickel; this occurred even though -400 mesh powder was used. The compacts are also slightly more water-permeable (see "Graphite Permeability Testing" in this report). A few more waste-free compacts will be made in which temperature

will be increased to provide more complete reaction. The goal is to demonstrate fabrication of this matrix material that is as good as the NUKEM material.

Graphite Matrix (Organic Binders) -

R. E. Bullock, General Atomic Company

Samples of carbonaceous bonding materials for encapsulating nuclear wastes are being fabricated at General Atomic Company and then shipped to PNL for evaluation of their water permeabilities. Four phases of sample preparation are planned:

1. green matrix rods without waste inclusions
2. baked matrix rods without waste inclusions
3. green rods with simulated waste inclusions
4. baked rods with simulated waste inclusions.

The first phase has now been completed, and preliminary permeability results received from PNL have been encouraging. Twenty-four green matrix rods without waste inclusions were shipped to PNL for evaluation, and six of the seven specimens evaluated to date have been found to be impermeable to water at a pressure of 1000 psi for the duration of the standard 24-hr test devised by PNL for determining water leachability. In particular, the polyimide (MC-600), the phenolic resin (Resinox 755), and the furan resin (QX-322) have all had zero permeability when no graphite filler was added to the binders. Likewise, the latter two resins had zero permeability for 70 wt% graphite filler in the binders, but the filler level in the polyimide had to be lowered from 70 to 45 wt% to give zero permeability.

Work is now under way on heat-treating the various matrices to temperatures of 400, 600, and 800°C. Subsequent permeability measurements will then be used to select the most favorable matrix type and heat-treatment

temperature for use in the final phases of the encapsulation work where simulated waste particles are to be incorporated into the matrix.

Matrix Characterization

Waste Form Evaluation - J. W. Wald

Evaluations of matrix waste forms have been heavily weighted toward the assessment of chemical durability. The leach testing that has been performed on a commercial and a defense-based waste glass and a commercial-based ceramic form, encapsulated in a variety of metal, glass and ceramic matrices, has illustrated a number of important considerations. Certain inert matrices will change the chemistry of leach solutions such that an environment more corrosive to the waste product will exist. Other materials are quite permeable to water under normal fabrication conditions, while some materials are most effective only if they form, intact, a complete envelope around the waste form. It appears that the best combination can be made only when waste product-matrix synergistics are considered.

More basic leach tests, described elsewhere in this report, indicate the lead matrix-borosilicate waste glass system offers a suitable combination. An as yet incompletely defined chemical protection system seems to exist that reduces leaching of the glass form by two orders of magnitude. Figure 2.1 illustrates the typical microstructural cross section of an as-fabricated matrix sample. As illustrated, lead has been detected by SEM examination in the glass at the glass/metal interface. Additionally, there appears to be a good bond between the glass waste form and the matrix metal, eliminating to a large extent possible

FIGURE 2.1. Microstructure of Lead Matrix-Encapsulated 76-68 Glass

leach solution pathways. Studies are currently being conducted to establish the kinetics of lead-matrix waste glass interactions at elevated temperatures as well as to model the behavior observed in Figure 2.1 by surface analysis of glass beads removed from the matrix after fabrication.

Graphite Leach Testing - W. J. Gray

Efforts have been made to measure the reaction of carbon with water in the presence of a ^{60}Co radiation field. All tests were

done in Pyrex[®] vessels at about 30°C using deionized water and powdered graphite.

Results shown in Table 2.2 are from tests conducted in an air atmosphere. Following irradiation, gas from the vessels was transferred directly into a gas chromatograph for analysis. The relative amounts of H_2 and CO_2 cannot be correlated with any of the possible reactions between water, air, and graphite. No gases other than air, H_2 and CO_2 were detected, although it is possible that small changes in the amount of O_2 could

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TABLE 2.2. Direct Analysis of Gas Produced in Gamma-Radiation Field

Graphite ^(a)	H ₂	CH ₄	CO	CO ₂	Dose Rate, Roentgens/hr	Time, hr
Yes }	6,860	-	-	1,260	3.2×10^5	24
No }	3,870	-	-	640	3.2×10^5	24
Yes }	9,940	-	-	410	3.2×10^5	24
No }	3,900	-	-	660	3.2×10^5	24
Yes }	10,000	-	-	520	1.6×10^5	24
No }	3,760	-	-	130	1.6×10^5	24

(a) Runs were made in three groups of two; one vessel contained graphite (yes) and one was a blank containing only water (no).

have gone undetected. It seemed possible that oxygen formed by the dissociation of water might be sorbed by the graphite. If the graphite were heated, the oxygen might desorb as CO or CO₂. Therefore, a series of tests was run where the graphite was degassed before the gas was analyzed by the chromatograph.

Following irradiation, the water was distilled from the vessel at about 100°C and collected in a dry ice trap while the gas (mostly air) was pumped into a bulb. Then the reaction vessel was heated to 500°C for 2 hr and the desorbed gas pumped into the same bulb. Analytical results for these gas samples are shown in Table 2.3. Results from the first set of vessels, which were not irradiated, indicated that there was some CH₄, CO and CO₂ initially on the graphite that was desorbed during the subsequent degassing treatment. Therefore, some of the vessels were loaded with graphite and degassed for 2 hr at 500°C before adding the water and sealing them. It does not appear that this had much effect on the results, however; the main feature of the data in Table 2.3 is essentially the same as in Table 2.2. Quite a lot of H₂ was generated by irradiation, and the amount increased substantially when graphite was present.

Irradiation had no measurable effect, however, on the other gases.

Table 2.4 shows data from two runs where the vessels were loaded with degassed water and helium rather than air. Also, the graphite had previously been degassed for an hour at about 2000°C. Following the runs, water was distilled from the vessels and they were degassed in the same manner described above for the data presented in Table 2.3. Obviously, a small amount of air got into the gas samples somewhere along the line. Again, irradiation produced a substantial amount of H₂ and the amount was increased when graphite was present. The amount of O₂ was roughly half the amount of H₂, suggesting a simple dissociation of water. The amounts of CH₄, CO and CO₂ present in the irradiated graphite sample are probably insignificant, particularly when considered together with the data in Table 2.3.

Data presented here show that graphite catalyzes the radiolysis of water. However, radiation caused no measurable reaction of the graphite with either water or oxygen.

Previous experiments at temperatures of 200 to 300°C have shown that graphite reacts with oxygen in the water rather than with the water itself. The reaction rate would

TABLE 2.3. Indirect Analysis of Gas Produced in Gamma-Radiation Field

Graphite ^(a)	Degassed	H ₂	CH ₄	CO	CO ₂	Dose Rate, Roentgens/hr	Time, hr
Yes }	No	-	82	1,033	2,332	0	20
No }	No	-	-	-	637	0	20
Yes }	No	32,500	77	919	3,708	8.0×10^5	20
No }	No	23,900	-	-	1,463	8.0×10^5	20
Yes }	Yes	-	1,150	188	1,416	0	68
No }	No	-	87	-	708	0	68
Yes }	Yes	80,600	370	643	3,940	8.0×10^5	68
No }	No	40,900	-	-	910	8.0×10^5	68
Yes }	Yes	-	188	342	1,500	0	23
Yes }	Yes	10,300	200	398	2,237	2.6×10^5	23
No }	Yes	5,846	57	-	1,289	2.6×10^5	23

(a) Each of the five runs contained one or two vessels with graphite (yes) and one blank containing only water (no).

TABLE 2.4. Indirect Analysis of Gas Produced in Helium Atmosphere In Gamma-Radiation Field

Graphite ^(a)	O ₂	N ₂	H ₂	CH ₄	CO	CO ₂	Dose Rate, Roentgens/hr	Time, hr
Yes }	1,250	7,255	-	-	-	189	0	68
No }	1,369	7,160	-	-	-	146	0	68
Yes }	13,500	7,889	28,100	103	228	2,013	8.0×10^5	68
No }	3,662	7,160	6,164	-	-	599	8.0×10^5	68

(a) Each of the two runs contained one vessel with graphite (yes) and one blank containing only water (no).

be much lower in an oxygen-free system. In the presence of gamma-radiation, however, there would be no oxygen-free water because of radiolysis. It is not possible to predict what effect gamma radiation would have on reaction rates at elevated temperatures. Unfortunately, that would also be a difficult experiment to perform. Therefore, no further carbon leaching experiments of any kind are planned.

Graphite Permeability Testing - W. J. Gray and L. R. Bunnell

The water permeability apparatus was redesigned slightly to allow higher pressures. It requires specimens 5/8 in. long and tapered from 0.625 in. dia on one end to 0.515 in. dia on the other end. The specimens were wrapped with Teflon tape and forced into a tapered hole in an aluminum block by the high-pressure water. This method has proved to make a very good seal

so that water does not go around the specimen. Most tests were run at 1000 psi water pressure; in recent tests the pressure was raised to 1500 psi.

Table 2.5 lists the matrix rods supplied by General Atomic Company. The as-received rods were "green;" that is, maximum heat treatment temperatures were about 150°C. Specimens were machined from some of these and permeability tested. Specimens containing A-240 pitch were too soft to be tested. All but one of the others was impermeable (flow rate $<10^{-9}$ ml/sec). Specimen M5 was permeable (flow rate $>10^{-6}$ ml/sec), but this result may not be typical of the M5 material in general, based upon subsequent tests described later.

To achieve the high-temperature stability and radiation resistance necessary for use as a matrix material, some carbonization by high-temperature heat treatment will be required. It is not known how much heat treatment the rods can stand before they become permeable, however. As a start in finding out, some rods were heated to 400°C at 67°/hr and then held at 400°C for 10 hr in an argon atmosphere. Table 2.5 shows that all but one rod looked good visually after the heat treatment.

Specimens were machined from the heat-treated rods that appeared sound. This caused the surfaces of some specimens to become highly cracked and pitted. Apparently the rods had a high density of very small cracks after heat treatment, and machining caused small pieces to fall out of the machined surface.

Permeability tests were run on specimens that survived the heat treatment and machining. Two remained impermeable (flow rate $<10^{-9}$ ml/sec), two were permeable (flow rate $>10^{-6}$ ml/sec), and two shattered in the specimen holder when pressure was applied.

It seems unlikely that the permeability of these materials could be improved by the heat treatment they received. Thus, the results for rod M5 are probably due to variations from one part of the original rod to another.

The cracks that occurred in the different rods during heat treatment and machining may have been caused by a too rapid heating rate. Specimens that shattered in the permeability apparatus may also have had small cracks that weakened them. Maximum compressive stresses expected from the pressure and geometry used were about 4700 psi. Sound specimens should be able to withstand that.

Two other materials were also permeability tested. One was a resin prepared by Fiber Materials, Inc. The other was NiS-bonded graphite prepared by NUKEM in the Federal Republic of Germany. No water penetrated either specimen during 23 hr at 1000 psi.

Matrix Cell Tests - C. Q. Buckwalter

To gain insights into waste form/matrix interaction, test cells were fabricated from candidate matrix material as shown in Figure 2.2. Waste glass PNL-76-68 was leached in these cells at the same conditions as in the MCC-1 test: 90°C deionized water, and 10 m^{-1} surface area to volume ratio. By comparing leachate results from the metal test cell with those of the suggested leach vessel, Teflon, comparative data are obtained to determine the effect of waste form/matrix interaction should the matrix be breached by water. Table 2.6 lists the leachate results of lead, titanium, and the reference Teflon container. The data indicate that the lead matrix decreases glass leaching by two orders of magnitude in all glass components detected. The effect on the container material is thought to be

TABLE 2.5. Permeability and Heat Treatment Results for GA Matrix Rods

Binder Type	Rod No.	Wt% Filler	Density, g/cm ³	Permeability ^(a)	Condition ^(b) After Heat Treatment	Condition After Machining	Permeability ^(a)
A-240 Pitch	M1	40	1.423	Extruded			
	M43	65	1.669				
	M30	75	1.759	Extruded	Good	Good	Shattered
MC-600 Polyimide	M19	0	1.092	Good	Good	Badly Pitted	
	M15	45	1.350	Good	Badly Cracked		
	M28	55	1.470				
	M6	60	1.655				
	M5	70	1.731	Poor	Good	Good	Good
	M20	75	1.613				
Resinox-755 Phenolic	M32	0	1.251	Good	Good	Badly Pitted	
	M34	40	1.511		Good	Good	Poor
	M37	60	1.645				
	M33	65	1.749				
	M16	70	1.719				
	M36	70	1.765	Good	Good	Good	Good
Resinox-755 + Resinox-754	M31	75	1.671				
	M12	0	1.226				
QX-322 Furan Resin	M4	70	1.722				
	M13	0	1.254	Good	Good	Badly Pitted	
	M18	60	1.645		Good	Good	Shattered
	M23	65	1.735				
	M17	70	1.750				
QX-322 + Resinox 755	M21	70	1.759	Good	Good	Good	Poor
	M39	70	1.762				

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

"Good" means no water penetrated the specimens.

"Poor" means water did penetrate the specimen.

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 to 400°C in 6 hr and held at 400°C for 10 hr.

81B464-1

FIGURE 2.2. Matrix Cell Leach Test Container

TABLE 2.6. Leach Results for 76-68 Glass in Matrix Cells^(a)

Cell Type	B	Mo	Na	Si	pH
Teflon	23.0	23.1	21.4	15.6	9.52
Lead	0.7	0.08	1.1	0.1	7.53
Titanium	32.1	35.5	35.4	24.2	9.49

(a) Experimental conditions: 90°C, SA/V = 10 m⁻¹, 14 days.

synergistic because the leaching of the lead apparently decreases by the same orders of magnitude as does a sample of lead leached by itself. Solid-state analysis of the lead container walls reveals no detectable glass constituents sorbed on the sides of the vessel. Leaching apparently increases with the titanium container; however, the effect is experimentally insignificant as it is on the same order of magnitude as Teflon. Titanium itself was inert to leaching.

Coated Particle Characterization - C. Q. Buckwalter

Glass marbles spiked with a small percentage of rare earth and cesium oxides were coated with metals selected for their known

durability. To test the relative durability, the static leach test known as MCC-1 was used as developed by the Materials Characterization Center. The experimental parameters tested were 90°C, deionized water, a surface-area-to-solution volume of 10 m⁻¹, with leaching time periods of 3, 7, 14, and 28 days. All samples were ultrasonically cleaned in absolute ethanol and leached in Teflon vessels cleaned as per MCC-1. After the specified time periods the pH of each room-temperature solution was measured and ICP, rare-earth, and cesium analyses were performed.

The results of leachate analysis indicate that all coatings present an effective barrier to leaching. Table 2.7 shows representative data of three metal coatings

TABLE 2.7. Leach Data for Plasma Spray Coatings on TDS-211 Glass Marbles

Coating	Thickness, μm	Leach Time, day	Normalized Elemental Loss, g/m ² ·day												
			Substrate						Coating						
			Ce	Cs	Nd	Sr	Na	Si	Al	Cr	Cu	Fe	Mo	Ni	Ti
None	0	3	<0.17	4.13	<0.08	1.80	2.63	2.53	-	-	-	-	-	-	-
		14	<0.04	1.21	<0.02	0.29	1.03	0.76	-	-	-	-	-	-	-
Al	600	3	<0.17	0.08	<0.08	<0.02	0.07	<0.003	0.003	-	-	-	-	-	-
		14	<0.04	0.05	<0.02	0.02	0.05	0.001	0.01	-	-	-	-	-	-
Pb	350		<0.17	0.02	<0.08	<0.02	0.01	<0.003	-	-	8.78	-	-	-	-
Sn Alloy	330		<0.17	0.03	<0.08	<0.02	0.003	<0.003	-	0.01	<0.82	<0.2	-	-	-

leached for 14 days. Significant durability gains for silicon are indicated by two to three orders of magnitude. Preserving the structural integrity of silicon, the major structural component in the glass mix, significantly enhances glass durability. Alkali ions are generally the most mobile species in a glass leaching experiment. Inhibition of the mobile ions, such as sodium and cesium, indicates that the barrier is effective for the remaining glass constituents. The conclusion is reached that the durability of the waste form is increased by the use of coatings.

RADIATION EFFECTS

Metamictization - R. E. Haaker and R. C. Ewing, University of New Mexico

A method was developed for growing single crystals of thorium-doped zircon. The crystals, Figure 2.3, contain enough thorium to be detected by SEM-EDS. For most elements, the limit of detection is about 2 wt%. The crystal size is small (0.2 to 0.3 mm) due to the short growth period of only 2 days. The hemispherical particles attached to the zircon crystal shown in Figure 2.3 are SiO_2 -rich glass.

Crystals of cerium-doped thorium silicates grown from a charge having a large excess of cerium were studied by SEM-EDS. Huttonite

FIGURE 2.3. Thorium-Doped Zircon Crystal

crystals grown at 1325°C from a charge having the desired molar proportions $0.9 \text{ ThO}_2:0.1 \text{ CeO}_2:\text{SiO}_2$ do not contain enough cerium to be detected by SEM-EDS. Huttonite, grown at 1325°C with a large excess of cerium, does contain enough cerium to be detected by EDS. Thorite crystals, however, grown at 1000°C even from a charge having a large excess of cerium do not contain enough cerium to be detected by SEM-EDS.

A method for producing high-purity polycrystalline zircon was developed. The

manuscript entitled "A Solution-Gelation Method for Preparing Polycrystalline Zircon" has been submitted to the Ceramic Bulletin. A suite of five natural zircons, showing a wide range of radiation effects, was sent to W. Weber for study at PNL.

Transmutation - W. J. Gray

Final measurements of the ^{134}Cs activity have been completed on samples that were irradiated in the high-flux isotope reactor (HFIR) for 3 months beginning in January 1979. Archive samples of all the materials were chemically analyzed to determine the actual amount of cesium present; most materials lost some cesium during preparation. Taking into account the actual amount of cesium present, 12.0% of the cesium was converted to ^{134}Cs rather than 20% as expected.

The third round of postirradiation examinations has been started. Only optical microscopy has been completed so far. No repolishing was required, so it was possible to examine the same areas as in the past. No changes were found in any samples. Density measurements are under way, and leach tests will begin in July.

X-ray diffraction measurements to date have been unsatisfactory. However, a new x-ray diffractometer for handling highly radioactive samples is now operational for cold samples (perhaps with some fine tuning still to be done). Work on nonradioactive pollucite has been started in preparation for examination of the pollucite irradiated in HFIR.

Hot Cell - C. A. Knox

The occurrence investigation is completed for the two incidents when contaminated solu-

tion was drawn back into lines in the operating gallery. A combination of poor operating procedure and operator error was the cause of both incidents. A final report was prepared and delivered to DOE.

The hot press and accessory equipment (see Figure 2.4) have been prepared for hot-cell installation but were not installed while the investigation was being completed in order to prevent unnecessary exposure to the corrosive cell atmosphere. In anticipation of receiving permission to restart cell activities soon, installation of this equipment has been started.

PROCESS AND EQUIPMENT DEVELOPMENT

Low-Temperature PyC Coatings - B. L. Blanco and M. F. Browning (BCL)

Reduced pressure fluidized-bed runs were made applying low-temperature PyC coatings to SPC-4E particles of varying sizes. In these runs, reagent concentration, reactor temperature and coating time were varied in an effort to improve coating quality. Preliminary tests indicated the following:

1. It was possible to fluidize larger SPC-4E particles by reducing the pressure.
2. Coating rates could be maintained at the same level as those obtained at atmospheric pressure using essentially the same parameters.
3. The porosity of the low-temperature PyC coatings appeared to be reduced; however, the coating continuity, adhesion and uniformity, as determined microscopically, was not significantly improved over that obtained at atmospheric pressure.

8102547-2

FIGURE 2.4. Hot Press and Accessory Equipment for Hot Cell Waste Form Fabrication

High-Temperature PyC Coatings - J. L. Kae
(GAC)

Investigations were started for coating an SRL composition calcine with a lead frit binder sintered at 1175°C for 1 hr. Coatings were deposited by chemical vapor deposition in a fluidized bed of particles. Before coating, the calcine was sieved to separate particles <417 μm in diameter from the charge for the coater. In an initial coating test, at 1150°C with carbon deposition through the decomposition of acetylene,

the batch of particles coalesced into one large agglomerate in the coater. It is thought that this occurred because the particles began to melt or to soften at this temperature; therefore, all subsequent coating studies were carried out at temperatures of 1100°C or less. The coating runs made to date are listed in Table 2.8. A series of four different coating runs were made in order to determine the best conditions for carbon coating of the calcine particles. The optimum conditions were a temperature of 1050°C and an acetylene flow that gave a

TABLE 2.8. Coating Runs Made to Date on SRL Composition Calcine

Coating No.	Temperature, °C	Coating Source Gas	Coating Deposition Rate, $\mu\text{m}/\text{min}$	Coating Thickness, μm	Comments
8322-129	1100	C_2H_2	0.5	32	Many broken coatings
8322-131	1100	C_2H_2	0.3	50	Some broken coatings
8423-81	1000	C_2H_2	-	-	No appreciable coatings
8423-83	1050	C_2H_2	3.1	185	Excellent coating
8323-142	700	SiH_4	0.5	90	Many broken coatings
8322-143	700	SiH_4	1.0	130	Excellent coating

coating rate of 3 $\mu\text{m}/\text{min}$. The particles of Run 8423-83 (Figure 2.5) had the best coating integrity, and these particles have been submitted to PNL for leach-testing.

Calcine particles were sealed with a silicon coating at 700°C so that carbon coatings could be deposited at higher temperatures. Two different coating runs were made to determine the best conditions. Coating breakage was eliminated by adjusting the SiH_4 flow so that the coating deposition rate was about 1 $\mu\text{m}/\text{min}$. A cross section of particles from the silicon coating batch 8322-143 is shown in Figure 2.6. Pyrocarbon coating of particles from this batch with the good silicon coating is currently in progress.

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

Simulated waste marbles were coated with aluminum for the lead encapsulation demonstration. The marbles were preheated to 300°C in ~7-kg batches. Each batch was coated for 20 min using the wire spray gun and marble agitator. The total weight of the uncoated marbles was 56 kg, and the coated marbles weighed 62 kg. The average

deposition rate was 2.3 kg/hr (5.0 lb/hr); higher rates have since been obtained.

Coated marbles were delivered to SRL for the comparative leach test. Two coating batches were sent: 1) 500 g of lead-coated marbles produced using the wire spray process and 2) 600 g of aluminum-coated marbles produced using the plasma spray process.

Installation of a METCO 7M[®] plasma spray coating system has been completed. Factory representatives assisted in the startup and testing of the unit. A chromium oxide-silica composite and a self-fusing molybdenum blend were plasma-sprayed by the new unit onto small batches of TDS 211 glass marbles in a vibrated agitator. The coatings are currently being evaluated.

A rotating marble agitator powered by a variable-speed cement mixer drive has been fabricated for use with the thermal spray guns. The base of the agitator barrel consists of a 4 mesh SS screen which contains the marbles while allowing heat and gas from the thermal spray gun to pass through.

[®]Registered trademark of METCO, Inc., Westbury, New York.

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X100

FIGURE 2.5. Cross Section of Particles Coated with PyC in Run 8423-83

81F800-1

X100

FIGURE 2.6. Cross Section of Particles Coated with Silicon in Run 8322-143

Metal Matrix Demonstration

Encapsulation - R. G. Nelson

A canister of coated marbles has been filled with pure lead using a vacuum casting technique. The canister measures 20 cm

(8 in.) dia by 91 cm (36 in.) length and contains 25 kg of aluminum-coated marbles 1 cm in diameter inside an inner container 18 cm (7 in.) dia by 61 cm (24 in.) long (Nelson, Nesbitt and Slate 1981). The marble-filled canister was preheated for 16 hr at 350°C. Four hours before pouring,

the preheat furnace was set at 400°C; then the 185 kg of lead were poured at 410°C. The duration of the pour was 1.5 to 2 min, considerably longer than the 1-min pour made previously (Nelson, Nesbitt and Slate 1981). The longer pour time was due to a slight modification of the pouring nozzle, and it resulted in overflowing the funnel and spilling about 18 kg of lead.

The lead level just covered the inner container, and the shrink cavity extended about 5 cm (2 in.) into the marbles. During sectioning of the canister it was noted that not a single marble was removed by the rough (4 teeth per inch) cutting action of the power hacksaw blade. Previous experience (Nelson, Nesbitt and Slate 1981) with uncoated marbles vacuum cast in a 90% Pb - 10% Sn alloy showed that a few of the marbles were removed during sectioning with the power hacksaw.

Metallographic examination of the aluminum-coated marbles in the lead matrix showed that the lead had completely infiltrated the marble stack. The porous 0.3 mm (0.012 in.) thick aluminum coating was also infiltrated with the lead. In a few instances the lead nearly reached the marble surface. This infiltration of the aluminum coating by the lead matrix forms a tight mechanical bond between the aluminum coating and the lead matrix.

Documentation - J. F. Nesbitt

A document entitled Nuclear Waste Encapsulation by Metal Matrix Casting, PNL-3750, has been issued. It describes several encapsulation casting processes developed or used at the Pacific Northwest Laboratory to embed simulated high-level wastes of two different forms (glass marbles and ceramic pellets) in metal matrices.

These demonstrations have shown that 5- to 10 mm-dia glass marbles can be encapsulated on an engineering scale with lead or lead alloys by gravity or vacuum processes. Marbles 12 mm in diameter were successfully encapsulated in a lead alloy on a production scale. Also, 4- to 9-mm-dia ceramic pellets in containers of various sizes were completely penetrated, and the individual pellets were encased with aluminum-12 wt% silicon alloy by vacuum processes. Indications are that of the casting processes tested, aluminum-12 wt% silicon alloy vacuum cast around ceramic pellets had the highest degree of infiltration or coverage of pellet surfaces.

REFERENCE

Nelson, R. G., J. F. Nesbitt and S. C. Slate. 1981. Nuclear-Waste Encapsulation by Metal-Matrix Casting. PNL-3750, Pacific Northwest Laboratory, Richland, Washington.

3. TMI ZEOLITE VITRIFICATION DEMONSTRATION PROGRAM

D. H. Siemens - Project 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

Approximately 790,000 gal of high-activity-level water at the Three Mile Island Unit 2 Nuclear Power Station will be decontaminated with the submerged demineralizer system (SDS). The SDS process flowsheet is shown in Figure 3.1. Based on samples of this water, there is estimated to be a total of 4.97×10^5 curies of activity present. This activity is primarily cesium (~96%) and strontium (~3%).

The cesium and strontium (therefore, the bulk of the activity) are sorbed onto zeolite. For final decontamination, the waste water is passed from the zeolite liners through an organic cation exchange resin and finally through a polishing bed containing layers of cation resin, anion resin and mixed resin. The zeolite is contained in stainless steel liners. Each liner contains ~8 ft³ of zeolite. Present plans are to load 60,000 curies of activity per liner.

The purpose of the program is to demonstrate a process to immobilize the SDS zeolite as a glass product. The process will be demonstrated (both nonradioactively and radioactively) from receipt of the liners containing the zeolite through preparation of the vitrified zeolite. The glass product

will be prepared by melting of the zeolite with glass formers in an in-can melter (ICM) at a temperature of 1000 to 1075°C. A conceptual ICM feed system is shown in Figure 3.2.

The demonstrations will be performed in the 324 Building. All nonradioactive activities will be performed in the Engineering Development Laboratory (EDL). The radioactive demonstration will be performed in the Radiochemical Engineering Cell Complex. Vitrification and effluent treatment equipment, already developed as part of the High-Level Waste Immobilization Program, is presently installed in the building and, to the extent practical, will be used in the ZVD Program.

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

Laboratory-scale tests were conducted to identify a suitable glass formulation for immobilizing the SDS zeolite. The objective of those tests was to identify a durable glass formulation with the maximum volume of zeolite incorporated into the final product. It was also desirable to find a composition that did not require costly pretreatment of the zeolite (crushing, grinding, etc.). The

FIGURE 3.1. Submerged Demineralizer System (SDS) Process Flowsheet

glass formulation selected for use with Linde Ionsiv IE-95[®] ion exchanger had a zeolite loading of ~70% by weight. However, a recent decision to add Linde Ionsiv A-51[®] ion exchanger to the IE-95 in an undetermined ratio has been made, and the final glass formulation has not been selected. The glasses tested were prepared with zeolite loaded with nonradioactive cesium and strontium and were subjected to visual examinations and leaching tests. Fluctuations in the cesium loading on the zeolite will not affect the vitrification process, as it will be designed on the basis of the zeolite and not the cesium loading.

[®]Registered trademark of the Linde Division of Union Carbide Corporation

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

Design, fabrication and installation of the vitrification system shown in Figure 3.2 is complete. The zeolite is dried by pulling heated air through the SDS liner (after the zeolite is dried, it is transferred into the mixer-feeder). Glass former is then added, and the mixture is homogenized within the mixer/feeder by tumbling. This mixture will then be added at a controlled rate to the canister by use of a variable-speed star valve. A tube-type furnace will be used to maintain the canister at 1050°C throughout the addition of the glass former/zeolite.

FIGURE 3.2. Zeolite Vitrification System

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 MCC-1 Static Leach Test Method and MCC-2 Static, High-Temperature Leach Test Method were approved by the MRB. Comparative studies of different waste-form materials are continuing for Savannah River Laboratory (SRL). In another study, the actinide concentrations of defense transuranic wastes were analyzed and the potential effects of the radiation on the properties of the wastes after conversion to immobile forms were assessed. Specialized equipment, such as the shielded x-ray diffractometer, a scanning electron microscope, a cyclone particle separator, and fines collection chamber, was installed to assist in studies of waste-form and engineered-barrier properties.

A State-of-the-Art Review of Materials Properties of Nuclear Waste Forms and a report summarizing the MCC Workshop on Compositional and Microstructural Analysis were published this quarter.

STANDARDIZED TEST METHODS - J. E. Mendel, M. D. Merz, D. M. Strachan, and W. J. Weber

Work is continuing on the preparation of all planned waste-form and engineered-barrier

test methods. These test methods were summarized in the last quarterly report (Chikalla and Powell 1981). Significant accomplishments this past quarter relative to these test methods are as follows:

- Both the MCC-1 Static Leach Test Method and the MCC-2 Static, High-Temperature Leach Test Method were approved by the full MRB for inclusion in the Nuclear Waste Materials Handbook.
- The MCC-6 Method for Testing Alpha-Decay Effects in Radioactive Waste Forms and the MCC-11 Tensile-Strength Test Method were reviewed by the MRB Procedures Panel and are being revised to reflect their comments.

TESTING - M. D. Merz, D. M. Strachan, and W. J. Weber

Testing in support of the MCC test methods is continuing. In particular, tests have been conducted on sieving analysis for the MCC-10 Brittle-Materials Impact Test. In addition, comparative testing, using MCC test methods, is under way for Savannah River Laboratory to provide data that will assist SRL in selecting waste forms. Being tested by all five MCC leach tests are glasses from SRL and Catholic University of America,

tailored ceramics from Rockwell Science Center, two types of SYNROC from Lawrence Livermore Laboratory, and pyrolytic carbon-coated sol-gel SYNROC particles from Oak Ridge National Laboratory. These materials will also be tested using MCC-7 (thermal phase stability), MCC-8 (vaporization), MCC-9 (gas pressurization), MCC-10 (impact), and MCC-11 (tensile strength); but the testing will be limited because some of these tests require more sample material than is currently available.

Actinide concentrations of defense transuranic (TRU) wastes were analyzed, and the potential effects of the radiation on the properties of the wastes after conversion to immobile forms were assessed. Conclusions based on this study, which was done in support of the MCC test methods, were that 1) accumulated beta-gamma doses will be 10^6 to 10^8 rad over a 10^5 -yr storage period and such doses should not significantly change physical properties of the waste forms and 2) alpha-decay doses will be 3 to 30×10^{16} decays/cm³ accumulated over a 10^5 -yr storage period and consequent changes in microstructure and phase stability should be negligible. Other conclusions will also be summarized in PNL-3913, An Assessment of Radiation Effects in Defense Transuranic Waste Forms.

A draft report of the MCC-1 Static Leach Test round robin and the associated analytical round robin is being reviewed and revised. This leach test round robin has made it possible to evaluate data obtained by 15 different operators using the same leach test method. The associated analytical round robin is yielding an estimate of how much of the overall variance in leach test data is due to lack of precision, or bias, in leachate analyses and how much is due to other factors such as variability in specimen surface characteristics. The resulting report describes the comprehensive statisti-

cal treatment that has been completed on the massive data base from these round robins.

TESTING EQUIPMENT - J. L. Daniel and M. D. Merz

The shielded x-ray diffractometer (SXR) was installed and is operating satisfactorily. The specimen chamber is enclosed in 4 in. of lead shielding, with provision for additional shielding if needed. A graphite monochromator and a solid-state, energy-dispersive detector allowed effective shielding of the detector for good signal-to-noise ratio.

The MCC scanning electron microscope (SEM) was installed. Point-to-point image resolution of better than 100 Å was achieved even at the long working distance (39 mm) to be used for study of radioactive materials. Both high-resolution, back-scattered and secondary electron imaging are provided. The microscope can now be used for low-level and nonradioactive specimens. A shielded enclosure is being designed to provide an additional 4 in. of lead shielding for hot nuclear waste studies. X-ray fluorescence capability will be added in August 1981.

Metallography equipment for sample preparation in the hot cell was received and is being modified for routine use by manipulators in the cell. Standard commercial metallographic saws, polishers, grinders, evaporator, and cleaning equipment are being used throughout. The specimen transfer interface between hot-cell interior and transfer cask has been designed to provide safe, efficient movement of prepared specimens via the cask from the hot cell to the SXR and SSEM. The interface allows direct insertion of specimens into the transfer cask with minimal surface contamination, while allowing for complete closure of the hot-cell ports when not in use.

The cyclone particle separator and the fines collection chamber were built and installed for use with the MCC-10 Brittle-Materials Impact Test Method. Also, static and cyclic-loaded test apparatus is being constructed for crack-initiation and crack-growth studies to develop stress corrosion test methods.

Construction continued on the radiation autoclave facility for radiation corrosion testing. The equipment will provide the basis for the MCC-105 Radiation Corrosion Test Method. The MCC is working with the Barriers Development Program at PNL, which has primary responsibility for operating the autoclave, to assist in establishing appropriate test parameters and capital support.

ANALYTICAL METHODS - J. L. Daniel

A report was published that summarizes the MCC Workshop on Compositional and Microstructural Analysis (Daniel et al. 1981). This document identifies the analytical methods favored by the workshop participants, discusses analytical areas that need attention, recommends ways to verify inter-laboratory correlation and comparability of analytical data, and lists specific standards and reference materials currently used in the laboratories represented. Among the conclusions discussed in the report are the following:

- Analytical round-robin tests of reference specimens should be conducted with the MCC-1 Static Leach Test Method round robin.
- Most laboratories are not sufficiently evaluating the statistical significance of analytical data.
- The analytical methods to be used to test MCC procedures should not be specified; this will permit each laboratory to use

its preferred methods. However, similar results from analysis of appropriate reference materials must be demonstrated.

- Since there are currently no certified materials entirely suitable for use as references to verify analytical procedures for nuclear waste materials, other generally available NBS standards should be used to check basic methods until specific reference materials are available.
- Surface analysis methods are of increasing importance in predicting long-term behavior of highly stable waste forms.
- Analytical data submitted to the MCC should always include a current analysis of the best available reference material or standard and a statement of the analytical precision for each element reported.

INFORMATION DISSEMINATION - R. D. Nelson, J. E. Mendel, and J. L. Hooper

A State-of-the-Art Review of Materials Properties of Nuclear Waste Forms, PNL-3802, was published this quarter. This document summarizes the existing data on physical properties, mechanical properties, chemical durability, vaporization, radiation effects, and thermal phase stability for the nuclear waste forms being developed for immobilization of high-level radioactive waste.

Work is continuing on the Nuclear Waste Materials Handbook, which will be issued in September. Experts in the field of handbook preparation have been consulted concerning the most efficient method of updating and monitoring the assigned handbooks. In addition, a format is being developed to facilitate access to, and use of, the needed data and test methods.

A paper, "Standard Tests for Nuclear Waste Materials," was presented to the International Seminar on Chemistry and Process

Engineering for High-Level Liquid Waste Solidification Meeting in Jülich, FRG, by R. D. Nelson, MCC Program Manager.

MCC WORKSHOPS - W. J. Weber and M. D. Merz

A second MCC Workshop on Irradiation Effects in Nuclear Waste Forms has been planned and will be held August 13-14, 1981, at Battelle Seattle Research Center in Seattle, Washington. The purpose of the workshop is to describe the current status of the MCC-6 Method for Preparation and Characterization of Actinide-Doped Waste Forms, examine the issues associated with other simulation techniques and ionization damage, and discuss additional test procedures that may be required.

A meeting on "Design-Relevant Stress Corrosion Cracking of Nuclear Waste Engineered Barriers" has been planned for August 6, 1981, at Pacific Northwest Laboratory. Ex-

perts on stress corrosion will discuss the determination of threshold stresses from crack-growth measurements. These discussions will provide the basis for developing the MCC-104 Stress-Corrosion, Crack-Growth Test Method.

REFERENCES

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- Daniel, J. L., D. M. Strachan, J. W. Shade, and M. T. Thomas. 1981. Materials Characterization Center Workshop on Compositional and Microstructural Analysis of Nuclear Waste Materials Summary Report. PNL-3832, Pacific Northwest Laboratory, Richland, Washington.
- Mendel, J. E. et al. 1981. A State-of-the-Art Review of Materials Properties of Nuclear Waste Forms. PNL-3802, Pacific Northwest Laboratory, Richland, Washington.

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

Activities for this quarter have focused on 1) obtaining data for the comparative assessment of TRU products and processes and 2) completing development work on low leach-rate waste forms.

Further characterization of plutonium-containing TRU waste treated to form monazite crystals has shown that plutonium is taken into the crystals. However, quantitative determination of the distribution of plutonium between crystals and matrix has not been possible due to the uniform distribution and small size ($\sim 1 \mu\text{m}$) of the crystals. Leach tests of second-generation basalt glass ceramics have continued to show that the crystallized waste form has significantly improved over its vitreous parent. Longer-term tests are needed, however, to evaluate potential pH effects; pH values have been quite different but now appear to be approaching each other after 28 days. A plutonium-containing second-generation basalt glass ceramic has been fabricated and is being leach tested. Tests were completed on aluminosilicate and borosilicate glasses to determine their tolerance to composition changes. The laboratory tests on viscosity and chemical durability indicate that waste variability will not be a serious problem.

Leach tests of 28 and 56 days have been completed on the comparative study samples.

Normalized mass loss for plutonium from each waste form is nearly constant with time, which indicates a saturation of the solution early in the test. The plutonium mass loss values are the lowest of the elements measured. Microstructural characterization of the samples has also been completed.

Estimates of capital, operating, transportation, and disposal costs of the six reference processes were completed. Cast cement has the lowest cost of the alternatives.

GLASS DEVELOPMENT - L. J. Ethridge and G. B. Mellinger

One characteristic of a successful waste immobilization system is that it must be able to accommodate expected variations in waste composition. Variations in waste composition must not lead to a product that is unacceptable from the standpoint of either product or processing. For this reason, we studied the effects of waste variability on the borosilicate and aluminosilicate glasses developed for vitrification of the Rocky Flats Plant sludge-ash mixture.

Properties studied were viscosity and chemical durability. Viscosity is an important processing property since excessive viscosity in glass might slow production or yield a poorly homogenized product. Alternatively, a very low viscosity melt might

lead to excessive refractory wear. Chemical durability is important because this property may significantly influence the rate of release of radionuclides in the waste repository. Three methods were used to measure chemical durability: the Soxhlet test, pH-4 tests (Mendel 1977) and the 14-day MCC-1 test.

Table 5.1 shows the defined waste composition and the ranges expected for each component. Twelve variants were chosen for testing; they were selected to produce the widest possible range of properties. Glasses were made using a waste loading of 50 wt% waste oxides. A glass containing waste high in SiO_2 and Al_2O_3 and low in alkali and alkaline earth was tested to determine the maximum viscosity that might occur. A glass with a minimum of SiO_2 , Al_2O_3 and TiO_2 but maximum alkali and alkaline earth was produced to determine minimum chemical durability and viscosity.

The viscosities of all glasses were found acceptable and were below the recommended

maximum of 200 poise at design process temperatures of 1050°C for the borosilicate and 1350°C for the aluminosilicate glass. None had a viscosity less than 20 poise. The minimum, maximum and average viscosity values are tabulated in Table 5.2.

Uniformly high chemical durabilities were found for all glasses and are shown in Table 5.2 along with a reference 76-68 high-level waste (HLW) glass. Soxhlet weight losses were all less than those found for 76-68 glass. Values for pH-4 were much higher than those for 76-68 glass, which was designed specifically to do well in this test. In the MCC-1 test, borosilicate glasses had normalized losses that were slightly less than those of 76-68. The aluminosilicate losses were much lower.

Based on the viscosity and chemical durability testing, we concluded that for either the borosilicate or aluminosilicate glass anticipated waste variations will not give an unacceptable product.

TABLE 5.1. As-Defined Composition of Rocky Flats Sludge-Ash Mixture, Anticipated Variation, and Variants Studied

Component	Wt%		Variants (a)			
	As Defined	Variation				
Al_2O_3	6.87	3.7 - 10.0	- + -	- + +	- + M	- - + ^(b)
CaO	7.52	3.5 - 12.5	- M M	⊕ M -	+ M -	⊕ - +
Fe_2O_3	16.03	13.8 - 22.0	⊕ M ⊕	+ + M	M + M	- - +
MgO	4.03	2.3 - 7.0	- M M	M M -	+ ⊖ -	⊕ - +
Na_2O	6.7	4.0 - 8.0	- - -	+ M ⊕	+ - ⊕	+ - +
P_2O_5	5.52	2.6 - 7.3	- M ⊕	+ M M	M M +	⊕ - +
SiO_2	41.66	34.0 - 48.0	+ + -	⊖ M M	M + M	- - +
TiO_2	7.16	5.0 - 10.0	⊕ M -	- M M	M ⊖ +	+ - +
K_2O	0.5	0.5				
ZnO	0.5	0.5				
Other	3.51	-				
	100.00					

(a) + is high value; - is low value; ⊕ is within 1% of high value; ⊖ is within 1% of low value; M is near middle of range.

(b) Low and high values are normalized to 99%.

TABLE 5.2. Summary of Viscosity and Chemical Durability Behavior of Borosilicate and Aluminosilicate Glasses

Material	Viscosity, ^(a) poise	Chemical Durability			
		Soxhlet, 24 hr, wt% loss	pH-4, 19 hr, wt% loss	MCC-1, 14 days, g/m ²	
				Na	Si
<u>Borosilicate</u>					
Low	20	0.7	0.3	8	7
High	170	1.2	5.6	17	11
Average	100	0.9	0.9	13	9
<u>Aluminosilicate</u>					
Low	30	0.3	<0.1	2	1
High	120	0.6	0.4	5	4
Average	70	0.4	0.1	4	3
76-68	200	1.6	<0.1	13	10

(a) Borosilicate and 76-68 were measured at 1050°C, aluminosilicate at 1350°C.

BASALT GLASS-CERAMIC CHARACTERIZATION -

L. A. Chick, R. O. Lokken, R. P. May and V. L. Coburn

In the previous quarter, the composition and heat treatments for the second-generation basalt glass ceramics (BGCs) were presented along with 7-day results from MCC-1 static leach testing. During this quarter, 28-day leach testing was completed, x-ray diffraction (XRD) phase identification was finished, and characterization by scanning-transmission electron microscope (STEM) was begun.

Table 5.3 lists the phases estimated by XRD. The major phases are an iron titanate that yields XRD peaks similar to spinel, and a pyroxene mineral similar to augite. An iron phase (hematite) and one or a few unknown phases are also found in the XRD patterns.

Figure 5.1 is a dark field-transmission electron micrograph of an ion-thinned section of specimen BGC-35-2, the most crystalline sample. Energy dispersive x-ray microanalysis, using an ultrathin window, determined the compositions at several points shown in the figure. These are identified

in Table 5.4. Included are three analyses of the residual glass matrix. These results generally agree with the XRD findings for BGC-35-2. They indicate that the "unknown" phases may be a calcium-alumino-silicate-phosphate and iron-alumino-magnesium-sodium-silicate.

Figures 5.2 and 5.3 show static (MCC-1) leaching data up to 28 days for the parent glasses versus the glass ceramics. Figure 5.2, which shows silicon release, reveals a four- to eightfold decrease in release upon heat treatment, depending upon the particular formulation. These curves are typical of all elements detected in solution. Notice that the silicon release rate for the glass ceramics begins to increase between 14 to 28 days. This is probably explained by the corresponding shift from acid to basic pH as shown in Figure 5.3. More OH⁻ becomes available to attack the SiO₂ network as the pH becomes more basic. Longer-term leaching tests are under way to investigate the increasing leach rates.

It is expected that the composition of the residual glass controls the leaching

TABLE 5.3. Basalt Glass Ceramic Crystallinity Determined by XRD

Sample	wt%				Total
	Hematite ^(a)	Spinel ^(b)	Pyroxene ^(c)	Unknown ^(d)	
BGC-35-1	7	8	18	1	34
BGC-35-2	-	19	20	5	44
BGC-50	6	9	15	2	32
BGC-63	2	14	13	6	35

- (a) Fe_2O_3 may contain Zr, Cr, Al, Ti or Mg as iron substitute-phase impurities.
- (b) $(\text{Fe}, \text{Ti})\text{Fe}_2\text{O}_4$ may have the same phase impurities as hematite. Also, it may have a slightly different structure than spinel according to preliminary STEM diffraction data.
- (c) $(\text{Mg}, \text{Ca}, \text{Al}, \text{Fe})\text{SiO}_3$ may contain Na and minor amounts of Cr, Ti, or Zn.
- (d) Several unidentified peaks in XRD scans could be attributed to phases seen in STEM work--Ca-Al-Si-P and Fe-Al-Mg-Na-Si.

FIGURE 5.1. Dark Field-Transmission Micrograph (40,000X) of Ion-Thinned Basalt Glass Ceramic BGC-35-2 Showing Areas and Crystals Analyzed

behavior of the glass ceramics. Table 5.5 compares the residual glass matrix composition (average of three analyses in Table 5.4 converted to oxides) with the parent glass composition (analysis by ICP). Evaluation of the matrix composition data in Table 5.4

shows that SiO_2 and Al_2O_3 are enriched from 59 to 90%, whereas Na_2O , MgO and CaO are depleted from 18 to 5% in the residual glass upon crystallization of the glass ceramic. This illustrates why the heat-treated glass ceramics leach much more slowly than the parent glasses, since it is well known that increasing the SiO_2 or Al_2O_3 contents of glasses increases their durability in neutral or basic environments, and that increasing Na_2O content, and in some cases MgO and CaO content, will tend to decrease durability.

MONAZITE FORMATION IN TAILORED TRU WASTE COMPOSITIONS - R. P. May

The mineral monazite (rare-earth phosphate) is a potential host phase for plutonium in TRU wastes. Monazite can be formed in TRU wastes by the "tailoring" of these simulated wastes with additions of rare earth oxides. The percent yield of monazite is primarily a function of heat treatment though adding excess phosphate also increases the percent yield (May 1981).

This quarter the yields of monazite and the microstructures of several samples that were prepared with thorium and with

TABLE 5.4. Basalt Glass Ceramic BGC-35-2 Compositions by Energy Dispersive X-ray Microanalysis, wt%

Identif. Analysis (Fig. 5.1)	Phase Type	O ^(a)	Na	Mg	Al	Si	P	Ca	Ti	Fe
A	Fe-Ti-O	14.3	0.8	2.4	1.4	0.4	--	0.2	16.3	64.3
B	Matrix	41.9	0.3	0.4	9.1	45.5	--	1.1	0.5	1.2
C	Pyroxene	34.5	1.1	14.1	4.1	32.0	--	5.3	0.6	8.4
D	Matrix	40.9	0.3	0.9	10.6	42.1	--	2.7	0.4	2.6
E	Pyroxene	31.7	2.0	15.5	3.8	26.6	--	12.3	0.7	7.6
F	Unidentified	19.5	3.1	5.6	6.4	3.7	--	2.3	3.4	56.1
G	Matrix	38.9	0.8	2.5	13.5	33.3	--	2.7	1.0	7.3
H	Ca-P-Si-O	28.3	--	0.7	7.6	23.2	12.0	26.0	0.5	1.8
I	Ca-P-Si-O	34.6	0.9	1.0	5.6	14.2	12.6	28.2	0.3	2.6

(a) Oxygen was determined directly with thin-window x-ray detector.

plutonium are reported. Two samples containing thorium were selected for replication using plutonium in an effort to determine the phase location and distribution of plutonium in heat-treated "tailored" TRU wastes. All samples were heat-treated identically: 1 hr melt at 1300°C; slow cool at 6°C/hr between 900 and 500°C and then reheated and held for 15 days at 800°C before cooling to room temperature. The two thorium samples were heat-treated in air; the plutonium samples were heat-treated in a nitrogen-filled glove box atmosphere. Table 5.6 summarizes the results obtained by semiquantitative x-ray diffraction.

Total crystallinity values for the plutonium samples were both about 75% of the total crystallinity of the thorium samples. This may be a result of the different atmospheres under which these two pairs of samples were heat-treated. The amount of RE phosphate formed in each pair of compositions is, however, very similar. Energy-dispersive analysis on a scanning electron microscope indicated that the monazite phase was significantly enriched in either thorium or plutonium. Quantitative analysis of the plutonium distribution by α -autoradiography

was not possible due to the submicron crystal size. These tests have shown that it is possible to incorporate plutonium into the monazite crystal in a complex chemistry, but further tests and development are needed to allow this approach to be used.

STATIC LEACH TESTS OF COMPARATIVE-STUDY

SAMPLES - F. P. Roberts, J. H. Westsik, Jr., and C. O. Harvey

Static leach testing of the six reference TRU waste forms being characterized in a comparative study has been partially completed. The testing employs the MCC-1 static leach test and the test matrix shown in Table 5.7, which includes both 40 and 90°C temperatures. To date, the 28-day tests at 40°C, and the 3-, 7-, 14-, 28-, and 56-day tests at 90°C have been completed. The waste forms were prepared in the laboratory and contain plutonium-bearing Rocky Flats Plant ash to enable a determination of plutonium and americium leach behavior. The plutonium activity in the waste forms ranged from 4 to 7 $\mu\text{Ci/g}$; the americium activity was about 7% that of the plutonium.

FIGURE 5.2. Silicon Release Versus Time for Static Leach (MCC-1) Test

FIGURE 5.3. pH Versus Time for Static Leach (MCC-1) Test

TABLE 5.5. Comparison of Compositions of BG-35 Parent Glass to Residual Glass in BGC-35-2 Glass Ceramic

Oxide	Parent ^(a) Glass BG-35, wt%	Residual ^(b) Glass in BGC-35-2, wt%
SiO ₂	47.7	72.2
P ₂ O ₅	2.3	--
Al ₂ O ₃	10.9	17.6
Na ₂ O	4.9	0.5
MgO	5.7	1.8
CaO	9.1	2.5
TiO ₂	4.1	0.9
Fe ₂ O ₃	14.6	4.5

(a) Analysis performed by KOH fusion followed by inductively coupled plasma atomic emission spectroscopy.

(b) Average of three analyses converted to oxide compositions. Analyses performed by energy dispersive x-ray microanalysis on a 200-keV STEM.

The MCC-1 static leach test was adhered to in all respects except that the leachate was acidified to a concentration of 2.0M at the end of the test instead of 0.16M as specified in the test procedure. The higher acid concentration was required to completely dissolve the plutonium adsorbed on leach vessel surfaces.

The elemental releases expressed as normalized mass loss ($\text{g}\cdot\text{m}^{-2}$) are given in Table 5.8 (the 40°C tests) and Table 5.9 (the 90°C tests). The leachate pH's determined at the end of the tests are also given. The following observations can be made from these data:

TABLE 5.6. Phase Determinations for Heat-Treated Tailored TRU Wastes (wt% crystallinity ± 1 wt%)

Compositions	TRU Wastes Plus 5 wt% Rare-earth Oxides and 15 wt% P ₂ O ₅			
	0.1 wt% Th	0.1 wt% Pu	0.1 wt% Th	0.1 wt% Pu
[Ca, Re]PO ₄	3	3.5	5.5	5.5
Ca-RE-B-Si-O	trace } 3	3.0 } 6.5	3.0 } 8.5	1.5 } 7
Fe ₂ O ₃	13	2	4	4
(Fe,Ti)Fe ₂ O ₄	} 3	} 6	4	} 3
Fe ₂ TiO ₅			4	
MgAl ₂ O ₄	--	--	2	3
Total	19	14.5	22.5	17

TABLE 5.7. Test Matrix for TRU Waste Form Leach Tests

90°C Tests	Days	3	7	14	28	56	91	182
	Number of Samples at Each Time							
Silicate solution					3			3
Brine solution					3			3
Deionized water		1	1	1	3	2	2	3
40°C Tests								
	Silicate solution				1			1
	Brine solution				1			1
	Deionized water				3			3

TABLE 5.8. Normalized Mass Losses, g/m², of TRU Waste Forms Leached 28 Days at 40°C

Leachant	Cast Cement	Cold-Pressed Cement	Borosilicate Glass	Alumino-Silicate Glass	Cold-Pressed Sintered Ceramic	Basalt Glass Ceramic
Deionized water						
Al	20.9 ± 0.8	10.6 ± 0.3	-	0.073 ± 0.011	0.23 ± 0.06	0.14 ± 0.02
Ca	87 ± 7	66 ± 3	0.34 ± 0.03	0.99 ± 0.13	18 ± 14	0.21 ± 0.07
Fe	0.092 ± 0.027	0.071 ± 0.052	-	0.26 ± 0.14	-	0.051 ± 0.054
Mg	-	-	0.36 ± 0.05	1.03 ± 0.17	5.9 ± 3.6	-
Na	876 ± 48	1160 ± 20	-	0.61 ± 0.46	1.4 ± 0.3	-
Si	1.4 ± 0.3	1.8 ± 1.3	0.32 ± 0.03	0.43 ± 0.05	0.26 ± 0.14	0.11 ± 0.02
Pu	2.3E-3 ± 2.4E-3	1.7E-3 ± 0.5E-3	0.030 ± 0.014	2.2E-3 ± 1.3E-3	6.7E-3 ± 3.3E-3	0.016 ± 0.004
pH	11.4	11.3	5.0	5.3	4.6	4.2
Brine						
Pu	0.024	0.068	0.017	2.6E-3	0.014	4.8E-3
pH	8.5	8.5	6.8	6.3	6.2	6.3
Silicate solution						
Al	11	2.4	-	0.081	0.066	0.062
Ca	49	24	0.074	0.038	13	0.070
Fe	0.057	4.7E-3	0.013	0.012	0.025	0.026
Mg	-	-	1.7	0.54	6.1	-
Na	820	980	-	-	-	-
Pu	2.1E-4	4.2E-3	1.4E-3	1.9E-3	0.012	0.011
pH	11.8	11.7	8.2	8.4	8.4	8.4

TABLE 5.9. Normalized Mass Losses, g/m², of TRU Waste Forms Leached 28 Days at 90°C

Leachant	Cast Cement	Cold-Pressed Cement	Borosilicate Glass	Alumino-Silicate Glass	Cold Pressed Sintered Ceramic	Basalt Glass Ceramic
Deionized water						
Al	18.8 ± 0.9	8.22 ± 0.09	3.24 ± 0.46	3.05 ± 0.81	0.41 ± 0.03	0.17 ± 0.13
Ca	48.3 ± 5.0	31.5 ± 5.9	4.52 ± 0.22	5.54 ± 1.26	9.03 ± 4.30	0.86 ± 0.15
Fe	0.11 ± 0.05	0.032 ± 0.03	-	1.9 ± 1.4	-	-
Mg	-	-	2.03 ± 1.13	6.53 ± 0.44	5.13 ± 2.51	0.67 ± 0.05
Na	1060 ± 140	1280 ± 180	15.3 ± 2.4	9.06 ± 0.46	3.66 ± 1.31	1.67 ± 0.60
Si	2.74 ± 0.34	5.34 ± 0.90	12.2 ± 2.4	6.67 ± 0.26	0.96 ± 0.11	1.02 ± 0.07
Pu	0.003 ± 0.004	0.0014 ± 0.0005	0.0029 ± 0.0007	0.0048 ± 0.0004	0.014 ± 0.003	0.032 ± 0.015
pH	11.8	11.7	9.5	8.7	5.4	5.6
Brine						
Pu	0.016 ± 0.007	0.081 ± 0.039	0.049 ± 0.002	0.0025 ± 0.0009	0.21 ± 0.10	0.15 ± 0.07
pH	8.5	8.5	7.1	6.3	4.2	3.5
Silicate solution						
Al	8.8 ± 0.4	2.9 ± 1.5	4.67 ± 0.18	2.78 ± 0.03	1.0 ± 0.6	1.92 ± 0.12
Ca	22.1 ± 3.1	0.60 ± 0.04	4.09 ± 0.72	1.34 ± 0.15	5.7 ± 2.3	0.69 ± 0.08
Fe	0.08 ± 0.008	0.16 ± 0.13	-	-	-	-
Mg	-	-	10.4 ± 6.0	6.49 ± 3.16	27.7 ± 9.2	0.44 ± 0.08
Na	1020 ± 40	1220 ± 70	-	3.54 ± 3.20	-	-
Si	-	0.62 ± 0.18	4.48 ± 0.31	2.74 ± 0.28	2.35 ± 0.48	2.30 ± 0.2
Pu	0.001 ± 0.002	0.01 ± 0.01	0.0048 ± 0.0004	0.10 ± 0.03	0.92 ± 0.04	0.066 ± 0.024
pH	11.7	11.6	9.4	9.5	9.1	9.3

- Plutonium releases are lowest for the two cements and highest for the two ceramics; the glasses are intermediate.
- A strong correlation between leachate pH and plutonium release is evident--the higher the pH, the lower the release.
- Plutonium releases are lower in deionized water than in brine or silicate solution, except for the borosilicate glass at 40°C.
- A poor correlation exists between the test temperature and plutonium release. This lack of correlation is due to large differences between the 40 and the 90°C tests.

Figure 5.4 presents the plutonium releases in deionized water at 90°C at 3, 7, 14, 28, and 56 days. Figure 5.5 gives release data for aluminum, calcium, sodium and silicon. Curves indicate that the total plutonium released is nearly constant with the measurement uncertainties. The other elements also appear to approach nearly constant values, in most cases within about 30 days. An apparent exception is sodium release in the cold-pressed sintered ceramic.

Additional tests in progress will extend the data to test durations of 182 days. These tests will be completed next quarter.

FIGURE 5.4. Releases in Deionized Water for TRU Waste Forms, Showing Normalized Mass Losses as a Function of Test Duration at 90°C

FIGURE 5.5. Elemental Releases in Deionized Water for TRU Waste Forms, Showing Normalized Mass Losses as a Function of Test Duration at 90°C. A. Aluminum releases; B. calcium releases; C. silicon releases; and D. sodium releases.

MICROSTRUCTURE EVALUATION OF REFERENCE WASTE FORMS - R. P. May

Crystalline-phase analysis has been completed on the six reference TRU waste forms. This analysis consisted of a detailed microstructural examination using optical metallography (MET), scanning electron microscopy (SEM) with energy-dispersive analysis capabilities (EDAX), α -autoradiography, and semiquantitative x-ray diffraction to identify and estimate the weight fraction of each crystalline component.

The results of this characterization for each waste form are as follows:

- Aluminosilicate glass: XRD, MET, and SEM with EDAX show this material to be uniform and vitreous under magnifications as high as 3000X. The α -autoradiograph shows the plutonium to be uniformly dispersed in the glass.
- Borosilicate glass: XRD, MET and SEM examination have shown a fine dispersion of micron-sized, rod-shaped crystals high in copper. About 2 wt% of this phase was present in the sample. A second crystalline phase, rich in zirconium and about 100 μm in diameter, was also detected by MET and SEM examinations. MET counting analysis indicates that this phase is present in the glass at <0.1 wt% and is thus undetectable by XRD. The α -autoradiograph of this sample shows that the zirconium-rich crystals are somewhat enriched in plutonium compared to the remainder of the glass sample.
- Basalt glass ceramic: MET examination shows a large number of fine and uniformly dispersed submicron-size crystals occupying perhaps a quarter of the glass volume. SEM examination shows only dendritic $(\text{Mg}, \text{Ti}, \text{Fe})\text{Fe}_2\text{O}_4$ crystals ranging from 2 to 7 μm in length and present

at about 2 wt% in the glass. XRD analysis shows that the phase that is optically visible is $(\text{Ca}, \text{Na})(\text{Mg}, \text{Fe}, \text{Al})(\text{Si}, \text{Al})_2\text{O}_6$ and is present at an estimated 25 wt%. This phase is compositionally similar to the residual glass, and this may be the reason that it is unobservable by SEM. The α -autoradiograph of this sample indicates that plutonium is dispersed uniformly in the material. But because the uniform dispersion is over a large number of small crystals, the crystallographic location of the plutonium in the sample is uncertain.

- Sintered silicate ceramic: Five identified crystalline phases are evident in this material. Two crystalline forms of SiO_2 were distinguishable by XRD--quartz (α - SiO_2) at ≈ 2 wt% and low cristobalite at ≈ 18 wt%. Two iron oxide phases were also observed in this ceramic. Hematite (α - Fe_2O_3) was present at ≈ 10 wt%, and a spinel-type crystal of the compositional form $(\text{Cr}, \text{Fe}, \text{Mg}, \text{Ni}, \text{Ti}, \text{Zn})(\text{Fe}, \text{Cr}, \text{Al})_2\text{O}_4$ was also noted at ≈ 6 wt%. A fifth crystalline phase observed is tentatively identified as CaMgP_2O_7 at ≈ 1 wt%. Both SiO_2 phases appear optically as dark irregular shapes on the order of 2 to 10 μm in size. The iron oxide phases are optically bright shapes ranging in size from submicron crystals of spinel to a block-shaped, 100- μm Fe_2O_3 crystal. Crystals of CaMgP_2O_7 were observed with SEM to occur on the surfaces of a hematite crystal. While this phosphate phase is the most likely host for plutonium, the presence of plutonium in this or any other phase could not be confirmed with either SEM-EDAX or α -autoradiography. Excluding the SiO_2 and hematite, nearly all crystals observed in this ceramic were typically under one micron. This is the chief

reason that the plutonium crystallographic location in this sample could not be determined. The α -autoradiograph does, however, show the plutonium definitely concentrated into selected areas.

- **Cement:** Four crystalline phases have been identified in the cold-pressed material, and there is at least one more phase as yet unidentified. Evident are ~10 wt% SiO_2 , ~5 wt% Ca_3SiO_5 and $\text{Ca}_2\text{Fe}_2\text{O}_5$, ~2 wt% $\text{Ca}(\text{OH})_2$, and about 5 wt% of an unknown phase. The cast cement has the same phase assemblage, but the total weight percent for each phase is reduced by one-third in this material. Both cements have the aggregate microstructures expected of this type of material, but the microstructural similarities end there. The cast cement has both open and closed porosity estimated at <10 vol%. The cold-pressed cement has ~2 vol% closed porosity. Radiographs for both these cements showed that plutonium is concentrated in some phase in these materials, but the phase involved has not yet been identified in these samples.

PROCESS EVALUATION - C. L. Timmerman,
R. L. Treat and J. G. Carter

The cost estimates for the six reference processes have been supplied by Kaiser Engineers. These estimates are based on construction of a new facility at Rocky Flats and the reference process descriptions published previously (Timmerman 1980). The cost estimates shown in Table 5.10 indicate that cement processes have the lowest total 30-year cost. A predominant factor in the

lower cost is the reduced labor requirement--also noted in the table. In-can glass-melting (ICGM) has a high container cost (\$10,000 per container), which dominates the cost of the process.

In addition to the processing costs, the transportation and repository costs have been estimated and are provided in Table 5.11, along with a total annual cost for each process. The transportation costs are based on \$1500 per TRUPACT shipment between the Rocky Flats Plant and the Waste Isolation Pilot Plant. The repository costs are based on \$88/ft³. Included is a comparison of the ICGM process which considers a \$10,000 canister and a \$1000 canister cost. Reduced canister costs can make the process competitive with noncement processes. Again, cast cement has the lowest overall annual cost. Detailed process descriptions and layouts have been completed for five of the processes. In general, overall facility volumes are approximately proportional to the process area volumes, as are capital costs.

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TABLE 5.10. Summary of Costs for Six Reference TRU Immobilization Processes with a New Facility,
Thousands of 1981 \$

Process	Construction, Including Engineering and Project Administration	30 Years Operation		30 Years Maintenance	Decommissioning	30-Year Facility Total
		Based On	Operating			
In-Can Glass Melting	\$33,000	24 hr/day, 300 days/year Use of SS Canisters	\$180,000	\$13,000	\$1,800	\$230,000
Joule-Heated Glass Melting	30,000	24 hr/day, 300 days/year Use of CS Drums	69,000	18,000	1,800	120,000
Glass Marble	33,000	24 hr/day, 300 days/year Use of CS Drums	70,000	20,000	1,800	125,000
Cast Cement	29,000	8 hr/day, 215 days/year Use of CS Drums	20,000	10,000	1,800	61,000
Pressed Cement	32,000	8 hr/day, 215 days/year Use of CS Drums	21,000	12,000	1,800	67,000
Cold-Pressed Sintered Ceramic	34,000	24 hr/day, 300 days/year Use of CS Drums	63,000	12,000	1,800	110,000

5.13

TABLE 5.11. Total Annual Costs for Six Reference Processes, Thousands of 1981 \$

	Processing	Transportation	Repository	Total
In-Can Glass Melting	7500 (\$10,000 can)	60	580	8100
In-Can Glass Melting	4700 (\$1000 can)	60	580	5300
Joule-Heated Glass Melting	4000	50	520	4600
Glass Marbles	4100	68	1000	5200
Cast Cement	2000	100	1600	3700
Pressed Cement	2200	150	2300	4700
Cold Pressed Sintered Ceramics	3700	120	1900	5700

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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

Construction of a materials storage and preparation facility has begun. The rinse/dry and compound handling systems for the vibratory finishing decontamination facility are in place, and work is in progress to complete the electrical and piping connections between these systems and the vibratory finisher. An air pallet was modified for use with the existing hydraulic lift table to support glove boxes during disassembly and sectioning. This air pallet and lift table combination should permit rapid repositioning of glove boxes during these operations. Cold testing and modification of a hydraulic web press were completed. The web press will be used as a nibbler to section the metallic portions of glove boxes. The modification consisted of adding a deeper die pocket to reduce misalignment of the die.

PRETREATMENT STUDIES

Construction began on a materials storage and preparation facility. This facility will be used to receive contaminated material, remove it from the shipping container, store it, and prepare it for the subsequent disassembly and sectioning operations.

The facility is divided into two chambers; the walls of each are standard sheet rock construction. The facility is equipped with HEPA (high-efficiency particulate air) filtered ventilation, and each chamber has an airlock for personnel access and large doors for the movement of material. Additionally, the preparation chamber is located in the high bay area of the 231-Z Building to provide sufficient headroom for unloading most standard-size shipping and storage containers.

The preparation chamber, 11 by 28 by 11 ft high, will be used to receive packaged contaminated material. The contaminated material will be removed from its container in this chamber, inspected for integrity, and repackaged as necessary to ensure the containment of contamination before storage in the adjoining storage chamber. The other function of this chamber is the preparation of contaminated material for placement into the sectioning/pretreatment facility. This work usually consists of removing all non-contaminated items such as pipe fittings, supports, nuts, etc., from the exterior of the glove boxes and other contaminated components. The preparation chamber will provide containment in case of breached glove box integrity resulting from grinding or burning operations.

The storage chamber, 25 by 38 by 10 ft high, will provide a contained, properly

ventilated area where the contaminated material can be stored and monitored until needed for the process demonstration studies. It will also permit ready access to the stored material for examination and for identifying the optimum preparation, sectioning and decontamination procedures.

DECONTAMINATION STUDIES

Significant progress was made in the installation of the rinse/dry, compound-handling, and compound-filtration systems that will be used with the high-production annular vibratory finisher. A diagram and a floor plan of these systems have been illustrated in a previous progress report (Chikalla and Powell 1981). These systems will be completely integrated with the annular vibratory finisher to provide a complete, semi-automated decontamination facility requiring only minimal operator attention.

The rinse/dry system will significantly advance the continuing development of this vibratory finishing decontamination technology. The rinsing and drying of material after decontamination by vibratory finishing has previously been a slow, labor-intensive operation. Although the vibratory finishing machine can easily decontaminate a wide range of sizes and shapes, commercially available rinse systems do not possess this same degree of flexibility. Therefore rinsing was done either manually by dipping or spraying or in dishwashers, which required hand loading of parts into racks.

The rinse/dry system (Figure 6.1) comprises a stainless steel hood containing a rinsing station, a drying station, a basket for handling material, and a hoist. The system is connected directly to the vibratory finisher unloading chute by a flexible bel-

lows. The stations, the basket, and the hoist are sized to handle the entire load from a vibratory finishing batch.

The rinse station consists of a tank equipped with a heater, a high-volume recirculation pump, and an air injection system. The action of this rinse tank is much like that of a hot tub or spa. The hot water in the tank is rapidly withdrawn from the top of the rinse tank, injected with air, and recirculated into the bottom of the tank through a series of concentric cone-shaped baffles. The result is a turbulent, boiling-like action of the hot rinse water.

The drying station is a chamber equipped with an air heater and a drain. Air is drawn through the heater, across the rinsed material, and into the vibratory finisher by the HEPA filtered exhaust system. The chamber drain is connected to the rinse system to recover any water carried out of the rinse tank with the basket.

In a typical operation, the decontaminated material drops from the vibratory finisher unloading chute, through the turbulent rinse water, and into the basket at the bottom of the rinse tank. The violent action of the water separates and rinses the material as it settles to the bottom of the basket. When the vibratory finisher has completed discharging, the basket containing the rinsed, decontaminated material is moved from the rinse station to the drying station by the hoist.

The compound handling system (Figure 6.2) consists of a 50-gal stainless steel holding tank equipped with two pumps, a compound metering system, and a spray ring assembly. The compound holding system, connected to the vibratory finisher drains by flexible connectors, directs the used vibratory finisher solution to the bottom of the holding tank. One of the two pumps is used to

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FIGURE 6.1. Rinse/Dry System for the High-Production Annular Vibratory Finisher Installed in the Decontamination Facility

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FIGURE 6.2. Compound Handling System for the High-Production Annular Vibratory Finisher Installed in the Decontamination Facility

recirculate the solution from the holding tank through a flowmeter and needle valve to the system that adds compound to the vibratory finisher; flow rates can be adjusted from 0 to 40 gal/hr. The pump's intake is positioned at midlevel of the holding tank to avoid the particulate matter that either settles to the bottom of the tank or floats on the compound solution. The second pump is used to clean out the holding tank; its inlet is located in a sump in the bottom of the tank. The compound metering system, consisting of an adjustable metering pump and a flowmeter, is used to mix fresh compound concentrate with water in proportions ranging from 0.5 to 5.0 oz of concentrate per gallon of water. The spray ring assembly is located around the periphery near the top of the tank interior. Producing a series of overlapping, fan-shaped jets of water, the spray ring rinses the interior surfaces of the compound tank.

All water used in the compound handling system comes from the rinse tank of the rinse/dry system. This cascading use of rinse water maintains clean water in the rinse tank while minimizing the overall volume of liquid waste produced by vibratory finishing.

Two modes of operation are possible with this compound handling system: flow-through, which uses the compound solution only once, and recycle, which recirculates the same batch of compound solution. While each mode has distinct advantages, the more effective one has not yet been determined. The flexibility of the new compound handling system should make the resolution of this question easier.

The compound filtration system consists of two independent filter chambers. Each chamber uses three 20-in.-high standard-wound filter elements. Normally, one cham-

ber is used to filter recirculated compound and one to filter the waste compound as it is pumped to the evaporator feed tank. The chambers, however, are connected by headers that allow the filter elements in one chamber to be changed during operation of the vibratory finisher while the other chamber provides the filtration. The compound filtration system is permanently attached to the bottom of a glove box for contamination control during changing of the filter elements.

SECTIONING STUDIES

A commercially available air pallet (Figure 6.3) was modified for use in the sectioning/pretreatment facility. The modifications consisted of attaching a skirt around the air pallet, to prevent the air cushions from being punctured by small, sharp bits of metal that might be on the sectioning/pretreatment facility floor, and an adaptor flange to hold the lift table in place on the pallet.

The air pallet will be used as the base for the lift table currently in use in the sectioning/pretreatment facility (Platt and Powell 1980). This combination of air pallet

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FIGURE 6.3. Air Pallet That Will Be Used as Base for the Lift Table

and lift table will allow repositioning of large and heavy components horizontally as well as vertically.

Air pallets have a long history of use in industry for transporting heavy items. Compressed air is forced through a series of air cushions located on the underside of the pallet. The compressed air forms a "frictionless" air cushion that elevates the air pallet less than 5/64 in. off the floor. This air cushion allows one man to easily move an air pallet loaded with items weighing hundreds of pounds.

A hydraulic web press was cold tested for use as a nibbler for sectioning the metallic portions of glove boxes. The web press is a "C" shaped tool with a punch and die in the open ends of the "C." The tool, normally used to punch holes in the web of beams at construction sites, can be maneuvered easily and can make horizontal and vertical punches.

Cold-testing of the web press revealed that a die pocket deeper than normal was necessary to reduce die misalignment while nibbling. Nibbling, which uses a series of overlapping holes to section, places uneven stresses on the punch. The deeper die pocket provides the support necessary to overcome these asymmetrical stresses.

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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

An amorphous or nearly amorphous sputter-deposited alloy of nickel containing about 10 atom% lanthanum and 11 atom% krypton has been developed for storage of ^{85}Kr . The combination of high-sputtering yield ($7.95 \text{ gA}^{-1}\text{h}^{-1}$), high krypton trapping rate [34 cm^3 of $\text{Kr}(\text{STP})/\text{g}$ of deposit], and reduced cost (\$60.13/kg) yields a material with significantly higher efficiency and the consequent lower costs than previous matrices. Using this alloy and the disposable unit described previously, the ^{85}Kr from a 2000 tonne/yr reprocessing plant would be contained in 304 storage units. Each deposit would require 116 hr, and thus five sputtering chambers would be required. Thermal properties of this alloy show two small exotherms centered at 400 and 620°C, respectively, but no major energy release is observed up to a temperature of 750°C.

ION IMPLANTATION OF KRYPTON IN SPUTTER-DEPOSITED GLASSY METAL - E. D. McClanahan, G. L. Tingey, R. W. Moss, and N. R. Gordon

Safe storage of the radioactive krypton (^{85}Kr) generated in nuclear power reactor fuels should be based on the following criteria:

1. minimum potential for accidental release of radioactive gas during storage

2. low probability of release during processing
3. minimum need for monitoring during storage
4. readily accessible for beneficial applications
5. minimized cost of process consistent with other criteria.

The process which appears to best meet these criteria at present is that of implanting krypton ions into a growing sputter-deposited metallic film (Tingey et al. 1979). With this process the krypton is atomically dispersed within the structure of a bulk metal deposit where it is released at an almost immeasurable rate at potential storage temperatures. Furthermore, the loading process occurs at reduced pressure ($\sim 10 \times 10^{-3}$ torr) and at room temperature, and, thus, hazardous quantities of gaseous krypton are never present in the process. This approach has good potential also for developing useful applications, and studies have already been proposed for producing heat sources containing enriched ^{85}Kr in metallic matrices.

The cost of the sputtering process appears competitive with other techniques for solid-state storage, and attempts are continuing to further reduce these costs. A major step forward was achieved in reducing the electrical power costs and time required for sputtering by the discovery that much more krypton could be incorporated into an amorphous or glassy metal alloy than in the

more common crystalline metal structures (Tingey et al. 1979; Bayne et al. 1979)

Several alloys have been tested that yield a glassy structure and can accommodate up to about 10 atom% krypton. The most efficient of the alloys and, thus, the most widely studied have been iron or nickel materials containing about 10 to 20 atom% yttrium. The high cost of yttrium (\$345.42/kg), however, has motivated a search for alternative materials that would still yield an amorphous structure and efficiently trap krypton. We had earlier concluded that amorphous sputter-deposited metals are favored when the atomic size differences are greatest. Therefore, we selected the metals that have large atomic radii to alloy with the smaller iron or nickel atom. Furthermore, it was decided to use atoms with structures and properties as similar as possible to those of yttrium. Following this rationale, we selected lanthanum, cerium, and titanium for examination. Krypton trapping rates for each of the three alloys were 34, 15, and 9 cm³ of Kr(STP)/g of deposit containing lanthanum, cerium, and titanium, respectively. Based on the high krypton loadings, we concluded that all three alloys yielded amorphous or nearly amorphous deposits, but the lanthanum-containing deposit was clearly superior to the other two. The cerium-containing deposit trapped very little krypton initially, but the rate increased with time up to a value approaching 25 cm³/g, yielding an average krypton content of 15 cm³/g of deposit. Thus the nickel-cerium alloy may prove to trap krypton at a rate near that of the nickel-lanthanum when a consistent run is conducted.

In addition to the high krypton content, the nickel-lanthanum alloy shows a signifi-

cantly higher sputtering yield (7.95 gA⁻¹h⁻¹) than other alloys tested previously. Thus the combination of increased sputtering yield, increased krypton trapping rate, and reduced cost of lanthanum (\$60.13/kg) very significantly increases efficiency and the related reduction in cost for containment of radioactive krypton. When the nickel-lanthanum alloy is compared with the other sputtered alloys listed in Table 6.1 of the previous quarterly report (Tingey 1981), it is clearly superior. The nickel-lanthanum alloy has a trapping rate of 6.60 μ of Kr(STP)/hr, leading to an electrical efficiency of 8.8×10^{-2} μ /kWh. Using the disposable chamber design, only five sputtering chambers would be required to implant all the krypton from a 2000 tonne/yr reprocessing plant. This would yield 304 storage units/yr with 116 hr required for each deposit.

On a related program sponsored by DOE, the thermal properties of the nickel-lanthanum-krypton alloy have also been measured. Differential scanning calorimetry runs have been completed in the temperature range from 25 to 750°C. When the sample is heated in argon, two small exothermic peaks are observed. The first occurs at about 400°C, with $\Delta H = -17$ cal/g. The second is a rather broad peak centered at about 620°C with $\Delta H = -35$ cal/g. If the sample is run in air, no significant change is observed in the 400°C exotherm, but another peak, centered at 622°C with $\Delta H = -178$ cal/g, completely masks the small higher temperature exotherm. This latter exotherm is attributed to oxidation of the sample. Within the temperature range studied, no major exotherm is observed that would cause concern for catastrophic stored energy release during transport or storage.

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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

Vacuum and sweep-gas thermal outgassing concepts were tested for the recovery of volatile fission products using irradiated Shippingport UO_2 fuel. A significant increase in ^{85}Kr , xenon and tritium release rates was observed when the sweep-gas equipment was modified to allow the fuel to be inserted into the 1500°C preheated furnace versus heating the fuel from 35°C to 1500°C over a 4-hr time period, using helium as the carrier gas. Preliminary results indicate that only 10 to 15% of the fission gas was removed from a section of zirconium-clad fuel heated under vacuum at 1500°C for 2 hr. Preparation of the literature survey document on thermal treatment continued during the quarter.

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

In previous studies, 1 g (1-2 pieces) of Shippingport UO_2 fuel was heated from 35°C to 1500°C over a 2-hr time period and then held at 1500°C for 4 hr. Greater than 90% of the xenon and krypton and 80% of the tritium was released after 6 hr using helium

as the sweep-gas. When the gas contained 6% $\text{H}_2 + \text{He}$, 100% of the tritium, 50% of the krypton, and 16% of the xenon were released in 6 hr. Similar results were obtained this quarter using powdered (5-30 mesh) UO_2 fuel, heated from 35°C to 1500°C over a 4-hr time period. However, when the sweep-gas equipment was modified to allow the fuel to be inserted directly into the 1500°C preheated furnace, a significant increase in the gas release rate was observed. As shown in Figures 8.1 and 8.2, greater than 90% of the xenon, krypton, and tritium was released from the fuel in 1 hr using helium as the sweep-gas. When the gas contained 6% $\text{H}_2 + \text{He}$, 96% of the tritium, 40% of the ^{85}Kr , and 27% of the xenon were released after 1 hr. Additional thermal sweep-gas experiments are scheduled for lower temperatures (1250°C and 1000°C).

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

The first vacuum outgassing test was completed in G-Cell at the 327 Building after months of installation and testing of equipment and associated instrumentation. Preliminary results indicate that only 10 to 15%

FIGURE 8.1. Tritium, Xenon and Krypton Release from Shippingport UO_2 Fuel as a Function of Time and Temperature - Helium Carrier Gas

FIGURE 8.2. Tritium, Xenon and Krypton Release from Shippingport UO_2 Fuel as a Function of Time and Temperature - 6% $\text{H}_2 + \text{Helium}$ Carrier Gas

of the fission gas was removed from the section (0.9 cm dia by 2.54 cm long) of zirconium-clad Shippingport UO_2 fuel. The fuel was heated under vacuum at $200^\circ\text{C}/\text{min}$ and held at 1500°C for 2 hr. Early termination of the expected 6-hr test was due to loss of vacuum when the fuel contained in a molybdenum foil touched the furnace wall, causing a pinhole leak. The loss of the first of three gas samples (due to a defective O-ring in the analytical laboratory) and the early termination of the test served mainly to test the equipment. The temperature of the heated system, the total pressure of the system, the partial pressures of selected gaseous components, a view (Figure 8.3) of the fuel using gamma radiography, and photomicrographs before and after heating were obtained during the first test. No fission gas was found in the cladding void space when the fuel pin was sectioned. The gas remaining in the heat-treated fuel will be determined. Preparations for the second experiment are now being completed. This test will involve crushed fuel pellets free from the cladding, heated at $200^\circ\text{C}/\text{min}$, and held at 1500°C for 4 hr.

FIGURE 8.3. View of the Vacuum Outgassing Furnace with Two 1/2-in. Zirconium-Clad Sections of Shippingport UO_2 Fuel, at 1500°C

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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

Scanning electron microscope (SEM) studies show that iodine distributes itself evenly throughout the matrix of silver mordenite (AgZ) and reduced silver mordenite (Ag°Z), but it is preferentially absorbed by the high-silver-content particles of Ag°Z. At low iodine loadings, e.g., 50 mg I/g AgZ or Ag°Z, the physical porosity of the zeolite particle affects the sorption of iodine.

Our studies on methyl iodide removal by Ag°Z have shown that the presence of water improves the removal efficiency of CH₃I with Ag°Z and that the presence of NO or NO_x improves the removal efficiency with Ag°Z.

Sodalite fixation studies indicated that the product made with kaolin clays was equal or superior to that made from laboratory chemicals.

SILVER SORBENT CHARACTERIZATION STUDIES

Scanning Electron Microscopy Studies -
J. E. Coleman and R. D. Scheele

During July-September 1980 (Chikalla and Powell 1980) we performed a series of analyses using scanning electron microscopy coupled with x-ray fluorescence elemental analyses on various iodine-loaded and

nonloaded silver-containing sorbents. Several interesting differences were seen among the different silver zeolites. In silver mordenite (AgZ) iodine was distributed evenly through the zeolite at 50% Ag use. In hydrogen-reduced silver mordenite (Ag°Z), 50% Ag use, the iodine was preferentially localized on silver particles distributed throughout the zeolite. Iodine sorbed by silver zeolite X (AgX) had a specific penetration depth that depended on iodine loading.

This quarter we performed a series of analyses on different iodine loadings of AgZ and Ag°Z to determine the effect of iodine content on its distribution in the zeolite particle. We also studied silver iodide to provide a reference for semiquantitative analysis of the iodine content of these materials. Figures 9.1-9.5 are 1000X magnifications of 50 and 150 mg I/g AgZ and 50, 150, and 200 mg I/g Ag°Z, respectively.

In the present study we found no significant deviation from our earlier study in the way that iodine loads into AgZ or Ag°Z. The iodine distributes itself evenly throughout AgZ and is preferentially absorbed by the silver particles in Ag°Z even beyond a 1:1 mole ratio of iodine to silver. This latter observation indicates that an iodine-silver "complex" formed.

20 μm

23989

FIGURE 9.1. 1000X SEM Micrograph of
50 mg I/g AgZ

20 μm

23994

FIGURE 9.2. 1000X SEM Micrograph of
150 mg I/g AgZ

20 μm

23932

FIGURE 9.3. 1000X SEM Micrograph of
50 mg I/g Ag°Z

20 μm

23938

FIGURE 9.4. 1000X SEM Micrograph of 150 mg I/g Ag°Z

An exception to the above distribution was seen for 50 mg I/g AgZ. In Figures 9.6 and 9.7 the two particles in the center of the micrographs with the lower porosity contain no iodine in their interior while their counterparts with an apparent higher porosity contained iodine. This phenomenon did not occur at higher iodine loadings.

In conclusion, we found that iodine distributes itself evenly throughout the matrix of AgZ and Ag°Z but is preferentially absorbed by the high silver content particles of Ag°Z. At low iodine loadings, ~50 mg I/g AgZ or Ag°Z, the physical porosity of the zeolite particle affects the sorption of iodine by the particle.

IODINE RECOVERY STUDIES - R. D. Scheele, C. L. Matsuzaki and L. L. Burger

In earlier studies performed by our laboratory (Platt and Powell 1979a,b), the

20 μm

23942

FIGURE 9.5. 1000X SEM Micrograph of 200 mg I/g Ag°Z

effects of carrier gas composition, temperature, and zeolite pretreatment on methyl iodide recovery by silver mordenite were studied. No difference existed when nitrogen or air was the carrier gas. Removal efficiency did improve at higher temperatures, 200 versus 100°C, and when the mordenite was pretreated with hydrogen.

The present work is being performed to determine the effects of temperature, the presence of dissolver off-gas contaminants such as nitric oxide and nitrogen dioxide, and the presence of water on the removal efficiency of methyl iodide by hydrogen-pretreated silver mordenite (Ag°Z). A statistical experimental study was designed to evaluate the effects of temperature, 100 to 200°C, and the effects of NO and NO₂, 0 to 2 vol%, in the gas stream.

As a prelude to the parametric study, two experiments were performed using reduced

200 μm

23987

FIGURE 9.6. 100X SEM Micrograph of 50 mg I/g Ag°Z

silver mordenite (Ag°Z) to determine the effect of water in the gas stream. Table 9.1 gives the typical operating parameters of the system. The bed was divided into three segments, each 5.0 cm deep. At the end of each segment a gas sampler was installed for gas chromatographic analysis of the effluent.

Figure 9.8 presents the experimental results at the typical operating conditions. Figure 9.9 presents the experimental results for Ag°Z when dry air ($\sim 4 \mu\text{mol H}_2\text{O}/\ell$) was

TABLE 9.1. Typical Operating Parameters

Bed length	15 cm
Bed diameter	2.5 cm
Face velocity	7.5 m/min
Bed temperature	150°C
Carrier gas	Ambient air ($\sim 500 \mu\text{mol H}_2\text{O}/\ell$)
Influent CH_3I	1.3×10^{-5} mole/ ℓ
Bed material	20-40 mesh

200 μm

23930

FIGURE 9.7. 100X SEM Micrograph of 50 mg I/g Ag°Z

the carrier gas. With ambient air, $500 \mu\text{mol H}_2\text{O}/\ell$, the decontamination factor (DF) dropped to 100 after <1450 min compared to <200 min with dry air. A small amount of water in the gas stream enhances CH_3I recovery. Comparison of data for the first segment effluent supports this conclusion.

We have performed several experiments to date to determine the effect of NO , NO_2 , or $\text{NO} + \text{NO}_2$ (NO_x). At 155°C with 1% NO and 1% NO_2 in the gas stream, elemental iodine was detected at the end of the bed in 1830 min. No CH_3I was detected after the first bed; the CH_3I reacted with the NO_x to form elemental iodine in the first 5.0-cm bed segment.

Similar results were obtained with 2% NO or 2% NO_2 in the gas stream. With 2% NO present, elemental iodine was detected in the effluent from the final bed segment after 1500 min of operation at 155°C . With

FIGURE 9.8. Methyl Iodide Trapping by Ag_2O , Typical Conditions (ambient air $\sim 500 \mu\text{mol H}_2\text{O/l}$)

FIGURE 9.9. Methyl Iodide Trapping by Ag_2O , Dry Air ($\sim 4 \mu\text{mol H}_2\text{O/l}$)

NO_2 elemental iodine was detected in less than 1320 min at 200 C and in 1860 min at 110 C. With either NO or NO_2 present, no CH_3I was detected after the first 5-cm bed.

Summarizing, the presence of water improves the removal efficiency of CH_3I by Ag Z, and NO, NO_2 or NO_x reacts with CH_3I to form elemental iodine. Thus with NO, NO_2 or NO_x present CH_3I capture should be equivalent to elemental iodine capture under similar conditions.

SODALITE PREPARATION STUDIES - W. I. Winters and R. G. Johnston

Earlier sodalite preparation used laboratory reagents as a source of aluminum and silicon, e.g., sodium aluminate and colloidal silica.

Preparation of sodalite from clay-based feeds has now been studied. Sodalite was formed by hot-pressing. Very low iodine losses were measured for all formulations that were tested, and strong, single-phase sodalite patterns were observed in the x-ray diffractograms of the various samples. High densities were observed (2.4 g/cm) in the products of two of the three clay formulations. Lower densities (2.1 g/cm) resulted from the formulation containing the clay with the fewest impurities. Considerable reaction was observed to have occurred in the feed material during initial preparation

steps, suggesting that direct sintering might be a viable process for producing sodalite with a clay-based feed material. A repeat of the HI-aluminosilicate gel hot-pressing experiment with a formulation of the correct stoichiometry confirmed that the high iodine losses observed in previous experiments were not solely the result of insufficient sodium in the original starting material. About five times the iodine lost from a comparable NaI gel feed was lost from the HI-based gel feed during pressing.

Preparation of clay-based sodalites using HI as the iodine source has begun. Additional hot-pressed specimens are being prepared from the gel feeds as well to provide sufficient samples for leach testing. Leach tests of both clay-based and reagent-based sodalites will begin shortly.

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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

Gamma spectrometry and microprobe analyses completed on the filter assembly from the spray calciner used during the Nuclear Waste Vitrification Project (NWVP) are providing measurements of ruthenium deposition within the sintered metal filters. It has been found that the filter cake is acting as a trap for semivolatile metal fission products. Only ruthenium has been found in significant quantities within the filter media.

TECHNICAL PROGRESS

Gamma spectrometry analyses of filter samples before and during sequential elutions with water and acid yielded the following observations:

- The dominant radionuclide in the filter wash liquid is cesium.
- Most of the cesium was removed by a water soak. Water is more effective than acid in removing the cesium.
- Europium was also removed with water, but at a lower rate than cesium.
- Most of the europium is removed by 0.5N HNO₃.
- There was only a slight reduction in the concentration of ruthenium with a water soak.

Based on these observations and assuming that europium is indicative of the behavior of the nonvolatile calcine, three distinct areas of materials are collected on the filters. The first layer has a composition typical of the calcined high-level waste product. The second layer is rich in cesium (compared to the europium), which indicates that cesium may be selectively volatilizing towards the filter. The third layer is predominantly ruthenium that has selectively moved toward the filter, either by volatility or by entrainment as fine particles. The second and third layers may be a mixture with the cesium-rich portion leaching away preferentially, leaving behind the ruthenium-rich portion.

Radiochemical analyses were also completed on samples taken from the calcine cake found on the filters. As expected, the filter cake is trapping volatile fission products. Enrichment over that of bulk calcine of 7.6 times for ruthenium, 1.9 times for cesium and 6.1 times for technetium were seen. Of these nuclides, only ruthenium was found in significant quantities within the filter itself.

Two stainless steel filter samples have been examined in the shielded electron microprobe. Elemental identification and location, with respect to filter depth, were determined for several fission products. For

both samples, the predominant fission product present was ruthenium. Most of the ruthenium was found within the front third of the filter cross-section.

Both samples were mounted in one mount, with the front surfaces facing the center of the mount. The samples were then polished and carbon-coated for electrical conductivity. X-ray spectra (by wavelength dispersive spectrometry) at low sample current (0.1 microamp) disclosed only the presence of ruthenium as a fission product. Cobalt and molybdenum were identified in the stainless matrix in addition to iron, chromium, nickel and manganese. At considerably higher sample current (0.9 microamp), cerium, praseodymium, neodymium and cesium fission products were also detected, but at much lower concentrations than ruthenium. Phosphorus was detected and could be a contaminant from the preparation processes. Silicon was also detected.

The distribution of ruthenium through the filter media was determined by simultaneously

monitoring the ruthenium and iron x-ray lines during a scan across the media. Monitoring the iron x-ray lines indicated the positions of pores in the filter, allowing the sites of ruthenium activity to be determined. Distribution maps of ruthenium, iron, molybdenum and cobalt were made on the front surface of the filter. The ruthenium is located on stainless surfaces (associated with the iron). Molybdenum and cobalt are distributed uniformly, identical to the iron distribution, and so represent components of the stainless steel filter. One spot of slightly enhanced molybdenum concentration was located that may represent some fission product molybdenum.

Distribution maps of ruthenium and iron were also made midway through the filter media. Spikes on the ruthenium traces of the filter traverse at midway positions indicate the presence of considerable deposits of fission product ruthenium.

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

Preliminary water balance calculations have been performed for the irrigated and ambient lysimeters at the Buried Waste Test Facility (BWTF). They indicate that up to 30% of the total precipitation is being lost, as drainage, from the irrigated lysimeter while the net storage or loss for the ambient caisson is too small for measurement.

Work is continuing in the effort to automate the weighing lysimeter measurements. First attempts failed due to insufficient stability of the voltage regulators used. Other designs are being tested to determine whether the desired accuracy is feasible with improved voltage regulation.

DATA ANALYSIS - T. L. Jones

Preliminary calculations of water balance have been performed for the BWTF lysimeters. Data from two lysimeters have been analyzed and are represented in Figure 11.1. One lysimeter was irrigated, so the total precipitation was approximately three times ambient levels. The other lysimeter received only ambient levels of precipitation. In Figure 11.1, the precipitation data are from rain gauges located on the BWTF plot. The

precipitation curve applies to both the ambient and irrigated lysimeters. The irrigation data are a record of water added to the irrigated lysimeter in addition to the normal precipitation. The drainage values represent the water removed through ceramic suction candles located in the bottom of the lysimeter. No water was removed from the ambient lysimeter until 1981. Neutron probe data show no significant change in the total water content of the lysimeters, so Figure 11.1 gives a rough approximation of the lysimeter water balance. The fact that no water was removed from the ambient lysimeter implies that the total evaporation was comparable to the total precipitation. Water was removed in 1981, indicating that there probably was some storage of water during 1979 and 1980, but these measurement techniques were too insensitive to account for small increases or decreases in water content. The results are quite different for the irrigated lysimeter, where up to 30% of the annual precipitation was drained from the lysimeter. It appears that the area soils are in a fine balance between evaporation and precipitation.

These results indicate that in a year of less than average precipitation, a net loss of water may be realized while in years of normal to high precipitation a net gain of

FIGURE 11.1. Meteorological Data from Buried Waste Test Facility

water would result. How this averages out over long time periods is still unknown. Also, these data are for bare soils. If vegetation were present, much lower drainage rates would be expected even under irrigated conditions.

FIELD ELEMENTS - R. R. Kirkham

The weighing lysimeter electronics are being analyzed and tested to determine the best measurement system. The scale is comprised of four load cells that have a combined output of ~ 13.5 mV for our weight ranges. This output has a sensitivity of ≈ 1 μ V/lb. The scale is accurate to ± 1 lb, and 1 lb weight loss is equivalent to 0.2 mm of evaporation. Daily evaporation rates range from 0.5 to 10 mm; therefore measure-

ments accurate to the 1-lb limit are desirable. This requires the accurate measurement of microvolt changes in a 13-mV signal. The only equipment available for continuous measurements is a DC-powered data logger. The data logger can measure a 13-mV signal only to ± 50 μ V; thus the load cell output must be carefully "conditioned" before measurement. The system being tested amplifies the signal to ~ 2.5 V and then subtracts out all but 10 to 15 mV. This conditioned signal may then be monitored by the data logger to the required accuracy. The first attempt at subtracting out part of the signal did not work due to an inferior voltage regulator. A precision regulator is on order, and meanwhile the stability of all other amplifiers and voltage regulators is being documented to decide whether the desired accuracy is feasible.

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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

Software development and calibration data acquisition for the ^{90}Sr bremsstrahlung detection technique are proceeding on schedule.

An open literature publication describing the results of the neutron activation analysis experiments on ^{90}Sr has been drafted.

The design manual for the tritium logging system has been drafted.

Investigation of the application of mass spectrometry to the in situ analysis of tritium has been initiated.

A ^{139}Ce source has been obtained for evaluation in x-ray fluorescence spectroscopy of actinides.

Technology developed in this program has been made available for application by other members of the scientific and technical community through specific discussions held with personnel from the United States Geological Survey in Idaho Falls, Idaho; UNC Nuclear Industries; the Radiological Sciences and Water and Land Resources Departments of Pacific Northwest Laboratory; Mound Laboratories in Miamisburg, Ohio; Evaluation Research Corporation in Oak Ridge, Tennessee; Battelle-Institut e.V. in Frankfurt, Germany; British Nuclear Fuels Limited in Seascale, United Kingdom; and the Kernforschungszentrum in Karlsruhe, Germany.

A paper entitled "In Situ Subterranean Determination of Actinides by High Resolution Gamma-Ray Spectrometry" was presented by R. L. Brodzinski at the International Symposium on Methods of Low Level Counting and Spectrometry, held in Berlin, April 6-10, 1981.

DEVELOPMENT OF LOGGING SYSTEMS CAPABLE OF MEASURING ^{90}Sr - R. L. Brodzinski, R. M. Campbell and L. A. McVey

Data reduction from the thermal neutron activation analysis experiments on ^{90}Sr has been completed, and an open literature publication describing the results of these experiments has been drafted. The potential sensitivity of this technique for in situ subterranean analysis of ^{90}Sr is being determined based on the results of these measurements, and this sensitivity will be compared to that obtainable with the bremsstrahlung technique developed earlier in this program.

Stringent calculations regarding the potential results of the proposed fast neutron activation analysis experiments have demonstrated insufficient probability for enhanced sensitivity of this technique over the thermal neutron activation analysis technique for the in situ subterranean analysis of ^{90}Sr to warrant further efforts in this

direction. Hence, the fast neutron activation analysis portion of these experiments will not be executed.

Preparation of the calibration facility for obtaining the input parameters for ^{90}Sr bremsstrahlung data reduction has continued. Initial data acquisition has been only for surface analyses. When all surface data have been obtained, the area will be drilled for subterranean calibrations. Computer code development for ^{90}Sr bremsstrahlung data reduction is expected to accelerate with the assistance of Dr. Walter Hensley, a new permanent staff member in our organization.

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

The design manual for the tritium logging system has been drafted. Work has resumed on the final assembly and the testing of the tritium logging system. A modification to the tritium logger is being considered that would replace the magnesium reduction furnace with a calcium carbide acetylene generator and hydrogen/palladium reducer. This change would eliminate the high-temperature furnace from the system, which could reduce potential problems encountered during operation in a confined space.

Discussions have been held with Martin Elliott and Mike Lynch of VG-Isotopes Ltd., Winsford, Cheshire, England, regarding application of mass spectrometry to the in situ analysis of tritium in shallow-land burial environments. This work was not scheduled until FY 1982, but because of the opportunity to initiate the task with a minimal financial commitment, the investigations were begun in the interest of efficiency. These initial studies indicate

a potential for real time, in situ analyses utilizing mass spectrometry at satisfactory sensitivity levels. More detailed investigation and experimentation will be necessary before a cost/benefit-effectiveness comparison can be made with the gas counter/nafiction sampler system currently under construction and the laser analysis study planned for FY 1982.

Discussions have been held with Jeff Bagby and Rodger Jensen from the United States Geological Survey in Idaho Falls, Idaho, regarding application of the ^{90}Sr and ^3H monitoring technologies developed in this program to measurement problems at the Idaho Falls site. Of most interest was the potential adaptation of the tritium monitoring system to the assay of tritium in water samples taken with an automated sampling system. If other, less expensive, monitoring methods cannot provide adequate sensitivity, the necessary modifications to our system will be determined in order to optimize it for their purposes.

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

A ^{139}Ce source has been obtained for evaluation as an in situ x-ray fluorescence isotopic excitation source for determination of actinides. The isotopic purity of this source has been determined and been found to be adequate for the purposes.

Discussions have been held with Al Larrick of UNC Nuclear Industries regarding in situ uranium measurement methods. Technology developed in this program, particularly actinide x-ray fluorescence technology, has been made available for use by UNC where applicable.

12.3

A seminar was presented by R. L. Brodzinski to personnel from the Radiological Sciences and Water and Land Resources Departments of Pacific Northwest Laboratory describing application of the actinide photon detection technology to transuranic monitoring and measurement requirements on the Hanford Site. The purpose of the seminar was to make the availability of the technology known to persons requiring data such as is obtainable with this technique for appropriate and efficient execution of their assigned tasks.

A paper entitled "In Situ Subterranean Determination of Actinides by High Resolution Gamma-Ray Spectrometry" was presented by R. L. Brodzinski to an audience of 178 scientists at the International Symposium on Methods of Low Level Counting and Spectrometry, held in Berlin, April 6-10, 1981. This paper, describing technology developed in this program, was very well received and appreciated by this international audience comprised largely of authoritative specialists in the field.

Discussions have also been held with Joe Garner and Harold Honius from Mound Laboratories in Miamisburg, Ohio, regarding application of the in situ actinide measurement technology developed in this program to the characterization of ^{238}Pu -contaminated areas at Mound and the monitoring of decontamination and decommissioning actions. Arrangements have been made to provide the technology, equipment, and operating personnel to Mound for evaluation experiments.

Discussions have been held with Don Jacobs and Keith Earnshaw from Evaluation Research Corporation in Oak Ridge, Tennessee, regard-

ing the effects of remedial action efforts at low-level waste sites. This information exchange was in conjunction with their work sponsored by the National Low Level Waste Management Program through Oak Ridge National Laboratories.

Discussions have been held with Hans Freund of Battelle-Institut e.V. regarding potential application of measurement technology developed in this program to monitoring large-scale decontamination and decommissioning of old reactor vessels and other large nuclear facilities.

Discussions have been held with Alan Marples of British Nuclear Fuels Limited, Seascale, Cumbria, United Kingdom, regarding technologies developed in this program on determination of ^{90}Sr concentrations by detection of bremsstrahlung radiation, in situ measurements of tritiated water, and quantitative analysis of transuranic elements in high gamma radiation environments. It is anticipated that these technologies will be extremely useful in hydrogeological survey and ground investigations at the Windscale and Calder Works.

Discussions have also been held with Reinhard Kraemer of the Kernforschungszentrum, Karlsruhe, Germany, regarding establishment of a Memorandum of Understanding on measurement and monitoring technology for low-level waste management under the Technical Exchange and Cooperative Agreement between the United States Department of Energy and the Federal Ministry for Research and Technology of the Federal Republic of Germany in the Field of Management of Radioactive Wastes.

Dr. Kraemer feels a memorandum in this area would be beneficial to both countries.

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

The package neutron counter for assaying transuranics has been tested in gamma-ray fields up to 35 R/hr with no adverse effects on operation. The potential exists for measuring 10 nCi/g of TRU in a gamma field of 1.5 million R/hr. Assay of a typical 200 l steel drum of low-level waste at the 10 nCi/g level is expected to take <1 min.

Procedures have been developed for accurate calibration of radionuclide spikes used to fabricate standard low-level waste packages.

Discussions have been held with scientists at Battelle-Institut e.V. in Frankfurt, Germany, and the Kernforschungszentrum in Karlsruhe, Germany, regarding some of their used and proposed waste packages and assay techniques.

WASTE RECEIPT INSTRUMENTATION DEVELOPMENT -

R. L. Brodzinski, L. A. McVey and E. A. Lepel

Optimization of the package neutron counter for assay of transuranics in waste disposal packages has been continued. One of the individual amplifier/discriminators, used to isolate $^{10}\text{BF}_3$ proportional neutron counters from one another, has been tested in a ^{60}Co irradiation facility. An array of

these neutron counters can be used to monitor the transuranic activities in low-level waste disposal packages by measuring the neutrons emitted by the actinides and their alpha particle interactions with light isotopes present in the package. To make measurements at the 10 nCi/g level in reasonable periods of time, a large number of these tubes will be required. If the signals from all tubes in the array are coupled prior to routing and storage, the small output pulses, generated in each tube due to interactions with gamma-rays emitted by the waste package, will pile up and be recorded as a false neutron event. The mini amplifier/discriminators designed in these laboratories prevent this pile-up by segregating the $^{10}\text{BF}_3$ tubes from each other until only processed neutron events are extracted.

A typical $^{10}\text{BF}_3$ neutron counter and its amplifier/discriminator were irradiated to various gamma dose levels in a ^{60}Co irradiation facility both with and without a steady neutron source present. The counter system was found to be totally unaffected by gamma-ray doses up to 35 R/hr, which means that any size package counter will also be able to handle gamma dose rates up to this level. With the addition of an optional lead shield, the counter could measure 10 nCi/g of transuranics from a waste package emitting

1.5 million R/hr of gamma activity. This is, of course, not the typical low-level waste package.

It is expected that the passive neutron counter system will be able to analyze a 200 l steel drum of low-level waste, emitting the maximum allowable gamma activity of 1 R/hr at 1 m, for transuranics at a sensitivity level of 10 nCi/g in <1 min.

Procedures have been perfected and documented for calibrating radionuclide spikes for use in the preparation of standard waste packages for quality control of assay instrumentation. Absolute uncertainties of <2% are now attainable, which will provide ample accuracy for preparation of the standards.

Discussions have been held with Hans Freund and Bob Sherriff of Battelle-Institut e.V., Frankfurt, Germany, regarding generation and disposal of large quantities of low-level waste during decommissioning operations of large nuclear facilities. Volumes of low-level waste received by disposal site operators in the United States are anticipated to reach unprecedented levels when large-scale decontamination and decommissioning efforts begin, and packaging and monitoring of these wastes will require a monumental effort. Currently low-level wastes in Germany are all disposed of in three standardized con-

tainers: the 200 l drum, a 400 l drum, and a large, shielded concrete cask.

Another packaging technique being considered by the Germans, primarily for high-level wastes, incorporates fabrication of an overpack by hot isostatic pressing. The waste form (calcine, vitrified glass, ceramic pellets, or whatever) is placed in a preformed aluminum oxide overpack, which is then sealed into a monolith by HIP. The procedure forms a container, a radiation shield, and another isolation barrier all at one time. In theory, the technique could be used for all types of waste if costs are not prohibitive. Another advantage of this technique would be the generation of standardized waste packages relatively easy to monitor and assay.

Discussions were held with Drs. Würz and Kraemer at the Kernforschungszentrum, Karlsruhe, Germany, regarding measurement and monitoring technology for assaying low-level waste packages. The Germans have a large passive neutron counter for assaying the TRU content of 200 l drums that is similar in design to the passive neutron counter being optimized for this purpose in these laboratories. The German system is capable of measuring 4 nCi/g in 20 min, and our counter is substantially more sophisticated, which should make rapid assay at satisfactory detection limits a reality.

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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

An experimental procedure employing multiple soil contactings was successful in pointing out that some apparently meaningful data with nickel and cobalt were really not meaningful. The behavior of nickel and cobalt when EDTA- or DPTA-containing solutions were contacted with soil was found to be highly dependent on the conditions allowed for complexation to occur before the soil contact was begun.

RESULTS

Work this quarter centered primarily on kinetic and solubility aspects of the behavior of nickel and cobalt complexes in solutions contacting Hanford soil. Many of the results reported last quarter for these elements are now known to have been incorrect insofar as general validity is concerned; instead, they were the result of the specific experimental conditions used. The experimental approach outlined last quarter was successful in pointing out the invalid results, however.

Perhaps the most useful procedure in demonstrating that the data were not generally valid has been to contact the equilibrated solution with a second batch of soil. If the K_d in the first contact is generally valid,

then the same value should be obtained in the second contact. Table 14.1 contains results of such tests in three different systems: Eu-EDTA, Ni-EDTA, and Ni-DTPA. Only in the europium case was the apparent K_d value in the second contact nearly equivalent to that in the first contact; in this case, even a third contact gave an equivalent value. Thus, this europium data point appears to be a good one. However, in the nickel experiments no sorption occurred in the second contacts, demonstrating that the first-contact results were not generally valid (even though they certainly looked good by themselves).

The initial attempts to explain these results with nickel centered on solubility effects, but additional results did not substantiate this hypothesis. However, it was found that the conditions (time and concentrations) of complex formation that prevail before the nickel solutions are contacted with soil greatly affect the behavior during soil contact. In the early work the radionuclide was spiked into the complexant solution only a few minutes before the soil contact was begun. This procedure is adequate with europium but not with nickel.

Some results obtained with nickel and EDTA indicate the importance of time of complexation before contact with soil. A solution containing $1 \times 10^{-7}M$ Ni and $3 \times 10^{-7}M$ Na_2EDTA was prepared, and portions were

TABLE 14.1. Apparent K_d Values in Successive Contacts with Soil

Solution	Contact Number	Contact Time, days	Apparent K_d , ml/g
Eu ($8 \times 10^{-9}M$) + Na ₂ EDTA ($1 \times 10^{-4}M$)	1	7	24
	2	7	37
	3	7	44
Ni ($1 \times 10^{-7}M$) + Na ₂ EDTA ($3 \times 10^{-6}M$)	1	6	180
		17	185
	2	7	0
Ni ($1 \times 10^{-7}M$) + Na ₂ EDTA ($3 \times 10^{-5}M$)	1	6	64
		17	52
	2	7	0
Ni ($2 \times 10^{-9}M$) + DTPA ($1 \times 10^{-8}M$) ^(a)	1	7	16
	2	3	20

(a) One day between preparing the solution and adding the soil in this case (versus only a few minutes in the other cases).

removed for contact with soil (0.010 g/ml solution) after various time intervals. When contact with soil was begun after only 1 min, only 3% of the nickel was found in solution after a 2-day contact. With a 15-min interval between solution preparation and contact with soil, 12% of the nickel remained in solution after a 2-day contact. Slow changes continued to occur in the stock solution as it aged longer; with 5-day and 19-day intervals between solution preparation and initiation of soil contact 29% and 41%, respectively, of the nickel remained in solution after a 2-day contact. The 15-min and the 5-day interval cases were also analyzed after longer soil-contact periods, and the results obtained were identical to those

after the 2-day contacts. Thus, the behavior of nickel in the soil contacts was independent of time of contact with soil but highly dependent on time allowed for complexation before the solution was contacted with soil.

Other results with nickel and EDTA indicate the importance of concentrations during the complexation period prior to contact with soil. In one experiment a $1 \times 10^{-7}M$ Na₂EDTA solution (containing $1 \times 10^{-9}M$ Ni) was aged one day before being contacted with soil for 5 days; no nickel then remained in solution. In another case a $1 \times 10^{-5}M$ Na₂EDTA + $1 \times 10^{-6}M$ Ni solution was aged one day before it was diluted 100-fold (to give the same EDTA concentration as the other experiment) and contacted with soil for 5 days; in this case all the nickel remained in solution. The extent of complexation after 1 day was obviously much higher in the more concentrated solution.

The situation with nickel and DTPA appears similar to that with nickel and EDTA. Preliminary work with cobalt suggests that it behaves similarly to nickel in these systems also. Stock solutions containing $1 \times 10^{-5}M$ nickel or cobalt and $2 \times 10^{-5}M$ EDTA or DTPA have been prepared and used to make dilutions for contact with soil. It is expected that these experiments, extended, plus multiple soil contactings will lead to generally meaningful data on the behavior of these complexes.

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.

The major portion of the body of the handbook has been drafted. Four main categories are presented in it:

1. Design and Engineering
2. Operation and Maintenance
3. Contamination Control and Decontamination
4. Administrative

In each category, approaches and methods for decreasing the generation of LLW are discussed. In addition, examples and cost/benefit analyses information are being prepared for inclusion in the main sections.

The methods to decrease the generation of low-level waste have been grouped into four main subject areas, facilitating the organization of available methods and providing for logical presentation of the techniques currently available. Wherever techniques apply to more than one major category, the technique is described in greater detail in the category deemed most appropriate.

Drafts have been prepared of several support appendices that will provide additional background information on decreasing the generation of low-level waste (LLW). These appendices discuss the need and philosophy of decreased generation of LLW as well as pro-

vide summary information concerning the present and projected generation rates of LLW.

Information dealing with methods to decrease the generation of LLW is either difficult to obtain or not available through documented sources. Basic conclusions concerning the effectiveness are occasionally available; however, in most cases, insufficient information exists to quantitatively evaluate the methods. Information currently available will be used to perform the cost/benefit analysis. Administrative controls appear to be a popular method for minimizing the generation of LLW, but unfortunately, pertinent techniques often must be analyzed from a subjective viewpoint due to the limited data available. On the other hand, many improvements have been made in the reuse or recycle of equipment by applying state-of-the-art decontamination methods. Since this material is reused, it is no longer considered waste, requiring disposal. Such work is documented, providing a sounder basis for cost/benefit analysis.

To adequately analyze the various techniques, more objective background material must be generated. Several examples will be included in the final recommendation.

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16. WASTE MANAGEMENT SYSTEM STUDIES

J. V. Robinson - Project Manager

The objectives of this program are to evaluate alternative systems for treatment and disposal of radioactive wastes and to develop information required to ensure effective 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 this past quarter. In addition, a new research task (Task 8) was added to the program as a complement to Task 4, and it will be described along with Task 4 below.

Task 1 is the revision and issuance of topical reports from FY 1980. Three reports are involved. The first has been cleared, printed and distributed. It is entitled Nuclear Waste Management and Environmental Mediation: An Exploratory Analysis (PNL-3678). The second report, entitled Implementation Research for Radioactive Waste Management (PNL-3814), regards the social science research needs in nuclear waste management. It was revised for a second time during last quarter and was sent to the PNL Project Manager, DOE Richland Operations (RL), and DOE Headquarters for clearance. The decision was made by DOE not to publish the document in its present form. Several meetings have been held with DOE staff since that decision to discuss the direction that the next revision should take. The report will be revised next quarter and sent back for clearance. The third report, entitled Long-Term Nuclear Waste Management: The

Problem of Retaining Information and Maintaining Surveillance for 100 Years (PNL-3914), was sent to the PNL Project Manager for review prior to submission to RL for clearance.

Task 2 is the public participation planning task. During this quarter both Stan Nealey and Tom Overcast met with DOE staff and MITRE staff regarding the public participation aspects of the National Plan for Radioactive Waste Management. Comments from Battelle Human Affairs Research Center (HARC) on Working Draft 3 were discussed. Now public comments on Working Draft 4 are being analyzed at HARC. Only a slight amount of work remains to be done on this task next quarter.

Task 3 is the completion and issuance of four reports on public perceptions of waste management facilities. All four reports received DOE clearance last quarter. One has been printed: Public Concerns and Choices Regarding Nuclear Waste Repositories (PNL-3797). The other three reports will be printed in July: Public Perceptions of Industrial Risks: The Context of Public Attitudes Toward Radioactive Waste (PNL-3799); Risk Perception, 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).

Task 4 is the comparative analysis of existing survey data on nuclear waste management. During last quarter a complementary task (Task 8) was added, which is a comparative analysis of existing survey data on all non-waste aspects of the nuclear fuel cycle. One report will be prepared for the two tasks. Numerous national and state surveys have been requested by HARC, and much of the data has already been received. More surveys will be received in July, and a report will be prepared by the end of next quarter.

Task 5 is the analysis of the waste management hearings process, including both legal hearings and public meetings. A first draft of this report was completed last quarter and was circulated to HARC staff for comments. The report will be put in final form and sent out for clearance next quarter.

Task 6 is the analysis of regions in the U.S. as they might have some bearing on state compacts regarding waste repositories. The various chapters of this report were integrated in June. The report is now being circulated at HARC for comments.

Task 7 is the analysis of the styles used to make decisions about waste management. A large portion of the report was written last quarter. A first draft will be available around the end of July, and the report will be finalized during the next quarter.

WASTE MANAGEMENT FACT BOOK - O. F. Hill

There exists a need for a pocket-sized, loose-leaf source book containing current, accurate information on topics related to nuclear waste management and directly related issues, e.g., nuclear power. Such a Waste Management Fact Book would provide a convenient and consistent reference source for DOE program officials and their contractors. Late this quarter PNL was autho-

rized by DOE-RL to proceed to develop such a fact book. The first task assigned was to develop a list of reliable references from which the data and information for the fact book would be derived.

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

The final report, Standardized Input for Environmental Impact Statements - Part I: Dose Calculations (PNL-3509), was published during May. A draft of Standardized Input for Environmental Impact Statements - Part II: Site Description was distributed for comment in June.

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

Task members attended Uranium Mill Tailings Remedial Action (UMTRA) EIS scoping meetings held in Salt Lake City, Utah; Tooele, Utah; and Durango, Colorado. The support task summary of issues raised at the Salt Lake City and Tooele scoping meetings was made available to Sandia Laboratories to assist them with the official scoping meeting summary. The support task summary of the Durango scoping meeting will also be provided to Sandia.

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

Dr. Raymond Murray, PNL consultant, completed his survey of DOE-approved publications in the area of nuclear waste management and related topics developed for the general

(a) For background information see PNL-3000-9, the prior report in this series.

public and submitted a report on his findings to the PNL Program Manager; the report was sent to DOE-RL and to V. Trice, DOE-HQ.

Also, a final draft of a report entitled Understanding Radioactive Waste Management, PNL-3570, was completed by Murray and submitted to the PNL Program Manager for review. PNL plans to submit it to DOE-RL for clearance next quarter.

Dr. Murray also presented a speech at the Annual Meeting of the National Science Teachers Association in New York City in April entitled "The Development of Educationally-Useful Information on Complex Technical Subjects." The speech used the work associated with developing PNL-3570 as a case study.

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

Under Carl Unruh's leadership, the second workshop on "Waste Management Health Physics" was presented April 20-23, 1981, at Headquarters to DOE-HQ Waste Management personnel and a few others. These courses resulted from the wishes of the Deputy Assistant Secretary for Nuclear Waste Management to provide his staff with a better understanding of health physics. Some 40 to 45 persons participated, including 5 or 6 from the Nuclear Regulatory Commission who particularly requested to attend. Notebooks with lecture notes were provided. A special 2-hr session for the nontechnical staff was also presented and was attended by about 20 individuals. The course received very favorable response.

(a) For background information see PNL-3000-9, the prior report in this series.

NUCLIDE TRANSPORT EXPERIMENTS^(b) - J. C. Laul

Comments were received from the Basalt Waste Isolation Project (BWIP) Office on a draft report entitled Disequilibria Measurements for Assessing the Transport of Selected Radionuclides: Sub-seabed Studies, PNL-3698. Based on the nature and extent of the comments, it was proposed that the PNL principal investigators (J. C. Laul and R. W. Perkins) present a seminar on the methodological approach to the BWIP staff and certain RL staff. We plan to present such a seminar in July if mutually agreeable arrangements can be made.

The Sub-seabed Project Office, which supplied the seabed sediments for the measurements that formed the basis for the analysis, suggested that the report be the basis for an article to submit for publication in a nuclear waste management journal.

DILUTION DISPOSAL OF RADIOACTIVE WASTES^(b) - G. L. Benson and A. R. Felmy

The draft report Near-Surface Geologic Disposal of Radioactive Waste - An Initial Assessment, PNL-3580, was revised by Water and Land Resources Department and submitted to the Project Manager at the close of the quarter. We plan to submit it to DOE-RL for clearance early next quarter.

EFFECTIVENESS OF WASTE MANAGEMENT CONTAINMENT SYSTEMS^(b) - J. W. Bartlett (TASC)

A report was published entitled Selection of Containment Systems for Commercial High-Level Waste Management, PNL-3803, which was prepared for The Analytical Services Corporation under contract to PNL.

(b) For background information see PNL-3000-7, an earlier report in this series.

WASTE MANAGEMENT DATABOOK^(a) - R. W. McKee

A report entitled Waste Management Data-book, PNL-3856, was submitted for clearance to DOE-RL. We were advised that RL does not

want the report published as a PNL UC-70 report, but that a limited number of copies could be prepared for use by DOE contractors. We are proceeding on that basis.

(a) For background information see PNL-3000-4, an earlier report in this series.

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.

Work continued on a survey of systems safety analysis methods and their application to nuclear waste management systems. A clearance draft of this report is nearing completion, and the report is to be published early next quarter.

Systems safety analysis is a formalized approach to safety that has evolved from use in the aerospace, defense and nuclear industries. In this approach, analytical methods are used to model the system of interest for the orderly acquisition of specific safety information. These methods can range from simple safety indices to detailed risk assessments.

This report reviews system safety analysis methods and examines their application to nuclear waste management systems. 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, Monte Carlo simulation, 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 aid in implementing the use of consistent and cost-effective safety methods throughout the DOE waste management programs.

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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.*

PROJECT MANAGEMENT - F. H. Dove

The mid-year review for the Office of Nuclear Waste Isolation (ONWI) occurred at PNL on May 18 and 19. Staff from INTERA Environmental Consultants, Inc., attended. Because the Basalt Reference Site Initial Assessment (RSIA) had already been extensively reviewed at ONWI, the mid-year review concentrated on explanation of AEGIS methodology development tasks.

Preparation of the Technology Program Plan (TPP) for FY-1982 began with discussions of a new AEGIS organization designed to be compatible with performance assessment elements of the work breakdown structure for the National Waste Terminal Storage (NWTS) Program. Review of the draft outlining SCEPTER Model Performance Requirements was begun as a necessary step in planning code development and integration tasks for the next fiscal year. Applications of AEGIS methodology are expected to focus on the Nevada Test Site (NTS). A draft copy of the TPP for general review has been rescheduled for completion by September 1, 1981.

The topical report Use of Geohydrologic Response Functions in the Assessment of Deep Nuclear Waste Repositories (PNL-3817) has been cleared and published. All Department of Energy (DOE) milestones for FY-1981 have been completed as scheduled. Also, topical report activity includes over 30 reports and journal articles that have been composed, reviewed, or edited by the AEGIS staff since October 1980.

METHODOLOGY DEVELOPMENT - R. W. Nelson

Recently two complementary approaches to the hydraulic conductivity inverse problem have been developed. A direct-circuit integral method, based upon a mathematical statement of mass conservation, yields a global solution to the inverse problem without calculating pathlines. Mathematical investigations of this method indicate that its continuity with respect to perturbation in input data is improved over previous methods of similar complexity. The second technique is based upon a variational principle and is expected to behave even

more smoothly with respect to input noise. The variational technique depends upon a good starting approximation to the conductivity. This initial approximation will be provided by the circuit integral method.

A summary of work accomplished in contaminant transport under uncertainty includes:

- The two computer codes developed have been named SCDE1D and SCDE2D. The last two characters distinguish the one-dimensional and two-dimensional versions. The other four characters are an acronym from Stochastic Convection Differential Equation.
- SCDE1D and SCDE2D have been compared by applying them to a one-dimensional problem for which an approximate analytical solution is known. The comparison is favorable.
- SCDE2D has been applied to a two-dimensional problem for which an approximate analytical solution is known (provided by A. G. Gibbs). The results were encouraging.
- SCDE2D has been applied to the Hanford data utilizing the covariance functions obtained by J. L. Devary through kriging techniques.
- The final draft of a document describing the numerical procedure and application of SCDE2D to the two-dimensional problem is 95% completed.

SITE APPLICATIONS - M. G. Foley

The basalt RSIA was presented in detail at ONWI on April 8. A summary of the analysis was included in the ONWI mid-year review for DOE on April 10, and a summary of the analysis was presented to DOE-Richland on April 23. The draft report, currently in clearance, reflects AEGIS interpretation of

the extensive data base contained in the Rockwell Integration Reports (RHO-BWI-ST-4, RHO-BWI-ST-5) and other more recent data (at which time drilling for boreholes DC-14 and DC-15 had not penetrated the Grande Rhonde Basalt). Revision of the draft report is in progress, and computer files associated with the calculations have been backed-up for long-term preservation.

The AEGIS evaluation of Environmental Protection Agency standard 40 CFR 191 and supporting documentation was submitted to ONWI on June 29, 1981. This evaluation--a compilation of technical reviews by AEGIS and other PNL staff--will be incorporated into the DOE response to the proposed standard. The evaluation concluded with the strong recommendation that the DOE reject the standard as proposed.

Five hundred "final" Monte Carlo simulations were performed with the Geologic Simulation Model, along with several smaller sensitivity analyses, following finalization of input data. Preparation of a draft final report is in progress, as is the final version of the summary input to the basalt RSIA report.

Documentation of the DITTY-1 dose code approached completion before work was halted in May.

A new task, 0305-Data Analysis, was approved and funded by ONWI for FY-1981. Work in this task will concentrate on evaluation of the quality and completeness of hydrologic data for potential repositories in domal and bedded salts of the Gulf Coast, Paradox Basin, and Permian Basin.

FUTURE ACTIVITIES

The documentation of the Fracture Flow Analysis of Dr. Strack will be continued at a reduced pace, but will be completed this fiscal year.

Analysis of data from the GSM Monte Carlo analyses will be completed, and the report PNL-3542-2 entitled Geologic Simulation Model for a Hypothetical Site in the Columbia Plateau: Volume II. Results will be prepared for submittal to NWTPD clearance.

In the data analysis task the top of the fresh-water and the base of fresh-water

potentiometric surfaces will be estimated for the salt dome region. Between 25 and 50 data points are available to estimate the top of the fresh water. More data may be available from the U.S. Geological Survey, perhaps several hundred points.

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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.*

LEACHING MECHANISMS - G. L. McVay

The effect of water radiolysis on elemental leaching from PNL 76-68 glass has been investigated as a function of temperature (in the range of 50 to 90°C) and of gamma irradiation dose rate. Degassed, deionized water was used as the leachate to prevent nitric acid generation. Radiolysis effects resulted in accelerated leaching over that found for the unirradiated analogs. Leach rate enhancements were most apparent at low temperatures and decreased in importance with increasing temperature. Enhanced leaching can be attributed to the formation of radiolysis products, since nitric acid formation was prevented. Also, earlier investigations have shown that gamma radiation-induced structural damage, if it occurs, has no discernible effect on glass leaching.

A dose-rate dependence of the leaching rate was found. An increase of two orders of magnitude in the dose rate resulted in an approximately 20% increase in the silicon leach rate at 70°C. The thickness of the

reaction zone on the glasses increased with increasing dose rate, with boron and sodium showing the greatest degree of selective leaching. However, cesium was found to re-sorb on the surfaces, resulting in a reduced degree of selective leaching.

ROCK-RADIONUCLIDE RETARDATION STUDIES -

J. F. Relyea

Fracture flow experiments have begun and are being coordinated with laboratory sorption experiments (determination of surface distribution coefficients, K_d). A comparison of batch, once-through-column and recirculating-column methods for retardation studies was made. The effects of groundwater composition on sorption of cesium, neptunium and plutonium by basalt-related solids was reported. Experimental uranium concentrations were compared to predictions made with several thermodynamic data bases. Adsorption of neptunium on kaolinite was studied as a function of both neptunium concentration and CaCl_2 concentration.

SOLUTION CHEMISTRY - D. Rai and
R. G. Strickert

A procedure has been developed at PNL to differentiate Pu(IV) from Pu(III) in 10^{-7} to 10^{-6} M Pu solutions using Arsenazo III. This procedure can be used in the study of plutonium compounds of low solubility. Results on the aqueous solubility of neptunium from doped glass beads indicate that the neptunium solution concentration is essentially the same as that in solutions contacting $\text{NpO}_2(\text{c})$. In addition, quinhydrone was shown to be an effective redox buffer ($E^\circ = 0.7 \text{ V}$). Additional osmium compounds were synthesized and tested (at Los Alamos National Laboratory) for use as redox buffers. The complexed $\text{Os(II)Cl(py)(bipy)}_2 / \text{Os(III)Cl(py)(bipy)}_2$ couple ($E^\circ = 0.43 \text{ V}$) appears to be stable for at least 10 days. A milestone report on technetium behavior under reduced condition (at Oak Ridge National Laboratory) was submitted and reviewed. Two important conclusions from the report were that technetium can be substantially removed from solutions contacting basalt and that the removal mechanism is associated with the reduction of technetium by the redox conditions existing in the suspension.

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

The PNL/Sandia waste package test components were submitted for surface and solid-state analysis at PNL and Sandia National Laboratories. A meeting was held to discuss the results to date. Several modifications were completed on the autoclave system that will be used for hot-cell testing.

SOURCE-TERM MODELING - W. L. Kuhn

Leach modeling for waste glasses is being pursued in terms of protective surface layers. A review of geochemical models for weathering of minerals shows they can be adapted as simple glass leach models. A review of post-test analyses planned for the PNL/Sandia waste package tests shows that surface analyses of the glass surface should contribute to developing realistic glass leach models.

GEOCHEMICAL MODELING AND SITE INVESTIGATION -
W. J. Deutsch

The thermochemical data estimated for nontronite last quarter were coded into the WATEQ data bank. Methods were investigated for estimating thermochemical properties of zeolites important in the ground-water environment. A supporting code for EQ3/EQ6 was rewritten to allow for expansion of the data base, and phosphate and plutonium are now on the primary data file. The process of building the mineral dissolution kinetics capability into the EQ6 code was initiated. The results of the basalt ground-water geochemical modeling study have been evaluated. The ground-water samples compute to be in equilibrium with calcite and a number of amorphous phases ($[\text{Fe}(\text{OH})_3]$, allophane, and SiO_2). If present in the aquifer, these reactive minerals will be influential in limiting or controlling the ground-water composition. In support of the salt dome site characterization studies, the concentration of ^{226}Ra in six core samples from two domes has been determined. Based on the estimate of uranium concentration from the radium measurements, it will be necessary to chemically separate uranium from the salt in

19.3

order to determine disequilibrium ratios as a measure of the stability of the domes.

FUTURE ACTIVITIES

Analyses for the PNL/Sandia waste package test will be completed and a status report prepared. Preparation of a leach model of waste glasses will continue; data from the existing literature will be added and WRIT experimental results incorporated. The minimal dissolution kinetics capability will begin to be built into the EQ6 computer code.

The uranium validation of the WATEQ3 geochemical model will be completed, and dating of the salt dome cores will continue.

Experiments to determine PuO_2 and NdO_2 solubilities will be conducted in an anoxic chamber. A series of thermal gradient experiments will be started, using Umtanum basalt and welded tuff along with either 76-68 glass or a simplified glass. Work with Np-laden ground water and kaolinite will continue to determine the dominant sorption mechanism.

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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.

All the cask-handling and shipping hardware has been fabricated and accepted. A special bail was added to the required hardware, which in turn was attached to the waste log to enable E-MAD to remove the waste log with their existing BWR grapple.

The cask-handling procedure is complete and approved. All training in reference to this program is complete.

The Pacific Northwest Laboratory's Operation Readiness Plan is complete and approved. This plan was reviewed by an Operation Readiness Review Board, and no significant changes were required.

Nuclear Assurance Corporation did not receive the certificate of compliance in time for PNL to meet the original scheduled shipping date. Additional information was furnished by PNL to NAC in support of obtaining this license amendment.

Once NAC receives authorization to ship the high-level waste log in their NLI 1/2 cask and DOE gives PNL permission to receive the cask, PNL will perform the dry run on the cask-handling equipment and subsequently load and ship the NWVP-2 waste log to E-MAD.

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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 multi-component backfill material that most nearly satisfies the prescribed attributes.

SUMMARY

The major activities during this reporting period have been 1) characterization of candidate backfill materials, 2) radionuclide sorption (K_d) measurements on candidate backfill materials, 3) measurement of backfill compaction properties, 4) determination of hydraulic conductivities and swelling pressures of bentonite and bentonite/sand mixtures, and 5) initiation of experiments designed to clarify the kinetics of backfill saturation.

TECHNICAL PROGRESS

Initial characterization of backfill materials has included x-ray diffraction (XRD) analysis, differential thermal analysis (DTA), and chemical analysis. Preliminary XRD analysis of five candidate backfill clays has been completed. Untreated sodium bentonite (CS-50[®]), treated sodium bentonite (Accofloc-350[®]), and untreated calcium bentonite are normal montmorillonites as expected. One treated sodium bentonite (Saline Seal[®]) is a mixed-layer clay containing a significant proportion of nonexpanding (illite) layers

within its crystal lattice. Ferrosand[®] is the 1M polymorph of the mineral glauconite. The chief impurities in the bentonites are feldspar and quartz. DTA scans of untreated sodium and calcium bentonite have been completed. DTA scans carried out at the standard heating rate of 10°C/min generally agree with published data for bentonites and indicate major water loss at ~115°C for sodium bentonite and 130°C for calcium bentonite. DTA scans carried out at lower heating rates indicate that kinetic effects can strongly affect DTA results. Scans carried out at 0.1°C/min, the lowest rate possible on the available equipment, indicate a shift of the major water loss endotherms to 70°C for sodium bentonite and 75°C for calcium bentonite. At the lower heating rate, loss of loosely bound water from the sodium bentonite is essentially complete at 100°C. These results indicate that published standard DTA curves cannot be used to accurately predict the water loss behavior for various clay minerals.

The compaction density of naturally occurring calcium bentonite was determined as a function of compaction pressure (55 to 221 MPa) and water content (0 to 28 wt% H₂O).

[®]CS-50, Accofloc-350, and Saline Seal are registered trademarks of the American Colloid Co.

[®]Ferrosand is a registered trademark of Hungerford and Terry, Inc.

Compared to previous results for sodium bentonite (CS-50), the compaction densities were lower at the same compaction pressure, but for the higher compaction pressures the results showed similar dependence on water content, with a density maximum at ~8 wt% water. Densities of 1.8, 2.01, 2.10, and 2.14 g/cm³ were obtained for 2.96-cm-dia pellets at 8 wt% H₂O content using compaction pressures of 55, 110, 166, and 221 MPa, respectively.

Batch distribution coefficients (K_d 's) for ¹²⁵I, ⁸⁵Sr, and ¹³⁷Cs with candidate backfill materials in synthetic Grande Ronde ground water have been measured for contact times of 14 and 28 days. The results indicate that strontium and cesium are retained by the clays and zeolites with K_d 's in the range of 10³ to 10⁴. Iodine was retained by pyrite, FeS₂, but the change of pH from 9.8 to 2.8 during the 28-day tests indicates that pyrite is probably not a desirable backfill component. Iodine K_d values were also obtained for other suggested backfill additives. Iodine K_d values of 10³ to 10⁴ were obtained for silver-treated silica and mordenite; Ag-, Cd-, and Pb-treated faujasite; and silver nitrate-treated bentonite clay. However, the stability of these materials in the backfill environment is uncertain. Technetium K_d values of ~7 x 10³ were obtained using iron metal and charcoal. No other materials have been identified for removal of technetium from ground waters.

Hydraulic conductivities and swelling pressures have been measured for sodium bentonite, calcium bentonite, and sodium bentonite/sand mixtures. Typical test results are listed in Table 21.1. Although the hydraulic conductivity of the calcium bentonite is higher than that of the sodium bentonite, and the swelling pressure is somewhat lower, the calcium bentonite may be acceptable as a backfill material.

Values for hydraulic conductivity can be used to evaluate the rates at which water will move through a backfill once it is saturated. They, however, provide little information about the time required for water to move through the backfill initially. A series of experiments have been initiated, using the existing permeameters, to help quantify this important parameter. Sodium bentonite (CS-50) was pressed at 138 MPa into 5-cm-dia cells to form cylinders of clay 0.5, 1.0, and 2.0 cm thick and with a density of 2.1 g/cm³. Grande Ronde ground water was then forced through the clay compacts by a hydraulic head of ~15 MPa. The initial results are shown in Table 21.2. The initial results are consistent with a model in which the hydration rate is controlled by the rate at which water can be forced through the already-saturated portions of the clay. Movement of water through 0.5 cm of clay required 4.6 days. If it is assumed that the first 0.5 cm of the 1 cm samples required

TABLE 21.1. Typical Permeability Tests Results

Backfill Material	Density, g/cm ³	Head, MPa	Hydraulic Gradient	Time, hr	Hydraulic Conductivity, cm/sec	Swelling Pressure, MPa
Na Bentonite	2.13	14.6	1.56 x 10 ⁵	766	5.6 x 10 ⁻¹³	58
Ca Bentonite	2.11	15.4	1.59 x 10 ⁵	617	1.6 x 10 ⁻¹²	31
50% Na Bentonite	2.09	16.7	1.73 x 10 ⁵	618	6.4 x 10 ⁻¹²	22
50% Sand (80-120 mesh)						

TABLE 21.2. Results of Preliminary Saturation Tests

Clay Thickness, cm	Hydraulic Head, MPa	Time to H ₂ O Breakthrough, Days
0.5	15.2	4.6
1.0	14.5	18.9
2.0	15.2	(a)
0.5	3.4	(b)

(a) No breakthrough in 30 days, estimated days to breakthrough = 80-120.

(b) No breakthrough in 22 days.

4.6 days, then the second 0.5 cm of the 1 cm sample required 13.8 days for water penetration.

Work during the next quarter will concentrate on measurement of sorption K_d 's, hydraulic conductivities, and saturation times. In FY-1982 work will be expanded to include material stability and compatibility and diffusion studies.

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 time periods of approximately 1000 years.

Fatigue-crack-growth rate tests are being used to evaluate susceptibility of titanium grades 2 and 12 to stress corrosion cracking in a Hanford basaltic ground water. Susceptibility is indicated by a frequency-dependent crack-growth rate or by a high crack-growth rate relative to an inert environment.

Fatigue-crack-growth rate tests run on two orientations of each titanium alloy at 90°C in simulated Hanford ground water at 1 Hz frequency showed no acceleration of crack-growth rate due to the ground water environment. The fluoride content of the ground water was then increased from the "normal" 37 ppm to 220 ppm to provide a more severe environment. Tests have now been run at 1 Hz and 0.1 Hz in this high-fluoride solution at 90°C. In addition, one orientation of grade 12 titanium was tested in high-purity deionized water. The data from these tests were analyzed by fitting the data to the equation

$$\frac{da}{dn} = c\Delta K^m$$

where da/dn is fatigue-crack-growth rate, ΔK = cyclic stress intensity, and c and m are regression coefficients from a power-curve fit. This procedure allows c and m to be compared for each test.

No significant difference was found between crack-growth rates obtained in the air

environment, normal fluoride Hanford ground water environment, or the high-fluoride Hanford ground water environment. Tests were then begun on grade 12 titanium, LT orientation, at 0.01 Hz. After four data points were obtained, an interruption in the water supply occurred and the test had to be terminated. The initial data points lie above the data scatterband of the high-frequency tests, indicating that a higher crack-growth rate occurred. However, the amount of data is insufficient to draw definite conclusions. Low-frequency tests in high-fluoride Hanford ground water will continue during the next reporting period.

Slow-strain-rate tests have been done on grades 2 and 12 titanium at displacement rates of 10^{-4} , 10^{-5} , 10^{-6} , and 10^{-7} in./sec in Hanford ground water at 250°C. Grade 12 has been tested in two orientations, and grade 2 has been tested in one orientation. Both titanium alloys exhibit a large loss of ductility with decreasing displacement rate, indicating environmentally induced damage. Fracture surfaces from specimens of both orientations of grade 12 titanium were examined in a scanning electron microscope for evidence of stress-corrosion cracking, either intergranular or transgranular. All surfaces are rough and dimpled, typical of the "normal" void-coalescence fracture mode.

One interesting feature observed is the presence of spherical particles on some fracture surfaces. These particles were found predominantly on specimens that were tested at the low displacement rates.

A test matrix for the first 12 months of testing in the radiation-corrosion facility has been constructed, and sample holders have been designed. Initial tests will include corrosion coupons; stressed corrosion specimens (U-bends); stressed, precracked specimens (wedge-opening load); and mechanical-degradation specimens (Charpy V-notch).

Safety reviews have been held regarding the irradiation/corrosion test facility by Pacific Northwest Laboratory and Hanford Engineering Development Laboratory. The

wrap-up of this phase should be completed in early July.

Future activities include the following:

- continuation of fatigue-crack-growth-rate tests of titanium alloys at low cyclic frequencies
- constant-elongation-rate tests (CERT) of titanium alloys performed in air environments to obtain control data
- fractographic examination of the surfaces of broken CERT specimens
- initiation of a screening test of selected cast ferrous materials in Hanford basalt ground water at 150°C
- startup of the irradiation/corrosion test facility.

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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.

SUMMARY

During the past quarter, a repository cost model was developed to facilitate the analysis of costs of mined geologic repositories in various media. The model was benchmarked to verify its accuracy, and a series of cases is now being run to analyze the cost sensitivity of media-dependent variables.

TECHNICAL PROGRESS

During this quarter, the repository cost model, RECON, was developed and completed. The model simulates ten cost centers in a repository: facility construction and equipment, shaft development, mine development and mined rock logistics, prestartup costs, waste receiving and packaging, other surface operations, underground waste handling, utilities, shaft sealing and decommissioning, and cost allocations by waste type. The model develops cash flow requirements based on cost streams from the above cost centers and calculates both total and levelized unit costs for up to five repositories in a single case.

The cost model was benchmarked using cost data from the draft Conceptual Reference Repository Design (CRRD) report for a repository in domed salt. The RECON estimates were \$4.5 billion, or within 5% of the CRRD estimate of \$4.7 billion.

Reference cases were then developed for generic spent fuel repositories in salt, granite, basalt, and tuff. The reference cases assume that 3 PWR or 8 BWR elements are packaged in 0.4-m-dia steel canisters with a 0.64-cm titanium skin. These are emplaced in holes with a carbon steel liner surrounded by a 0.3-m annulus of bentonite. The reference packages are the same for each medium. All other parameters that were not readily identifiable as being media-dependent were also held constant for each medium. Media-dependent variables included rock density, unit mining and rock handling costs, unit backfilling costs, hole spacing, extraction ratio, repository depth, room dimensions, hole drilling costs, and limiting thermal density criteria.

Costs for the reference repositories are summarized in Table 23.1. The driving factors in the cost estimates (and the reason that the estimates in Table 23.1 differ significantly from the CRRD estimate) are the packaging and hole-lining concepts, as shown in the unit cost breakdown in Table 23.2. If fewer spent fuel elements are packaged per canister, these costs become even more significant. Table 23.2 also indicates that for repositories that are similar in all non-media-related aspects salt would be the least expensive medium, due chiefly to lower hole-drilling costs and, to a lesser extent, lower mining costs.

In the next quarter the sensitivity of costs to changes in media-dependent variables will be examined using the RECON model, and least-cost scenarios will be

defined for each medium. The results will be published in a topical report in the following quarter.

TABLE 23.1. Reference Repository Costs in Various Media

	Medium			
	<u>Salt</u>	<u>Granite</u>	<u>Basalt</u>	<u>Tuff</u>
Total cost, billions of 1981 dollars	7.6	9.0	8.0	8.4
Unit cost of spent fuel disposal, \$/kg heavy metal	82	98	107	92

TABLE 23.2. Unit Cost Analysis for Reference Case Repositories, \$/kg Heavy Metal

	Medium			
	<u>Salt</u>	<u>Granite</u>	<u>Basalt</u>	<u>Tuff</u>
Facility construction and equipment	15	16	18	16
Shafts	2	2	3	1
Mining	3	7	8	5
Waste operations labor	13	12	13	13
Packaging	21	21	21	21
Hole preparation and lining	10	20	21	17
Other	<u>18</u>	<u>20</u>	<u>23</u>	<u>19</u>
Total	82	98	107	92

24. ANALYSIS OF SPENT FUEL POLICY IMPLEMENTATION

M. K. White - Project Manager

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

The collection of data for the fee update was begun. The updated spent fuel management requirements reported in DOE/SR-007 were assessed to determine the appropriate away-from-reactor basin and reporting schedule. The Conceptual Reference Repository Description (CRRD) issued by the Office of Nuclear Waste Isolation (ONWI) was evaluated to determine whether the cost data are adequate for use in the fee calculation. Calculations of the base case logistics and facility requirements for the fee report were begun.

A meeting was held at DOE Headquarters on June 16 to discuss data requirements for an updated disposal fee estimate. It was decided that the update should include an estimate of the fee for high-level waste disposal. Pacific Northwest Laboratory will provide to ONWI by the end of July a reference schedule for light water reactor and fast breeder reactor high-level waste (HLW) receipts at the repository. The repository

cost estimates for both spent fuel and HLW disposal will be provided to PNL by October 30, 1981.

Work is continuing on the computer model users' manual. Methodology descriptions previously planned for the fee update report will be included in the users' manual since the fee update will no longer include a storage fee. An outline of the report will be forwarded to Savannah River Laboratory (SRL) in July.

A report is being prepared that describes methodology for valuing spent fuel and estimating the value of current inventories. Methodology development is partially complete. The method for inventory valuation will depend on the degree of detail for spent fuel isotopic composition in the Stoller data base. SRL will be consulted to determine what data are available. An outline of the report will be forwarded to SRL in July.

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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

The draft of the International Survey of Spent Fuel Storage Experience was finalized at a June 1981 Consultant Group meeting in Vienna.

Specimens are being examined at PNL from spent fuel pool components exposed in the Zion (PWR), La Crosse (BWR) and RBOF (AFR) pools

Studies are continuing to examine important factors that contribute to stress corrosion cracking of 304 stainless steels (SS) under spent fuel pool conditions.

PROGRAM MANAGEMENT

A paper, "Technical Bases for Interim Storage," was prepared for the ANS topical meeting, Technical Bases for Nuclear Fuel Cycle Policy, to be held in Newport, Rhode Island, September 20-23, 1981.

INTERNATIONAL

The International Atomic Energy Agency (IAEA, Vienna) and the Nuclear Energy Agency (NEA, Paris) are cooperating on an international survey of spent fuel storage experience. Survey responses have been received from 19 countries. The responses were sum-

marized in a draft report which has been sent to the responding countries for comment. The report was finalized by an IAEA Consultant Group at a June 1981 meeting in Vienna.

SPENT FUEL EXAMINATIONS

The paper entitled "Spent Fuel Behavior in Water Pools" (Paper No. 168; PNL-SA-9055) was presented at CORROSION/81 in Toronto on April 8. An abstract for a proposed paper, "Interim Storage of Spent High-Burnup LWR Fuel" (PNL-SA-9697-A), was submitted for the ENS/ANS Topical Meeting on Nuclear Fuel Cycles and Waste Disposal to be held in Brussels in April 1982.

Shippingport Fuel Examination

Work is continuing to prepare the final report on the hot-cell examination of fuel rods from fuel bundles 0551 and 0074. The Shippingport fuel examination report is expected to be issued about September 30, 1981. R. W. Klingensmith (Battelle Columbus Laboratories) visited PNL on May 27 and delivered detailed information on the hot-cell procedures and the associated quality assurance measures needed for inclusion in the report and requested by BCL.

A letter was sent to W. G. O'Quinn of the Savannah River Operations Office (SRO) of DOE containing the information we have been able to assemble for the Appendix A agreement; this is needed before the remaining fuel rods can be shipped to a storage facility. A reply was received from L. C. Sjoström, SRO, indicating that the fuel is acceptable for receipt and long-term storage in the RBOF (Receiving Basin for Off-Site Fuel) at the Savannah River Plant.

Connecticut Yankee Fuel Examination

Efforts are continuing to finalize the report on hot-cell examination of stainless-clad fuel assembly S004. We expect to issue the Connecticut Yankee fuel examination report on schedule (September 1981).

Selected rods from Assemblies G11 and H07 (EPRI/NUSCO examination) are to be used in the reconstitution of fuel bundle S004; some characteristics of those rods (e.g., cladding seam weld and end cap weld areas) that are of particular interest to this program have been evaluated and will be reported under the PNL program.

Oconee Failed Fuel Examination

As suggested by Babcock and Wilcox Company, PNL contacted Duke Power Company early in April about the possibility of examining (at the Oconee spent fuel pool) one or two Oconee-1 fuel bundles, which contain defective Zircaloy-clad fuel rods, that have been stored in borated water for 6 years. PNL estimates that much of the needed information could be obtained with about 1 week of activity. We are particularly interested in a visual inspection that produces high-quality, high-resolution color prints of fuel rod

areas associated with the defects. The Duke Power personnel suggested we also consider inspecting the fuel bundle(s) by sipping.

SPENT FUEL POOL COMPONENT EXAMINATIONS

Examinations are proceeding on specimens from spent fuel pool components exposed in the following spent fuel pools:

Zion (PWR):

stainless steel fuel rack

La Crosse (BWR):

stainless steel fuel rack

boronated stainless steel fuel rack

boral curtain

RBOF (AFR):

stainless steel table section

aluminum spacer (yet to be received).

MECHANISM STUDIES

A paper entitled "An Evaluation of Stress Corrosion Cracking of Sensitized 304 SS in Low Temperature Borated Water," PNL-SA-9387, has been prepared for the Second International Conference on the Environmental Degradation of Engineering Materials to be held September 21-23, 1981, at the Virginia Polytechnic Institute.

Intergranular stress corrosion cracking (IG SCC) has been observed during constant axial load tests of furnace-sensitized, high-carbon 304 SS in borated water (2000 ppm boron as boric acid) with 15 ppm Cl^- at 35°C. The specimen was removed from the Three Mile Island pipe material (0.07 wt% carbon), was sensitized (24 hr, 620°C), and was loaded to a stress of 1.5 times the yield stress for 700 hr. Intergranular cracks propagated

through 85% of the specimen cross-section. Constant extension rate tests (CERT) of an identical specimen showed a decrease in ductility, but no IG SCC.

Constant axial load tests have also been completed on two as-welded TMI pipe specimens. Both specimens were loaded sequentially to stresses of 1.0, 1.25 and finally 1.5 times their yield stress for 700 hr at each stress level. Again, the presence of chloride ions was essential for IG SCC to occur. The specimen exposed to a boric acid solution without Cl^- at 35°C showed no evi-

dence of corrosion or stress corrosion, while the second specimen, with ~2 ppm Cl^- in solution, exhibited IG cracking through ~30% of the cross-section. This cracking occurred during testing at the highest stress level.

No evidence of IG SCC has yet been observed in furnace-sensitized or as-welded specimens without the addition of chloride to the borated water solution. Axial load experiments on furnace-sensitized and as-welded 304 SS are continuing to determine the importance of the level of sensitization and specific-environment chemistry on IG SCC.

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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.

SUMMARY

The computational capabilities required for modeling postulated accidents in spent fuel basins have been fully implemented. Analysis of one of the hypothesized accidents using fresh fuel conditions has been completed.

MODEL DEVELOPMENT

The objectives of this program require the capability to model the time-dependent neutronics and thermal-hydraulics behavior of a system comprised of an array of spent fuel in a nonpressurized water environment. The two-dimensional, time-dependent neutron-

ics program TWIGL and the thermal-hydraulics analysis code COBRA were selected for use in the analysis. The two codes were modified, combined and enhanced in previous quarters. Testing of the code was completed during this quarter.

ANALYSIS

A postulated accident involving the separation of a 3 x 3 array of fresh fuel from a borated rack has been modeled. Efforts are currently being directed toward modeling the more realistic case where credit is taken for the fissile depletion associated with spent fuel.

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

Tailing core samples have been obtained from the 1981 field test area and are being analyzed for radium content, chemical composition, density, particle size distribution, and water-leachable elements. In the seal-stability studies it was found that 1) emulsified asphalt can be slowly biodegraded, 2) no single organism can utilize all components of the asphalt, and 3) inhibition or toxicity to bacteria occurs when a mixed colony grows on asphalt.

Planning continued for the 1981 joint field test, including meetings at Grand Junction, Colorado, and Salt Lake City, Utah, with RAECO, PNL and Sandia personnel to finalize plans for the earthen cover and column test plots. The earthen cover system will consist of four test plots using soil and clay covers. The specific materials to be used have not yet been selected. Instrumentation for the earthen cover systems will include moisture blocks, thermocouples, and access tubes for neutron moisture measurements and downhole logging. The column tests will have soil gas probes and alpha detectors in addition to the moisture blocks and thermocouples.

The first part of the field test was started with removal of the overburden from the asphalt emulsion test area and scraping

of vegetation from the other test areas. Radon flux measurements were made on the asphalt and earthen cover test areas.

TAILINGS CHARACTERIZATION - M. R. Elmore and J. M. Sauer

Field samples were collected at Grand Junction during April 6-12 from an area representing the summer 1981 field test site. Fifteen sample points on a 3 x 5-ft geometric pattern were made by coring with three 3-ft Shelby tubes at each hole. The tubes were sealed with wax and shipped to PNL for analysis. Each 3-ft core sample was separated into 1-ft sections, which were then split into four equal samples. These samples will be used to determine the following characteristics of the tailings:

- radium content and emanation coefficients
- bulk density
- moisture content
- particle size distribution
- chemical composition
- water-leachable components.

Field densities were determined, with corrections allowed in some samples where compaction was caused by pushing the Shelby tubes into the tailings. Average density of the tailings was 77 lb/ft³, varying from an average of 72 lb/ft³ on the west side of the test plot to 84 lb/ft³ on the east.

Moisture contents of all the samples were also made by oven-drying the samples overnight. Sample moistures varied from 17.5% on the west half to 9.7% for the east half of the test plot. Radium counting, emanation coefficient determinations, particle size distributions, chemical analyses, and water leaching tests are now under way.

ASPHALT SEAL STABILITY - D. A. Nelson and C. F. Voss

Three aspects of seal stability were investigated this quarter: biodegradation, aqueous leaching, and oxidation. A mixed bacterial colony known for its ability to utilize heavy oils was used in the biodegradation study. There, bacteria definitely utilized the emulsified asphalt as a carbon source for growth. However, the growth dynamics were quite complex and the overall rate of the growth appeared to be very slow. A major complication was that some bacterial byproducts were toxic or inhibitory to others in the mixed colony. Consequently, the variable and complex dynamics of growth were difficult to measure by counting and turbidity techniques. It does appear at this time that the following assumptions can be made:

- Emulsified asphalt can be biodegraded.
- No single organism can utilize all components of the asphalt.
- Inhibition or toxicity to bacteria occurs when a mixed colony grows on asphalt.

Four aqueous leaching cells were dismantled after 6.5 months of operation. Two solid asphalt samples and two admix samples were examined. No disturbance was noted in the admix samples or the surrounding sand. There was, however, evidence of cold flow in the pure asphalt samples, and some discoloration of sand was noted under one of the pure

asphalt samples. The leachate (distilled water or brine) was extracted with dichloromethane. In all samples there was a 0.03 to 0.05% weight loss (based on asphalt) regardless of whether they had been exposed to brine or distilled water. This assumed a 20% asphalt content in the admix samples. It must be emphasized that this weight loss was due to 6.5 months of constant exposure to recycling water or brine. The leachate residues will be examined by gas chromatography.

An authentic 35-year-old asphalt sample was examined using an infrared technique developed by Claime Peterson of the Laramie Energy Technology Center. After considerable initial difficulty, the procedure has been found to be a superb way to quantitatively measure oxidation products (acids, anhydrides and ketones) in asphalt. Samples of emulsified asphalt collected in 1980 and 1981 from the Grand Junction site show none of these byproducts of oxidation. Sample holders have also been designed and constructed for laser-Raman spectroscopy. This procedure will measure oxygen uptake (versus time) by asphalt.

Core samples of the 1980 Grand Junction test seal were taken during April and sent to Scott Schuler for laboratory testing. The laboratory in Albuquerque will perform a number of triaxial tests to determine the asphalt response to thermomechanical loading. A variety of ASTM asphalt tests will also be performed to allow a comparison with other asphalts.

Four of the core samples were tested at PNL to determine the percentage of asphalt, aggregate and air in the seal. Average thickness of the seal from the sampling points was 2.64 in. (6.7 cm) with a standard deviation of 0.18 in. The results of the asphalt extractions are shown in Table 27.1.

TABLE 27.1. Asphalt Content of Core Samples Taken from 1980 Test Area

<u>Sample</u>	<u>Asphalt Content, wt%</u>
B1-028.0 ^(a)	19.8
C1-045.7	23.1
D2-066.8	23.4
F1-102.8	<u>25.8</u>
Avg	23.0

(a) This number designates the distance north (in feet) from the south edge of the seal, at which the core was taken.

SEAL FORMULATION - R. L. McDowell and H. D. Freeman

Tests were run on several asphalt emulsion/concrete sand mixtures to determine the optimum curing time before compaction of the seal. It was found that if the moisture content of the sand was initially less than 10 wt%, the seal could be compacted in about 14 days. However, if the moisture content of the sand exceeded 10 wt%, the optimum curing time was about 23 days. It is apparent from this test that the concrete sand moisture content should be monitored during the seal application if minimum time is desired between application and compaction of the seal.

RADON DIFFUSION MEASUREMENTS - H. D. Freeman

Radon diffusion measurements have been run on various asphalt seals prepared by Petroleum Sciences, Inc., and PNL. The data collected from these tests have been analyzed with a transient model computer program to determine the effective diffusion coefficients for radon through the seal. The results of this analysis are presented in Table 27.2.

As can be seen from the diffusion coefficients, several seal formulations are equally effective in stopping radon. The factors that must be considered in choosing the best seal formulation are 1) economics, 2) behavior of the admix in the seal application machinery, and 3) long-term stability of the seal.

FIELD TEST - J. N. Hartley

The site for the 1981 field test was surveyed, staked out, and sampled as discussed in the section on laboratory characterization. Also preliminary flux measurements were made; they ranged from 31 to 840 pCi/m².sec. The overall test area (450 x 250 ft) is located on the southeast side of the tailings pile.

A meeting was held in Grand Junction to discuss the field test and, in particular, the earthen cover systems. Those attending were J. N. Hartley, H. D. Freeman, G. W. Gee, J. T. Zellmer, V. C. Rogers, and P. O'Brien. It was concluded that four earthen cover systems would be applied and tested in 50 x 100-ft test plots. The systems include 1) 10-ft typical Grand Junction overburden type 1; 2) 10-ft typical Grand Junction overburden type 2; 3) 2-ft clay type 1 plus 8-ft overburden type 1. Also to be included in the test will be six 6-ft-dia column tests to compare results with the larger test plots. One of the columns will be used for the "admiral's" test (apply enough earthen cover to reduce radon flux to below 2 pCi/m².sec EPA standard).

Contracts were completed for the field test, including those for 1) general contractor, 2) cold mix paver, 3) distributor truck, and 4) asphalt emulsion.

At a meeting held in Salt Lake City with Vern Rogers and Associate Engineering

TABLE 27.2. Calculated Effective Diffusion Coefficients for Radon Through Asphalt Seals

Seal Description	D_e , cm^2/sec
25-84A Hot Asphalt Macadam Mix	2.02×10^{-6}
25-84B Hot Asphalt Macadam Mix	2.30×10^{-6}
25-84C Cationic Rapid Set Emulsion Macadam Mix	4.24×10^{-6}
25-125C Hot Asphalt Hydraulic Mix	2.02×10^{-6}
25-125D Hot Asphalt Hydraulic Mix	3.36×10^{-6}
78 mV (150-200 pen) Cationic Emulsion Seal	3.37×10^{-6}
78 mV (85-100 pen) Cationic Emulsion Seal	4.39×10^{-6}
78 mV D (85-100 pen) Cationic Emulsion Seal	4.86×10^{-6}
25-128 D-SS1h Nonionic Emulsion Seal	2.27×10^{-6}
25-129C-CSS Cationic Emulsion Seal	3.19×10^{-6}
Arco 2400 Cationic Emulsion	4.35×10^{-6}

Corporation (RAECO) plans were reviewed for the earthen cover portion of the field test. Those attending were J. N. Hartley, M. R. Elmore and H. D. Freeman for PNL and V. Rogers, K. Nielsen, A. Sutherland, and D. Rich from RAECO. RAECO's contribution to the field test effort was reviewed. Their primary responsibilities will be to 1) characterize selected cover materials, including soil properties and effective diffusivity; 2) determine radium content and emanation of tailings; 3) provide manpower during installation of earthen covers; and 4) monitor effectiveness of covers in conjunction with PNL monitoring activities. Questions were raised at the meeting as to what size of columns should be used for column tests. PNL suggested 6-ft-dia columns while RAECO suggested 4-ft-dia columns. Instrumentation of the columns was reviewed, with the recommendation that gas samples and temperature and moisture measurements are to be made at 2-ft intervals.

The column tests will include: 1) four columns with soil configurations similar to those of the large earthen cover test plots, 2) two columns similar to multilayer test

plots, and 3) one column similar to asphalt-emulsion system. All columns will have 6 ft of tailings to avoid the surrounding environment's affecting the source term. In addition, an "admiral's test" column will be installed by RAECO.

The field test layout is shown in Figures 27.1 and 27.2.

The field test began June 1 with the removal of 2 to 10 in. of overburden from the asphalt emulsion test plot. Vegetation was scraped off the earthen cover and multilayer test areas to provide a smooth surface for radon flux measurements and seal application. Radon flux measurement test points were surveyed and staked out for the entire joint field test area. One hundred and ten radon flux measurements were completed on the asphalt emulsion and earthen cover test areas. Moisture blocks and thermocouples were placed in 16 locations in the asphalt emulsion and earthen cover systems. These will be monitored periodically to determine the temperature and moisture below the seals.

A revised field test schedule is included for reference. The major activities are scheduled as follows:

FIGURE 27.1. Multiview Sketch of 1981 Field Test Site

FIGURE 27.2. 1981 Joint Field Test Site Layout

Site preparation	June 1-12
Site characterization	June 15-26
Asphalt emulsion seal application	July 6-10
Earthen cover application	July 6-31
Multilayer cover application	July 13-31
Reclamation	Sept. 8-30
Radon flux monitoring	Sept. 8-30

Application Technology - J. L. Buelt and E. G. Baker

The cold-mix paver to be used in this summer's field test was modified for a higher production rate and subjected to a brief screening test. Since the production rate had been previously limited to the pumping capacity of the asphalt emulsion, an additional pump operated in parallel with

the original was installed. With this pump, the asphalt seal production rate was increased from 1000 kg of dry aggregate per minute to 1800 kg/min, an increase of 80%.

During the screening test, an asphalt seal 75 m long was paved to check out the equipment. Some recommendations were made by various industrial experts observing the test. The most pertinent comments include the following:

- Slow the aggregate feed belt to half speed while doubling the gate height. This will keep more weight on the belt, eliminating fluctuations in aggregate flow rate.
- Use the storage tank on the cold-mix paver as a surge tank while pumping from the asphalt tanker truck. This will eliminate any possibilities of cavities at the higher emulsion flow rates.

- At the higher production rate, the dump trucks supplying aggregate to the cold-mix paver must be coordinated well to allow continuous production.

These recommendations are being incorporated for this summer's field tests.

Based on the results of the cold-mix paver test runs in Holbrook, Arizona, a new conveyor motor has been purchased for the paver to help control the aggregate flow rate. The subcontract for the asphalt emulsion distributor truck was approved and returned by the subcontractor.

Final preparations were made for the asphalt emulsion application at the joint field test in Grand Junction, Colorado. All subcontracts are in place and 49,000 gal of CMS-2 Cationic Asphalt Emulsion has been purchased from Armak Co. Final site preparation and equipment check-out will take place July 6 and 7. The 1-acre test plot will be paved July 8-10. Black Rock Construction will do the paving using a modified Midland cold-mix paver. Additional equipment will be provided by Walton Trucking Co. and Don Arnold Construction.

Cost comparisons of earthen and asphalt covers for the Salt Lake and Durango sites

were made after obtaining cost estimates for various tasks from local contractors. Our goal is to compare the two types of systems as a function of the amount of earthen cover required. Results of the earthen cover field tests can then be used to determine which cover method is the more economical for the two selected sites.

Grand Junction Site Monitoring -

H. D. Freeman

A trip to Grand Junction was made during the week of April 6-12 to monitor the 1980 test site. Radon flux measurements were made on 37 test locations to determine the effectiveness of the seal in reducing the radon exhalation. Radon fluxes ranged from 0.1 to 262 pCi/m²·sec on locations over the entire seal. In areas over the seal made with the cold-mix paver fluxes ranged from 0.1 to 1.8 pCi/m²·sec, showing that this seal is still very effective. Table 27.3 shows the radon fluxes measured during April 1981. For comparison the fluxes taken in November and September 1980 are also shown. The effectiveness of each seal is shown in Table 27.4.

TABLE 27.3. Radon Flux Measurements at Grand Junction 1980 Test Site

	April 1981 ^(a)	Nov. 1980 ^(a)	Sept. 1980 ^(b)		April 1981 ^(a)	Nov. 1980 ^(a)	Sept. 1980 ^(b)
1 A	--	--	12.9	12 A	--	1.1	0.6
B	--	--	4.3	B	0.1	--	0.2
C	12.7	--	178.4	C	--	--	0.1
D	2.6	--	0.9	D	--	0.7	0.1
2 A	--	--	344.5	13 A	--	0.5	0.3
B	1.1	--	0.7	B	--	--	0.1
C	--	--	81.0	C	0.3	0.4	0.1
D	--	--	20.0	D	--	0.6	0.2
3 A	5.1	--	--	14 A	0.5	--	0.2
B	5.0	--	1.4	B	--	--	0.1
C	262.0 ^(c)	--	3.3	C	--	0.6	0.3
D	--	--	2.3	D	0.4	0.4	0.1
4 A	1.6	--	--	15 A	0.1	--	0.3
B	--	--	--	B	--	0.9	0.2
C	--	--	1.8	C	--	0.8	0.2
D	72.4 ^(c)	--	--	D	--	--	0.1
5 A	--	--	6.5	16 A	--	0.4	0
B	1.0	--	--	B	--	55.8	0.2
C	--	--	3.1	C	0.2	0.6	0.02
D	1.4	--	0.6	D	--	--	0.002
6 A	--	0.9	0.3	17 A	--	--	0.04
B	--	2.0	0.6	B	--	0.4	0.008
C	4.5	--	4.7	C	--	--	0.02
D	0.6	--	0.5	D	0.2	0.3	0.03
7 A	--	0.4	0.5	18 A	0.1, 0.3	--	0.4
B	0.3	0.7	0.3	B	--	231.6	0.4
C	--	--	1.2	C	--	0.4	0.1
D	--	--	70.1	D	--	--	0
8 A	0.2	--	0.3	19 A	0.1	0.3	0.14
B	--	0.3	0.3	B	--	--	0.2
C	--	--	0.3	C	--	--	0.1
D	2.3	--	0.5	D	--	0.6	0
9 A	--	0.5	0.6	20 A	--	0.4	0.2
B	0.3	--	0.3	B	1.8	--	0.2
C	--	--	0.4	C	--	0.4	0.03
D	--	--	0.6	D	0.1	0.4	0.1
10 A	--	0.7	0.4	E	329.6 ^(d)	--	589
B	--	--	0.5	F	160.7 ^(d)	--	176
C	0.4	--	0.5	G	--	--	251
D	--	--	0.6	H	15.2 ^(d)	--	216
11 A	--	0.6	0.01	I	9.8 ^(d)	--	169
B	--	--	0.1	J	45.0 ^(d)	--	123
C	--	0.5	0.04	K	0.1 ^(d)	--	0.6
D	0.2	0.5	0.04	L	--	--	550

(a) Measurements made on top of 1-4 ft of overburden.

(b) Measurements made directly on asphalt seals.

(c) Measurements taken close to the edge of the seal, which allows radon to diffuse to the radon measurement system. This makes the data very questionable.

(d) Measurements made on outside edges of seal.

TABLE 27.4. Comparison of Radon Fluxes from Various Seals (April 1981)

	<u>Flux Range</u>	<u>Average</u>
Soil stabilizer seal	1.1 - 12.6 ^(a)	5.5
Fog seal	0.4 - 2.3	1.3
Hot rubberized seal	0.6 - 4.5	1.9
Cold-mix paver seal	0.1 - 1.8	0.3

(a) Excludes measurements taken on the edge of the seal.

28. LINER EVALUATION FOR URANIUM MILL TAILINGS

J. L. Buelt - Project Manager

The objective of this project is to evaluate the effectiveness of prospective lining materials for preventing moisture transport of radionuclides and hazardous chemicals from uranium mill tailings over a long-term period.

SUMMARY

To determine their long-term stability, eight selected liner materials have been exposed to conditions in the laboratory that accelerated their degradation. Permeability coefficients, which have been determined for each of eleven testing cycles throughout the exposure period, are used to evaluate the rates of degradation. Based on the results of the laboratory tests and a comparative cost evaluation, catalytic airblown asphalt and sodium bentonite will be the liner materials used in the 1981 field test at the Grand Junction, Colorado, tailings site.

ASPHALT AND SYNTHETIC LINER STUDIES -

S. M. Barnes

The liner testing period, designed to simulate long-term liner aging, was completed this quarter. The liners were exposed for 3 months in 60-cm-dia columns to the conditions designed to accelerate the aging process. The liner aging was accelerated for the asphalt liners by exposure to elevated temperatures, strongly acidic solutions, and an oxygen cover gas.

In addition to the accelerated aging conditions, the liners were subjected to substrate subsidence modeling. The substrate subsidence was simulated by creating a void beneath the liner in the exposure column.

The size of the void was determined by subsidence calculations for a generic tailings storage site assuming a tailings depth of 6 m and an overburden depth of 3 m. Fluid was removed from a sealed reservoir installed beneath the liners, thus creating the desired void area.

Accelerated Test Results

The permeability of the various liners was measured at known time intervals (generally 1 week) to determine the degradation of the liners versus exposure time. The results of these permeability tests are plotted in Figure 28.1. The permeability of the liners was determined by measuring the volume of fluid passing through the liner material over a period of time with a known pressure exerted on the fluid. The thicknesses of the liners were estimated, and the permeabilities were calculated with the following formula:

$$K = \frac{VL}{APt}$$

K = permeability, cm/sec

V = fluid passing through liner, cm³

L = assumed liner thickness, cm

A = liner surface area, cm²P = applied pressure, cm - H₂O

t = time, sec.

FIGURE 28.1. Changes in Permeability Coefficients for Asphalt Liners

The volume change during the testing periods was determined by one of two methods: 1) measuring the fluid loss from above the liner or 2) collecting and measuring the solution passing through the liner. The particular measurement method for a selected liner was based on the permeability range for each liner. Liners with higher permeability were measured by fluid collection, and those with lower permeabilities were measured by fluid loss.

The test data indicate an increased permeability over the test cycle for all the liners except the catalytic airblown asphalt (CAA) membrane. The permeability spikes between days 40 and 50 for the CAA liner are due to an experimental error caused by the method of sealing the liners to the test cylinder. The large permeability increase

measured for the asphalt-rubber membrane was due to tearing of the liner where it joined the exposure cylinder. The tears were discovered by post-testing visual inspection.

The subsidence simulation was performed on test day 49, as represented in Figure 28.1. The generic subsidence calculations predicted a subsidence of about 1 cm per 50 cm horizontal length along the impoundment walls for a tailings pile with a 1 to 5 side-wall slope. In the exposure columns this relates to ~1 cm subsidence at the cylinder centerline. The liners were actually subjected to a 1.5-cm subsidence to the centerline for conservatism.

The liner displaying the largest effect of the subsidence is the asphalt-rubber membrane. The tears discovered in this membrane explain the increased permeability since the effect of the subsidence would be to create or enlarge the tears. The catalytic airblown asphalt membrane permeability

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spike during this period is probably due to the experimental error discussed above rather than the subsidence simulation. The fact that this liner eventually regained its previous permeability supports this theory.

Field Test Liner Selection

The candidate liner materials were evaluated using three criteria to select the material for installation at the Grand Junction test site. The selection criteria were a permeability effectiveness factor, the change of permeability with time, and installation cost. The permeability effectiveness factor is defined as the permeability averaged over the final three testing cycles divided by the proposed field liner thickness. The effectiveness factors and installation costs for the liners are listed in Table 28.1. Catalytic airblown asphalt was selected for the FY 1981 field test because permeability actually decreased with time, while those of other materials increased. The selection was based also on a low permeability effectiveness factor and relatively low installation costs.

CLAY LINERS - V. Q. Hale

Much the same approach was used in determining the long-term characteristics of the four clay liners whose accelerated tests were also completed this quarter. However, aging mechanisms for clays depend primarily on the ion exchange rates of sodium with calcium; thus temperature, oxygen concentration, and acidity are not significant factors, as they are with asphalts. Therefore, aging was accelerated by forcing an adequate number of liner pore volumes of leachate solution through the liner. The four clay liners tested were composed of Durango soils, three of which were amended with different bentonites. The initial readings at the beginning of the exposure period revealed that the clay liners did not achieve equal rates of permeability because of differences in individual installations. Accordingly, direct comparisons among clay liner materials are not entirely meaningful. Therefore the liners were evaluated individually upon the rate at which they lose their sealing ability. The results are related to time by

TABLE 28.1. Liner Permeability Effectiveness Factors and Installation Costs

<u>Liner</u>	<u>Average Final Permeabilities, cm/sec</u>	<u>Assumed Thickness, cm</u>	<u>Thickness Ratio</u>	<u>Effectiveness Factor</u>	<u>Installation Cost, \$/m²</u>
Asphalt-Concrete	7 (10 ⁻⁸)	7.6	0.75	6.9 (10 ⁻⁹)	9.60
Hypalon	2 (10 ⁻¹⁰)	0.2	1.71	1.7 (10 ⁻⁹)	7.80
Asphalt-Rubber Membrane	2 (10 ⁻⁶)	0.5	0.65	2.6 (10 ⁻⁶)	4.40
Catalytic Airblown Asphalt Membrane	7 (10 ⁻⁹)	0.6	0.67	7.8 (10 ⁻⁹)	4.30

calculating the number of pore volumes of leachate passing through the liner.

As with the asphalt liners, bladders located under the three bentonite liners were collapsed to simulate subsidence as it might occur in the field. This was a test to determine to what extent the liners would be disrupted and would self-heal. Both the Saline Seal 100 and the GSR-60[®] displayed an immediate increase in permeability followed by decreasing permeability in successive tests. The sodium-bentonite showed a slight increase in permeability following the simulated subsidence test, but has not shown any recovery or self-healing. However, the permeability coefficient for this material following the last test was still

below the coefficient measured when it was first installed; this is because of a steady decline in permeability before the bladder was collapsed. Figure 28.2 shows the changes in permeability coefficients and the number of pore volumes of leachate that have passed throughout the testing period. Of the four clay materials tested, only the sodium bentonite maintained its initial permeability.

In these tests, the sodium-bentonite has been shown to hold up well based on this technical evaluation. Also, economic comparisons with the other bentonite amendments show it to be the most cost effective material. Therefore, a natural soil amended with sodium bentonite was selected with catalytic blown asphalt for the 1981 Grand Junction field test.

[®]Saline Seal 100 and GSR-60 are registered trademarks of the American Colloid Co.

FIGURE 28.2. Changes in Permeability Coefficients for Clay Liners

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.

SUMMARY

During the third quarter of FY 1981, the program accomplished the following:

- tested several clay/gravel and gel/gravel mixes to investigate their use as radon diffusion barriers
- analyzed field and laboratory data, using steady-state and transient radon diffusion models
- began development of a two-dimensional radon diffusion code for multilayer barriers systems
- conducted a site visit in Grand Junction, Colorado, in preparation for the summer field studies
- analyzed Grand Junction samples for moisture content distribution, etc.
- developed a system for measuring time-dependent radon diffusion coefficients.

MATERIAL TESTS AND MODELING - M. E. Dodson
and D. W. Mayer

Tests on several clay/gravel and gel/gravel mixes were conducted to investigate their use as radon diffusion barriers; i.e., materials that would hold water against drainage and reduce the air-filled porosity. The gel/gravel mixes were produced by adding chemical constituents to the clay/gravel

mixes. Initially, iron sulfate and lime were added to produce a hydroxide gel that retained water under 1 bar applied pressure. Additional tests with aluminum sulfate and lime also proved successful. Gel/gravel mixes created by adding sulfates or limes caused no significant decrease in the density of the mixtures.

For Grand Junction conditions, a 1-bar pressure test was conducted to simulate the expected equilibrium drainage of the clay/gravel layer. To date, when iron or aluminum hydroxide is added to the clay/gravel mixture, significant decreases in drainage are achieved. Samples with alum and lime added showed significant increases in equilibrium water contents. The retained water is bound water, which decreases the air-filled porosity and hence the radon diffusion. Radon diffusion tests of both iron and aluminum gel mixtures have produced results comparable to asphalt in terms of radon attenuation properties. Diffusion coefficients for several of the mixes are shown in Table 29.1.

Laboratory permeabilities for clay/gravel and gel/gravel mixes, measured by the falling-head method, yielded values ranging from 10^{-6} to 10^{-8} cm/sec. Mixtures at higher bulk densities exhibited the lowest permeability. The dependence of permeability on

TABLE 29.1. Measured Diffusion Coefficients for Various Compacted Soil/Gravel Mixtures and Gel

Cover Material	Bulk Density, g/cm ³	Volumetric Water Content, cm ³ /cm ³	Air-Filled Porosity, cm ³ /cm ³	Diffusion Coefficient, cm ² /sec
A-(soil/gravel)	2.00	0.196	0.063	8.1E-6
A-(soil/gravel)	2.00	0.102	0.157	1.4E-5
GSR-60® (clay/gravel)	1.71	0.207	0.160	4.6E-4
Gel 1 (soil-gel/gravel)	1.97	0.246	0.027	1.5E-6
Gel 2 (soil-gel/gravel)	1.76	0.273	0.080	4.2E-6
Gel 3 (soil-gel/gravel)	1.77	0.262	0.087	6.6E-6

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bulk density suggests that to achieve permeabilities below 10^{-7} cm/sec the cover material should have a density of at least 1.90 g/cm³. Samples of the clay/gravel and gel/gravel mixes are also being tested to determine maximum compaction density and optimum moisture content. Analyses of water-retention curves for mill tailings samples, including slimes, sands, and sand/slime mixes are also in progress.

Both steady-state and transient radon diffusion models were used to analyze field and laboratory data. The modified version of RADON1, which computes the moisture content required in a layer to achieve a specified surface radon flux, has been tested and applied to plots of the 1980 field site. The transient diffusion code RNDI1D has been used to find the time required to reach a steady-state surface flux. This analysis was made for several different coefficient values and tailings pile configurations. Results from the RAECO code at Rogers and Associates compared well with those from RADON1, thus verifying the RADON1 computational scheme. Table 29.2 shows the comparisons between RADON1 and RAECO in describing one-dimensional radon diffusion through multilayers. The multidimensional heat conduction code TRUMP has been put on

the PDP 11/70 computer and made operational for diffusion modeling. Several runs have been made that simulate the RNDI1D runs while determining diffusion coefficients. Radon decay is not included in the present version of TRUMP, requiring additional modification of the code to attain an operational two-dimensional radon diffusion model. This work will be accomplished in the next quarter.

The one-dimensional partially saturated flow model UNSATV is now running on the PDP 11/70. Work has begun on the one-dimensional partially saturated flow analysis using the A+ and A- soil data. This analysis will use as initial conditions the characteristics of nearly saturated A+ soil. One year will be simulated using wet-year data. The resulting moisture distribution will then be used as initial conditions for a 4-dry-years simulation using the A+ soil and for a single dry year using the A- soil.

FIELD MEASUREMENTS - J. T. Zellmer,
D. R. Sherwood, and B. E. Opitz

A meeting was held in Grand Junction, Colorado, to assess the summer field program and to inspect the test plots. For the multilayer test plot, two treatments using

TABLE 29.2. Comparison of RADON1 and RAECO One-Dimensional Radon Diffusion Codes

Layer	Depth, m	Diffusion Coefficient, cm^2/sec	Total Porosity, cm^3/cm^3	Radium, pCi/g	Exit Flux, $\text{pCi m}^{-2} \text{sec}^{-1}$	
					RADON1	RAECO
1	15.5-9.5	0.0138	0.46	1600	85.4	84.9
2	9.5-8.5	0.0138	0.46	1200	-79.5	-79.3
3	8.5-8.0	0.0138	0.46	1800	14.8	14.6
4	8.0-5.0	0.0138	0.46	1500	95.0	94.5
5	5.0-1.0	0.0138	0.46	1300	583.0	580.0
6	1.0-0	0.0145	0.47	0	429.0	427.0

compacted clay/gravel mixes are being planned. These mixes will be designed to minimize the air-filled porosity of the radon control layer. Additional tests are being planned to assess single-layer earthen covers 3 m (10 ft) thick, using locally available fill materials, and also to assess a composite cover, 3 m thick, containing a compacted clay covered by earth fill. Six large culverts (1.2 to 1.8 m in diameter) will also be filled and packed with tailings and cover materials using several configurations of both single and composite systems. On at least one of the single-cover test columns, sufficient material will be placed to reduce the radon flux at the surface to $<2 \text{ pCi m}^{-2} \text{sec}^{-1}$.

General site preparations were made for the summer field study. The sampling grids and test locations were surveyed. Each grid and test location was located in relation to permanent markers established at the site. These markers also provided elevation control in preparing a contour map of the test plot.

Field measurements will include radon flux measurements and soil radium content analysis. For this purpose a sodium-iodide detector system was installed at the laboratory provided by DOE. The detector was calibrated and tested against standard samples. Plans are under way to have radium

standards on hand while at Grand Junction. Samples from last year's tests will be re-counted and used as standards for calibration and efficiency determinations. Once these preliminary steps are completed, radium contents in the soil and tailings can be determined at the site.

Forty-five core samples of tailings, ~0.8 m long, acquired from the tailings surface to depths of 2.5 m, were taken at the test site in Grand Junction. Radon emanation coefficients, water contents, and densities were determined on 135 subsamples of tailings materials. Attempts will be made to relate the radon source term, computed from the measured parameters, with the actual radon flux measurements.

Radon measurements at the 1980 Grand Junction test site in May indicate that some drainage has occurred in the clay/gravel layer on several covered plots, resulting in increased radon surface flux measurements. Water contents have increased in the surface covers of all plots due to irrigation but have not offset the apparent drainage of the clay/gravel layer. Volumetric water contents of the surface covers in May ranged from 12 to 18 vol%, an increase of 4 to 6 vol%, resulting in only a slight decrease in air-filled porosity. The neutron probe used for water content determination was calibrated for the field site.

Three small radon test plots, consisting of two gel tests and one bentonite test, were designed and completed. The test boxes were 0.9 x 1.5 m, and the thicknesses varied according to the tests. The gel tests were made up at depths of 15 and 30 cm with a composition of 15% alum and 5% lime mixed with the standard A- mix. The bentonite test plot was a 35-cm-thick layer of 12% commercial bentonite, 3% lime and 85% A- mix, and rested 1 cm above the tailings on a thin layer of the existing overburden. Radon measurements taken on all three plots will be counted early in the next quarter.

COVER OPTIMIZATION - Rogers and Associates

The Task 1 report from Rogers and Associates on the cover optimization model RAECO is in final review. The draft report on experimental verification of the cover optimization model (Task 2) has been completed but has required some major revisions. Task 2 work has resulted in the development of a time-dependent radon diffusion coefficient measurement system. The system is yielding results that agree well with literature values for air and soil materials. Diffusion coefficient reproducibility is $\pm 15\%$ for radon diffusivity in air and has been found equally good for diffusion coefficients in soil materials. The initial tests with soils tested at various water contents and densities confirm that radon diffusivity

correlates more closely with air-filled porosity than with soil water content. Observation of a three- to fivefold difference in results between measured surface flux and fluxes computed from measured radon concentrations has led to a careful reevaluation of radon flux measurements, water contents, and densities.

Monitoring of radon continues on composite cover test columns to which 2 liters of added moisture have been applied to internal clay layers. The steady-state radon flux values have not been reached. Monitoring of bare-surface radon fluxes has been completed. Radon flux measurements have begun on elevated moisture test columns. In these tests the water is precisely controlled by specially constructed hanging water columns. Water tension control in a hydraulically isolated layer is accomplished by using porous ceramic cups to supply and extract the water under controlled water tension (potential) conditions.

Field monitoring of water contents was continued at five selected field sites. Compilation of atmospheric data continued for Task 4. These data are being used to correlate equilibrium water contents in earthen cover materials with site locations. The correlation will assist in predicting the influence of stored soil water on long-term radon control of earthen covers.

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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

The major effort this quarter was to finalize the design and produce a quantity of pellets (PCD system) needed to undertake the field study at the Grand Junction uranium tailings site. The pellets are to be molded into small cylinders measuring 9 x 9 mm from a low-density polyethylene material mixed with carbon black as a carrier and trifluralin as the bioactive agent.

The prairie dogs dug through the rock barriers made from small stones (1.5 in.) at the Grand Junction site. There was, however, no evidence of any penetrations of the asphalt emulsion seal lying just below the rock barrier. The small ground squirrel did not penetrate any barriers, including the 1.5-in. rocks in the Hanford tests.

DEVELOPMENT OF POLYMERIC CARRIER/DELIVERY (PCD) SYSTEMS - W. E. Skiens and F. G. Burton

The design of the slow-release pellets (PCD system) for the first major field study at Grand Junction, Colorado, has been completed, and preparation for their fabrication is near completion. The size and shape of the pellets, concentration of trifluralin, polymer type, and the amount of filler are as follows. The pellets are cylinders, 9 x 9 mm, molded from a low-density polyethylene material with a melt index of 22.

The formulation will include 30 pph carbon black as filler to increase the herbicide reservoir within the pellet and to slow the release rate of trifluralin.

The 24-cavity mold to produce the pellets is nearing completion. It is estimated that the mold when in operation will produce between 2500 to 3000 pellets per hour. Sufficient pellets to supply the field study should be available 1 wk after startup.

PHYTOTOXICITY AND DEGRADATION STUDIES - D. A. Cataldo

Studies are continuing with the 9 x 9 mm pellets designed for use in Colorado. These extended studies are designed to determine 1) the influence of soil moisture levels on release rates and equilibrium soil levels of trifluralin with time and 2) the diffusion rates of trifluralin released from the PCD devices in soils. Both of these studies will require analyses at 30-day intervals over a 240-day period to ensure that each system is at equilibrium.

Soil moisture studies were conducted at 6, 12 and 18% in a Ritzville silt loam soil. After 90 days, soil concentrations of trifluralin were 27, 8 and 8 ppm for the 6, 12 and 18% moisture treatments, respectively. All are within the effective soil concentrations required to inhibit root growth.

Diffusion studies, needed to determine both the effective biocide zone in soils and to ensure limited migration of trifluralin from the barrier zone, will require additional effort. It now appears, after 90 days of study, that the effective biocide zone will extend no more than 4 cm above and below the pellet placement zone.

ANIMAL INTRUSION STUDY - K. A. Gano

Grand Junction Test Site

In September 1980, a 1-ft-thick layer of rocks 1.5-in. in diameter was placed over a section of the asphalt emulsion seal. The rock layer was then covered with ~1 ft of soil (Figure 30.1). Enclosures were built over this rock and soil barrier. The wire mesh was extended into the backfill beyond the above-ground enclosure. Prairie dogs were then placed in the enclosures and observed.

The final inspection of this experiment was made during the quarter. Diagrams were made and photographs were taken to document the burrowing activity within the enclosures. There was no evidence of any penetrations of the asphalt emulsion seal by the prairie

dogs. Many of the rocks had been excavated, and the tunnels passed through the backfill and the rock layer. Tunnels had been dug in all pens until the animals found a place where the wire mesh did not reach the seal; they then were able to tunnel beneath the perimeter fence and escape. The conclusion is that the rock used in the field test was too small and that the size and mass of the rocks used in a barrier must be correlated with the weight of the animal. A barrier using the small rocks was effective in preventing intrusion by the smaller ground squirrels in the Hanford tests.

Hanford Test Site

A facility was constructed at Hanford to test the effectiveness of crushed rock as a barrier against animal intrusions into radon seals placed over uranium tailings. Eight enclosures were constructed by burying open-ended wooden boxes into the soil with the upper end level with the soil surface. Each box measured 4 x 4 x 4 ft. The buried box was then surrounded with wire mesh (Figure 30.2) to ensure that burrowing occurred only within the box.

FIGURE 30.1. Barrier Configuration Used at Grand Junction Test Site

FIGURE 30.2. Enclosure Used To Test Burrowing Rodents Against Various Barrier Designs

The various barrier configurations were placed in the buried boxes as shown in Figure 30.3. There were three barrier configurations and one control, with one replicate of each. The configurations were 1) a crushed rock layer placed over a clay mix seal, 2) a crushed rock layer placed over an asphalt emulsion seal, and 3) an asphalt emulsion seal only. Eighteen inches of top soil was placed over each barrier configuration. The controls had 48 in. of top soil with no barrier.

Ground squirrels were placed in the enclosures and allowed to dig in the boxes for at least 8 wk. In April 1981 the squirrels were removed from their pens, and the tunnels were studied. To permit this, a trench was dug alongside each box and the side panel removed. This exposed the barriers and tunnels without disturbing the seal configuration.

The top soil was carefully removed and the tunneling diagrammed. The ground squirrels had not penetrated the crushed rock layers over the multilayer seal or over the asphalt emulsion seal; nor did they penetrate the asphalt seal without a rock barrier. Tunnels and nest chambers had been constructed at the barrier interface in all cases. However, the animals in the control boxes had excavated tunnels and made nest chambers to a depth greater than 3 ft, showing that ground squirrels generally burrow deeper than the 18 in. of soil cover placed over each barrier.

After the ground squirrel study was completed, the burrow boxes were reconstructed by replacing the wooden side panels and the top soil over the same types of barriers. Prairie dogs were then introduced to pens; the females were spayed to prevent propagation of the species in case they escaped

FIGURE 30.3. Three Different Barrier Configurations Tested at Hanford. A control was used to compare burrowing without a barrier.

during the study. Prairie dogs are three to four times larger than the ground squirrels and much stronger burrowers. Common to many areas of the West, they are likely to be the most powerful burrowing rodent encountered

at uranium tailings piles. This study is now in progress and the prairie dogs will be maintained for at least 8 wk. The animals will be removed and the burrow boxes examined in the same manner as before.

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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 provide for compatibility with sealant/barrier systems and are suited to soils and climates at inactive uranium tailings sites.

SUMMARY

The project has undergone a scope change during this quarter and will now emphasize the use of rock covers for surface stabilization. The product of this revised effort will be a set of guidelines to aid in deciding on surface stabilization designs. Site-specific revegetation recommendations will not be made as was originally planned.

Vegetation and soil moisture sampling were initiated at the Grand Junction Test Site. Farmington, New Mexico, was chosen as the location for the second test site.

Regional soil and vegetation sampling was begun. Sampling on the Colorado Plateau and in northwest Colorado was completed.

Work continued on constructing mathematical models of soil erosion and soil water dynamics. A lysimeter study was initiated on the Arid Lands Ecology (ALE) Reserve to study the effects of rock covers on the evaporation of water from soil.

PROJECT MANAGEMENT - L. L. Cadwell,
P. A. Beedlow, and N. R. Hinds

This quarter, the scope of the revegetation project was changed to emphasize the use of rock covers rather than vegetation for surface stabilization of inactive uranium tailings. Under current scoping,

site-specific recommendations will not be made. The product of the revised effort will be a set of guidelines to aid the architectural engineer in deciding on surface stabilization designs. In contrast, our original intent was to deliver site-specific revegetation guidelines. The scope change significantly altered the objectives of the project.

TEST PLOTS - P. A. Beedlow, L. L. Cadwell,
M. C. McShane, J. L. Downs-Berg, and
J. R. Skalski

The original objectives of the test plot task were 1) to identify interactions resulting from the sealant/barrier systems that would limit, modify or otherwise influence the effectiveness of vegetation for stabilizing the surface of the mill tailings and 2) to evaluate the probable effectiveness of selected revegetation strategies. The revised objectives are 1) to evaluate the interactions between vegetation and sealant/barrier systems and 2) to evaluate the effects of rock covers on soil water and vegetation establishment.

Tests to evaluate the interactions between vegetation and sealant/barrier systems are being conducted at the Grand Junction Test Site. An irrigation system was installed on the site in April to ensure seed germination

and maintenance for vegetative cover. Monthly soil moisture measurements were initiated in March. In May the site was sampled for germination from the fall seeding. Grasses and forbs from the applied seed mixture were present as well as two invading weed species. Plant species sown in November that had germinated were: *Agropyron* sp (wheatgrass), *Atriplex* sp (salt-bush), *Oryzopsis hymenoides* (Indian rice-grass), *Puccinelli lemmoni* (Lemmon's alkali grass), *Sporobolus airoides* (alkali sacaton) *Amaranthus retroflexus* (redroot pigweed), and *Sphaeralcea coccinea* (scarlet globe-mallow). Two invading species, *Salsola kali* (Russian thistle) and *Kochia prostrata* (prostrate summercypress), were also present. Germination data are summarized in Table 31.1. Seeded grasses dominated at germination along with *Salsola kali*, a volunteer. These data indicate that germination was not uni-

form across the site. No statistical correlation between germination and soil moisture was found.

Farmington, New Mexico, was chosen as the location for a new test site to be constructed in late summer. At this site we will evaluate the effects of rock covers on soil moisture and plant establishment. The experimental design will be finalized in July.

DATA ACQUISITION AND FIELD SAMPLING -

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

The original objectives of this task were 1) to collect site-specific data on characteristics of the inactive tailings sites and 2) to review tolerance of candidate plant species for revegetation and make preliminary selections of species to be used to stabilize the surface at each site. Because

TABLE 31.1. Plant Germination on Grand Junction Test Plot
May 18, 1981^(a)

	Individuals Counted	Mean Density, Indiv/m ²	Plot Frequency, %(b)	Maximum Individuals Occurring in One Plot, %(c)
<i>Agropyron</i> spp	491	43.8	62.5	9.2
<i>Puccinelli lemmoni</i>	148	13.2	32.1	10.1
<i>Salsola kali</i>	90	8.0	42.9	4.4
<i>Amaranthus retroflexus</i>	67	6.0	29.5	7.5
<i>Oryzopsis hymenoides</i>	50	4.5	23.2	22.0
<i>Kochia prostrata</i>	37	3.3	17.9	10.8
Grass spp	22	2.0	2.7	77.3
Other species ^(d)	20	1.8	8.0	15.0

(a) Total number of plots, 112; size, 0.1 m² (standard Daubenmire frame); total number of individual plants counted, 925.

(b) Percent plot frequency = the number of plots in which a species was present divided by the total number of plots (112).

(c) Number of individuals in the plot having the greatest count divided by the total number of individuals for that species multiplied by 100.

(d) *Sporobolus airoides*, *Halogeton glomeratus*, *Hilaria jamesii*, *Sphaeralcea coccinea*, *Chenopodiaceae* spp, *Distichlis stricta*.

of the scope change, the emphasis of this task is now on collecting regional data needed to support the other tasks. The revised objectives are as follows: 1) to determine the climatic and edaphic influences on plant community structure (cover, density, rooting profile), 2) to provide necessary data to develop a predictive model for estimating revegetation potential, 3) to provide data necessary for erosion modeling, and 4) to determine availability of rock cover materials.

Twenty of the inactive uranium tailings sites were grouped, using a cluster-analysis based on climatic data, into three general regions: the Colorado Plateau--Four Corners area (Grand Junction, Naturita, Slick Rock, Shiprock, Monument Valley, Tuba City, Mexican Hat, and Green River); the west slope of the Colorado Rockies (Ambrosia Lake, Durango, Gunnison, Rifle, and Baggs); and the Northern Great Plains (Belfield, Bowman, Riverton, and Spook).

Sampling is limited to the major natural vegetative communities representative of these three areas. In each region, vegetative cover is sampled on soil types similar to those likely to be used as topsoil for a particular tailings pile. Soil units are chosen with the help of a soil scientist and local soil conservation service personnel. The criteria used in choosing soil types include extent (percent coverage of a county), depth, and texture. The actual location of sampling within a selected soil type depends upon accessibility, ownership, and range condition. At a chosen sampling location, a line intercept method is used to estimate shrub and bunchgrass cover. Ten 50-m transects are run through each area. Daubenmire plots are used to estimate grass and forb coverage. They are placed at 10-m intervals along the 500-m transect. All cover measure-

ments are taken by species. A surface soil sample is taken every 100 m for pH measurement. Soil cores, collected at 20-cm increments to 1 m, are taken at the beginning, middle and end points of the 500-m transect. These will be analyzed for texture, organic matter content, particle size, electrical conductivity, and macronutrients.

During the third quarter of FY-1981, sampling was completed in the Colorado Plateau-Four Corners area and was begun on the west slope of the Colorado Rockies. Information was collected on soils sampled in these regions and the associated vegetation. Information is available on the following counties: Mesa, Montrose, San Miguel, Rifle, and Moffat, in Colorado; San Juan in New Mexico; Apache in Arizona; San Juan and Grand in Utah; and Carbon in Wyoming.

The following soil units were sampled: Glenburg (slope 0-3%, sandy loam); Avalon (3-12%, loam); Fruita (3-8%, loam); Billings (0-3%, silty clay loam); Clovis-Progresso (3-12%, fine loam); Minchy (1-10%, fine sandy loam); Los (0-6%, sandy loam); C-18 (0-6%, sandy loam); Aneth-Sheppard (1-8%, loamy fine sand); Palma-Clovis (0-8%, sandy loam); Tours-Navajo Trail (0-3%, silt loam); Monue-Sheppard (1-12%, loamy fine sand); Nakai (2-6%, very fine sandy loam); Sager (0-4%, silt loam); Typic Torriflorents (0-3%, silt loam); Kim (3-6%, loam); Potts (3-6%, loam); Rock River (3-12%, loam); Camborthids (3-12%, loam); Floutsch-Cushool (3-6%, sandy loam); Ryan Park-Elk Mountain (2-7%, fine sand).

RIPRAP STUDIES - P. A. Beedlow, R. H. Sauer, T. J. Bander, 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. The approach and specific models were discussed in the previous quarterly report. Progress this quarter consisted of work on the mathematical models and the construction of a lysimeter study on ALE.

A procedure for calculating the annual wind erosion from a tailings pile has been implemented. The procedure is based on the wind erosion equation developed by W. S. Chepil and modified by N. P. Woodruff and T. H. Siddoway. The charts and tables used by J. D. Nelson and T. A. Shepherd can be used to obtain numerical values for the amount of wind soil loss as a function of five basic parameters. The five parameters are:

1. Soil wind erodibility factor (determined by the type of soil and particle size distribution; also slopes can be factored in).
2. Soil surface roughness factor (a measure of the amount of ridges or small undulations of the tailings pile; a conservative estimate would be to assume this factor equal to one).
3. Equivalent field length (determined by size of tailings pile, prevailing wind erosion direction, and any barriers such as wind breaks).
4. Local wind erosion climatic factor (based on mean annual wind velocity, precipitation and evaporation; this accounts for conditions that would cause severe soil blowing at times).
5. Vegetative factor (determined by quantity of surface residue and kind of vegetative cover).

Using the charts and graphs, the variation of soil loss as a function of any one of the above parameters can easily be plotted. For example, keeping parameters 1 through 4 unchanged, the soil wind erosion loss for a

particular tailings pile can be plotted as a function of different forms of vegetative cover.

The effects of vegetation and rock covers on soil moisture are being studied via an unsaturated flow model (UNSATV). The modeling effort has accomplished the following:

- Soil-water characteristic curves have been developed for the Grand Junction clay/gravel layer. These curves more closely match the characteristics of the clay/gravel layer as installed than do the previous curves developed from laboratory data.
- The UNSATV partially saturated flow model has been modified to handle the transpiration from a plant community having canopy coverage of 29% *Artemisia tridentata*; 2% *Atriplex confertifolia*; 2.5% *Agropyron*; and 2.5% *Bromus tectorum*.

Since UNSATV was originally developed for one plant species only, the above plant community has been modeled as a composite of the four plant species using the percentages as weighting factors. This has required modifications to the subroutines in UNSATV that account for plant transpiration and root density distribution.

The presence of rock cover on uranium tailings piles could retard evaporation and produce a significant increase in soil moisture. To determine the extent of this problem, a series of 25 lysimeters is being constructed at ALE Reserve on the Hanford site. Ten of the lysimeters will contain instrumentation to measure soil moisture and soil temperature. Various aggregate sizes and cover depths will be compared to bare soil to determine evaporation rate, soil temperature and soil moisture contents.

The lysimeter study is being conducted by Dr. John Batey of Indiana Central University, who is serving a 10-wk National Science Foundation appointment at PNL this summer.

ECONOMIC EVALUATIONS

The literature search has been completed. The Department of Highways has been contacted in several states to obtain regional estimates of excavation, grading, and revegetation costs. Some of this information has already arrived. Information has also been

ordered on riprap from the National Crushed Stone Association. Native Plants has sent some data on the cost of various plant species. Also the Environmental Protection Agency has volunteered to send some detailed cost information based on their work in waste disposal costs. These data, however, have not arrived.

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