Nuclear Waste Management Quarterly Progress Report July Through September 1980

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

November 1980

**Prepared for the U.S. Department of Energy
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NUCLEAR WASTE MANAGEMENT
QUARTERLY PROGRESS REPORT
JULY THROUGH SEPTEMBER 1980

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

November 1980

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 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 April Through June 1979, PNL-3000-6.

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1. HIGH-LEVEL WASTE IMMOBILIZATION

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T. A. Golding - Project Administrator

The primary objective of the High-Level Waste Immobilization Program (HLWIP) is to develop and demonstrate technology for converting high-level radioactive waste to a glass form and for packaging it for disposal in a repository. This effort includes the development of suitable glass forms for existing waste (Western New York Nuclear Service Center, defense) and future wastes (commercial, alternative fuel cycles). A secondary objective is the application of the process and equipment technology to alternative waste forms (supercalcine, matrices, etc.). Government agencies and commercial industry will be assisted in applying this technology to their specific applications.

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

Work Element 1.3.1 Waste Form Development and Characterization

Work Element 1.3.2 Process and Equipment Development.

SUMMARY

Simulated defense and commercial waste glasses were formulated that have significantly better leach rates at 90°C in static deionized water than do current reference glasses.

Test data concerning the effects of cracks on leaching of glass show that the surface within cracks does not contribute to leaching as much as does the external surface.

Static fracture toughness tests of grade 12 titanium plate have shown that a different trend in toughness versus temperature exists for two different orientations of this material, depending on whether static or dynamic test methods are used.

In fatigue-crack-growth rate tests of titanium grades 2 and 12 conducted in both a Hanford ground-water solution and laboratory air at 90 to 94°C, no evidence was found that the ground water accelerated the rate of crack growth.

Metal U-bend samples were discharged from the 250°C Hanford ground-water screening test after the second 90-day exposure period. Oxygen was held to <50 ppb in this test. The titanium alloys showed the least corrosion (essentially no weight change) of the materials tested. Stainless steels and nickel-base alloys were next best. Copper, copper-nickel alloys, and cast irons showed the greatest attack. No samples cracked.

Basalt fragments leached in a flowing autoclave system at 250°C were found to behave like basalt undergoing natural weathering; the same elements are leached but at an accelerated rate.

Reconstruction and restart of the liquid-fed ceramic melter were achieved on schedule. Air inleakage to the rebuilt melter was reduced by a factor of 10 compared to performance before reconstruction.

Two canisters of glass were made in the spray calciner/in-can melter (SC/ICM), demonstrating two mixing concepts. The

first canister was sparged while filling, and the second was fed frit slurried into the feed.

Reconstruction of the calcine-fed ceramic melter (CFCM), now redesignated pilot-scale ceramic melter (PSCM), is nearly complete. The new melter will be compatible with direct liquid feeding and experimental power boosting methods as well as continued operations directly coupled to a spray calciner. Changes to the melter consisted mainly of improvements to insulation, electrodes, lid, and discharge throat.

Radioactive operations of the in-cell spray calciner/in-can melter were begun with a simulated waste feed spiked with ^{99}Tc and ^{131}I . Preliminary results show extensive volatilization of iodine, as expected.

The final draft of the Spray Calciner/In-Can Melter Technical Manual was issued on schedule to meet the Department of Energy headquarters milestone.

WASTE FORM DEVELOPMENT AND CHARACTERIZATION (1.3.1)

The goals of this task are to develop waste forms such as glass and evaluate their properties and to develop and evaluate engineered barriers capable of containing wastes for time periods up to 1000 years.

Leach tests at 90°C in static deionized water show that leach rates of highly durable defense and commercial waste glasses are about a factor of 10 lower than those of reference glasses. This durability difference diminishes as the temperature is raised; at 200°C there is no significant difference in the leach rates. The formulation changes that cause increased durability are not yet fully understood, but they seem to involve increased levels of SiO_2 as well as the pres-

ence of Al_2O_3 and Fe_2O_3 and their proportion with respect to the alkali oxides. Most of the high-durability compositions tested had higher melting temperatures than the reference glasses. However, at least one of the improved glasses is compatible with processing in existing PNL melting equipment; the others could be processed in the higher temperature equipment commonly in use in the commercial glass industry. As expected, volatilities at the melting temperature were higher for the higher melting temperature, improved durability glasses than for the reference glasses. The higher volatilities might be compensated for by specific design of the off-gas system for improved treatment of off-gas and recovery of volatile materials. The highly durable glasses deserve further study in view of their significantly lower leach rates at temperatures below 150°C.

Studies are under way on the leaching behavior of waste glass containing cracks. Cracks were simulated by stacking, in a fixture, glass wafers spaced apart by platinum wires. Crack thickness was dependent upon wire size, and depth upon pellet diameter, and the number of cracks per unit length of cylinder was determined by height of pellets. Both static (leachate unchanged) and dynamic (leachate periodically changed) tests are being made. Preliminary results from both tests show that crack surfaces leach at rates one and one-half to three times lower than do outer surfaces.

Mechanical and environmental tests were performed on candidate metallic, ceramic, and polymeric materials to determine their usefulness as long-lived barrier elements in nuclear waste packages.

In-depth mechanical testing emphasized titanium alloys, grades 2 (commercial purity) and 12 (0.8% nickel, 0.3% molybdenum).

Static fracture toughness tests of grade 12 were completed recently for specimens having crack planes both parallel to and perpendicular to the rolling direction. In dynamic tests the fracture toughness at 250°C increased significantly for specimens with crack planes in the transverse orientation, but toughness of specimens with longitudinally oriented crack planes increased only slightly. A different trend was observed in the static tests, where the toughness in both orientations increased substantially.

Fatigue-crack-growth rate tests of titanium grades 2 and 12 were conducted at 90 to 94°C in a Hanford basaltic ground-water solution using specimens with cracks longitudinal and transverse to the rolling direction. Time-dependent environmental interaction was assessed by using frequencies from 0.1 to 10 Hz. Tests were also performed in air as an additional measure of environmental influence. Fatigue-crack-growth rate tests are considered a sensitive indicator of environmental attack because they expose unoxidized metal to the environment under severe stress and constraint.

Analysis of the fatigue-crack-growth rate yielded the following conclusions:

- 1) Fatigue-crack growth rate properties of grade 2 titanium are better than those of grade 12 titanium, regardless of crack orientation, in air and in a simulated repository environment.
- 2) Both titanium alloys are more resistant to crack growth if cracked transversely rather than longitudinally.
- 3) No evidence indicates that the simulated repository environment affects the crack-growth properties of either titanium alloy.

In addition to the testing portion of this work, a study has been completed that reviews and summarizes the methods used to

predict the susceptibility of metals to ground-water crack-growth enhancement. The information gained from this report will be used for planning future enviromechanical tests.

Corrosion samples were discharged from the 250°C Hanford low-oxygen ground-water test after the second 90-day period of exposure. The specimens were examined, weighed, cleaned, weighed, dye-penetrant checked, and cleaned, then restressed and returned to the test with a medium oxygen concentration (~5 ppm).

The samples evaluated were not cracked. After 6 months' exposure, total weight changes with deposited material removed showed stainless steels, Inconel, Hastelloy, and Incolloys between -2 mg/dm² and -10 mg/dm²; titanium alloys between +2 and -1/2 mg/dm²; and Zircaloy at +12 mg/dm². Stripping of deposited oxides and most corrosion product oxides produced the following weight losses: copper -170 mg/dm²; copper-nickel (70-30) -670 mg/dm²; and cast iron -786 mg/dm². No evidence of localized corrosion was observed except in one cast iron specimen, which displayed a local area of severe pitting. Comparison of weight changes for the first 3 months to the last 3 months showed little change except for Zircaloy-2, which appeared to lose weight in the second period.

Comparison by electron microscopy of autoclave-leached basalt fragments with naturally weathered fragments showed that leaching in the autoclaves simulates leaching in the field except that the rate is accelerated.

In both cases silicon, iron, and potassium were leached from the basalt, with calcium, magnesium, and titanium remaining nearly constant and zinc increasing in the leached zone. Although (due to the higher

temperature) we are actually leaching elements from the basalt at a greater rate than occurs in natural weathering, the faster ground-water flow during the autoclave tests would tend to offset the increased leach rate in respect to the alteration of the ground-water chemistry.

PROCESS AND EQUIPMENT DEVELOPMENT (1.3.2)

This task provides the process and equipment technology to produce glass and glass-ceramics for high-level waste immobilization. Specific equipment being developed includes the spray calciner, liquid-fed ceramic melter, in-can melter, and calcine-fed ceramic melter. Verification tests to confirm that waste processing technology is ready for plant application are part of the effort.

Laboratory melt tests investigating foaming in simulated defense wastes continued with tests of the effects of: 1) carbon and sodium sulfate content, 2) waste loading in the glass, 3) addition of barium metaphosphate, and 4) exclusion of oxygen during melting. Results show that: 1) although the C-NaSO₄ interaction is not a major cause of foaming, optimizing the carbon content can reduce foaming, 2) reducing waste loading in glass to 14% or less is effective but not satisfactory because it requires that twice as much glass be produced to vitrify the same amount of waste, 3) addition of barium metaphosphate (1 to 2%) produced foam height 26% less than that of control samples, and 4) use of calcine heated to 1000°C in CO and melted with frit under a nitrogen atmosphere foamed very little but did produce some metal in the glass.

Reconstruction and restart of the liquid-fed ceramic melter were achieved on schedule. Operation was demonstrated by a test in which

simulated defense waste was slurry-fed to the melter. Approximately 4000 kg of glass were produced in 145 hr of operation, and a steady-state processing rate of 39 kg/hr was achieved. Air inleakage was reduced by a factor of 10 compared to that occurring before reconstruction.

A full-scale spray calciner/in-can melter (SC/ICM) run was made to test two concepts for improved mixing in the ICM process. Sparging of the canister as it filled during conventional calciner operation, and calciner operation with all frit slurried into the waste feed were the methods under investigation. A run summary is presented in Table 1.1. Calciner wall temperatures were maintained at 400°C (compared to 700°C normally) during filling of the second canister to prevent the glass forming compounds from sticking to the calciner walls; consequently, processing rates for this canister were relatively low.

Preliminary examination indicates that crystalline forms exist in both cans. The first can appeared to have more metal nodules formed than the second.

TABLE 1.1. Summary of Full-Scale Spray Calciner Run No. 39

<u>First Canister (Sparged)</u>	<u>Conditions</u>
Operating time	14.3 hr
Liters of waste processed	11880 l at 80.7 g oxide/l 12000 l at 92.4 g oxide/l
Max. feed rate	295 l/hr
Avg. feed rate	271 l/hr
<u>Second Canister (Slurried Frit)</u>	
Operating time	57 hr
Liters of waste processed	11100 l at 375 g oxide/l 1680 l at 293 g oxide/l
Max. feed rate	~67 l/hr
Avg. feed rate	49 l/hr

Reassembly of the calcine-fed ceramic melter (CFCM) is very nearly complete. Since this redesigned melter will not be limited exclusively to a direct-coupled calcine feed system, its name has been changed to pilot-scale ceramic melter (PSCM). The redesigned system will allow use of the melter to continue experiments directly coupled to a spray calciner, or to conduct exploratory evaluation of direct liquid feeding with other power-boosting techniques, including plasma torch, fuel combustion, and microwave heating.

Changes to the melter consist mainly of improved floor insulation to increase glass temperature near the bottom of the tank and to minimize glass leakage through the floor, repositioned and better-fitting tank wall insulating blocks to limit glass migration, reshaped electrodes to direct current flow away from the melter walls and provide more uniform increase in current density from top of the pool to the floor, and elevation of the tank lid to allow thicker lid insulation accompanied by a reduction in the number of penetrations.

Perhaps the single most important change was made in the discharge throat area.

There the original loosely stacked insulation blocks were replaced by a single large block drilled to provide a discharge channel. The new design eliminates the many cracks and horizontal surfaces present in the original and allows access for an air bubbler to airlift discharge a portion of the melt.

After completion of nonradioactive tests of the in-cell spray calciner/in-can melter, radioactive operations were initiated by processing 13 l of simulated waste feed spiked with ^{99}Tc and ^{131}I . Preliminary analysis of off-gas samples drawn from the calciner, venturi scrubber, and packed scrubber indicates extensive volatilization of the iodine, as expected.

The final draft of the Spray Calciner/In-Can Melter High-Level Waste Solidification Technical Manual, PNL-3495, was issued in September, meeting DOE-HQ Milestone 2602-1 on schedule. The manual summarizes the development of spray calciner/in-can melter process and equipment technology and provides source data for design, safety analysis, environmental assessments, and application of the technology.

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 glass ceramics, coatings, and matrices that are included in the multibarrier concept.

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

Work Element 1.3.1 Waste Form Development and Characterization

Work Element 1.3.2 Process and Equipment Development.

SUMMARY

As-received SPC-4P supercalcine powders have been characterized. The powders have a high residual nitrate content (~ 13 wt%) and relatively high surface area ($31 \text{ m}^2/\text{g}$). Eighty to 90% of the powder has an equivalent spherical diameter in the 0.8 to $2 \mu\text{m}$ range.

Samples of glass marbles encapsulated in titanium and glass matrices have been fabricated for characterization. A nickel-sulfur-bonded graphite matrix has been received from NUKEM in West Germany. This matrix consists of graphite flakes which are surrounded and infiltrated by a NiS binder. Leach testing of the graphite matrix is under way.

Calculations were performed to determine doses to various matrix materials from waste glass marbles. It is estimated that the 1000-yr cumulative gamma and alpha dose from defense waste glass marbles will be 10^9 to 10^{10} rads and 10^6 to 10^7 rads, respectively. Doses due to commercial HLW marbles would range approximately one order of magnitude higher.

Waste form/matrix reactions during thermal anneals have been observed only in the case of glass waste forms incorporated in pure lead matrices. Supercalcine SPC-4 has not shown any signs of interaction with metal matrices.

Studies continue at Battelle Columbus Laboratories (BCL) to develop chemical vapor-deposited (CVD) coaters capable of depositing pyrolytic carbon (PyC) on large-diameter substrates at low temperatures. A total of 27 coating runs have been conducted on $\sim 13\text{-mm}$ simulated PNL waste glass marbles.

A supplement to D-Cell Operations Safety Requirements has been prepared to include crystalline waste form fabrication. A hot-pressing system has been fabricated and tested for installation into D-Cell. The press uses either alumina or graphite dies and is capable of operating in air, inert gas, or reducing atmospheres.

Leach tests have been conducted on eight carbon materials using deionized water in an air atmosphere. The reaction rates are falling within about an order of magnitude

of one another. At 300°C, the highest test temperature, average reaction rate is 10^{-6} g/cm²·day.

Disc pelletizer and pin mixer installation is complete. A series of tests were run using both devices. Savannah River Laboratory (SRL) calcine and frit and supercalcine powder have been pelletized.

Approximately 100 kg of disc pelletized supercalcine was sintered using an Inconel canister placed in an in-can-melter furnace. The sintered pellets had a surface coating, indicating a possible reaction with alumina carrier material during sintering. Several sintering tests were also conducted using a vertical sintering kiln. The furnace exit jammed, resulting in only about one-third of the pellets being adequately sintered.

An engineering-scale process demonstration for encapsulating marbles in a lead matrix was completed. The product of this demonstration was a canister, 40 cm dia by 213 cm long, containing 300 kg of glass marbles encapsulated in 1400 kg of lead.

In another matrix demonstration, uncoated supercalcine pellets were encapsulated in aluminum-12 wt% silicon alloy. A canister, 20 cm dia by 91 cm long, was produced containing 33 kg of supercalcine pellets and 46 kg of aluminum alloy.

Low-temperature PyC coatings have been successfully applied to quartz particles using the PNL fluidized bed coater. Average coating thickness on the 32 x 48-mesh particles was 12 μ m. Design of an engineering-scale large-particle coater system has been completed. The coater, which is screw-agitated, will be supplied by BCL.

One paper was presented, two reports received clearance, and one report was issued for comments during the quarter.

WASTE FORM DEVELOPMENT AND CHARACTERIZATION

Ceramic Development – R. O. Lokken

As-received SPC-4P supercalcine had high residual nitrate content due to relatively low calciner barrel temperatures (565 to 655°C). Thermogravimetric analysis of the material revealed high weight losses in air up to ~550°C, at which point denitration appeared essentially complete. Cumulative weight loss at 600°C was 13 wt%. The total weight loss from the material after a soak time of 2 hr at 1200°C was 25.4 wt%. As a result of the low calcining temperature, the surface area measured by BET^(a) was relatively high at 30.7 m²/g. The high BET surface was due to particle agglomeration and porosity rather than fine particle size. Sedimentation measurements indicated that 80 to 90% of the powder had equivalent spherical diameters in the 0.8 to 2 μ m range.

Pellets of as-received SPC-4P supercalcine developed voids in the centers when sintered for 2 hr at 1200°C. The voids are believed to be caused by a high sintering rate (due to the high surface area) creating a "skin" of high-density material on the outer surfaces followed by consolidation from the inside. Preheating the powder at 600°C before pressing resulted in sintered pellets free of voids. The effect of sintering temperature on density was similar to that observed in previous formulations of SPC-4 supercalcine.⁽¹⁾ The density increases with temperature up to 1200°C and decreases slightly thereafter.

(a) Brunauer-Emmett-Teller equation used for surface area determinations by computing the monolayer area.

Matrix Development - J. W. Wald,
W. E. Gurwell, A. M. Nolan, and L. R. Bunnell

Samples of titanium and glass matrix waste forms containing glass marbles were fabricated. Two titanium matrix waste form samples were made by hot pressing at 170,000 psi and 800°C for 10 sec, with essentially complete densification achieved. There are some cracks in the titanium oriented perpendicularly to the pressing direction. These may be due to springback of the glass when the pressure is relieved, and if so, cooling under pressure is needed. The flint glass marbles deformed to an elliptical cross section. The waste glass marbles (of unknown composition and an immersion density 2.82 g/cm³) were fluid enough to infiltrate the adjacent titanium powder but not the outer envelope of titanium 1 cm thick.

Two glass [Corning Code 7570^(a)] matrix waste form samples were pressed for 10 sec at 170,000 psi and either 570°C ($\sim 10^4$ poise) or 500°C ($\sim 10^6$ poise). Essentially full densification of the glass matrix was achieved. Another glass (Code 7570) matrix waste form sample was fabricated by pressing in a graphite die at 570°C and very low pressure, 2 psi, for about 12 hr. The matrix is about 95% dense. It appears that the light waste marbles (TDS-211, 2.73 g/cm³) floated to the top of the dense (5.42 g/cm³) matrix glass. Pressing at somewhat lower temperature, higher pressure and shorter time should produce a much better waste form.

A sample of NiS-bonded graphite from NUKEM in West Germany was examined by optical metallography and scanning electron microscopy (SEM). Both showed the graphite flakes to be surrounded and infiltrated by the binder. Minor differences in nickel/sulfur

ratio were detected when comparing different areas of binder, but the reaction appeared complete. X-ray diffraction identified the binder as NiS; there are at least six different nickel sulfides. Structurally the material seems to be a good high-level waste (HLW) matrix. Samples have been cut from the NiS-bonded graphite and submitted for leach testing. No data are available yet. NiS is reported,⁽²⁾ however, to be water-soluble to the extent of 3.6×10^{-3} g/l at 18°C. It may be possible to find a similar compound (perhaps another sulfide) that can be formed in situ by reaction but is less soluble.

Calculations were performed to determine doses to the various matrix materials under consideration. Two different waste sources were considered: solidified high-level wastes and SRL wastes. To simplify the calculations, the least dense waste form (borosilicate glass) was assumed since this results in the highest dose to the matrix material. Only two matrix materials, spanning the range of densities of all materials to be considered, were analyzed. Doses to other matrix materials, for a given waste source, will fall between the doses to these two materials, in order of density. Both gamma and alpha doses were estimated for ages of wastes ranging from 2 yr to 1000 yr. The results are summarized in Table 2.1 for 1000-yr cumulative dose.

The results indicate that the alpha doses to the matrix material are several orders of magnitude lower than the gamma doses and are confined to a small shell surrounding each waste marble. Gamma doses accumulated over 1000 yr are quite high and may approach the range of significant radiation effects, depending on the materials and physical properties being considered.

(a) Corning Glass Works, Corning, New York.

TABLE 2.1. Accumulated Gamma and Alpha Dose for Matrix Materials from Encapsulated Borosilicate Glass Marbles

Waste Source	Matrix Material	1000-yr Cumulative Gamma Dose, rads	1000-yr Cumulative Alpha Dose, rads
PW-9 ^(a)	EPDM Rubber ^(c)	1.8×10^{11}	7.4×10^5
PW-9	90% Pb-10% Sn ^(d)	4.9×10^{10}	1.0×10^5
SRL ^(b)	EPDM Rubber	9.6×10^9	2.1×10^7
SRL	90% Pb-10% Sn	1.9×10^9	2.8×10^6

(a) 2-yr-old high-level waste.

(b) 5-year-old defense waste.

(c) $\rho = 0.9 \text{ g/cm}^3$.

(d) $\rho = 10.5 \text{ g/cm}^3$.

The kinetics of reactions between a glass waste form and lead and lead alloys and between a ceramic waste form and lead and aluminum metal alloys were investigated. These studies, initiated as a collaborative effort with the Hahn-Meitner Institute in Berlin, include two glass waste forms, PNL-76-68 and HMI MOD-102, and supercalcine, SPC-4, incorporated in lead and lead-10% tin and lead and aluminum-12% silicon metal alloys, respectively. The two main objectives of this study are to 1) establish the reaction kinetics when waste form-metal matrix reactions occur and 2) to evaluate the potential effects on the leach behavior when reactions occur.

Reactions have been observed only in the case of the glass waste forms incorporated in the lead matrix. Both glasses, although compositionally different, seem to behave similarly. When treated at temperatures of 550°C for periods of 24 hr or longer, the discrete glass/metal interface is replaced by an intermixed "reaction zone." Additional time/temperature treatments will be required to establish kinetics; characterization of the reaction zone, however, indicated that molybdenum tends to migrate from the glass phase into the metal matrix. Preliminary leach testing has not indicated significant

degradation of the waste form composite as a result of this separation. Supercalcine SPC-4 has shown no signs of interaction with the metal matrix when treated in the molten metal state for periods of up to 1 week.

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

Coating development activities at BCL emphasize low-temperature pyrolytic carbon (PyC) chemical vapor-deposited (CVD) coatings, large-particle coaters (SAC), and the coating of glass marbles. Technology developed at BCL is continuously being transferred to PNL for process demonstration.

Based on the appearance of the typical low-temperature PyC coatings prepared thus far in the program, it was decided that both coating quality and coating rate could be improved in the fluidized bed, as well as the SAC system, if homogeneous gas-phase nucleation of PyC could be inhibited and/or heterogeneous deposition promoted. One method to achieve this is to reduce the $\text{Ni}(\text{CO})_4$ catalyst concentration. Accordingly, this parameter was studied more extensively with emphasis on establishing a lower practical limit. The best-appearing PyC coating prepared in the fluidized bed

was applied at $\sim 470^\circ\text{C}$ from a gas mixture containing an ~ 1.5 mole% acetylene, ~ 0.006 mole% $\text{Ni}(\text{CO})_4$ and the balance hydrogen.

An alternative approach to reducing gas-phase nucleation was also started. If one assumes that the low-temperature PyC coatings are formed preferentially on nickel nuclei, then PyC gas-phase nucleation could be minimized by eliminating nickel nuclei in the gas phase. Techniques studied to implement this approach are: 1) deposit nickel and PyC sequentially so that the full concentration of the nickel and carbon precursors are not mixed at temperature, 2) stabilize or use a nickel precursor more stable than nickel carbonyl so that gas-phase nucleation of nickel does not occur at the temperatures required to deposit PyC, and/ or 3) use a more stable catalyst precursor that contains a metal other than nickel, e.g., cobalt or iron.

Screw-agitated coaters (SAC) have remained primarily the same as discussed in previous quarterly reports, except for feed tube modifications. The more significant design changes have been in introducing the reagents so as to reduce nickel plugging and to increase the coating rate. A 304 stainless steel, water-cooled, jacketed metal catalyst feed tube was used to reduce clogging problems due to premature decomposition of the catalyst. Four auger designs were tested extensively to determine bed circulation times and patterns. Auger variations included 25 to 64-mm pitch, 38 to 76-mm auger diameter, and 6 to 25-mm shaft diameter.

In the SAC, unlike the fluidized-bed reactor, heat transfer could be a limitation, especially if acetylene is introduced without preheating, as is being done when both the carbon and nickel reactants are introduced at the bottom of the coater. To provide some preheating to the C_2H_2 , experi-

ments were performed in which the C_2H_2 was supplied to the system through a stainless steel tube extending from the top of the coater and terminating near the bottom. Neither the coating rate nor coating quality were significantly improved by use of preheated C_2H_2 .

The preliminary approach to applying PyC coatings in the SAC system was to use 6-mm alumina balls as substrates. Once preliminary coating parameters were defined, coating runs were made in the two SAC systems using PNL glass marbles (~ 13 mm average dia). Twenty-seven runs were made with glass marbles. The coating runs have emphasized 1) continuing experimental parameter study in an effort to increase both the coating rate and coating quality and 2) identifying any problems associated with coating glass marbles. All runs have been made using acetylene (C_2H_2), hydrogen (H_2), and nickel carbonyl [$\text{Ni}(\text{CO})_4$] as the reagents. One run carbon monoxide (CO) was added to the gas stream in an effort to reduce gas-phase nucleation.

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

High-level waste from the Nuclear Waste Vitrification Project will be fabricated into crystalline waste pellets in 324 D-Cell. A supplement to D-Cell Operation Safety Requirements has been prepared to cover crystalline waste form fabrication.

Cold-testing of a pellet-pressing system and sintering furnace for hot crystalline waste form fabrication was reported in the previous quarterly report. A hot-pressing system for air, inert gas, or reducing atmosphere operation at temperatures to 1350°C is being assembled as an additional fabrication technique. The system is based on one

previously used by Cowan at Los Alamos.⁽³⁾

A previously cold-pressed pellet is placed in an alumina hot-pressing die that is $\sim 1/8$ in. larger in diameter than the pellet. Granular-fused zirconia is placed at both ends of the pellet and in the annular space between the pellet and die to prevent reaction or sintering between the alumina and the sample. Surrounding the die is a resistance heating-element furnace, designed and fabricated to fit between the posts of the hydraulic press used for cold-pressing. The system is capable of temperatures to 1350°C. Cowan reported that the alumina dies in his system withstood pressures of 20,000 psi at 1000°C, 15,000 psi at 1100°C, 10,000 psi at 1200°C, and 5000 psi at 1325°C.

Another die system constructed of graphite has also been fabricated. The graphite die is capable of 4000 psi over the entire temperature range of the furnace. It must, however, be protected from oxidation by an inert or reducing gas purge. It has not yet been determined whether the as-fabricated clearances between furnace components and between

the furnace and the load train are tight enough to keep air inleakage from oxidizing the graphite.

The hot-pressing furnace has been assembled and operated successfully to 1300°C. The alumina die and load train have been tested at room temperature with satisfactory results in a hydraulic press at 5000 psi. The system is currently being prepared for demonstrating its suitability for hot-pressing in air using the alumina die, and in Ar-4% H_2 using the graphite die.

Carbon Leaching - W. J. Gray

Leach tests have been conducted on the eight materials listed in Table 2.2 using deionized water in an air atmosphere. The first three materials are powders; the last five are ~ 500 - μm dia particles. The two materials with outer coatings of silicon carbide also have inner coatings of pyrolytic carbon. The surface areas listed in Table 2.2 are preliminary and may be changed in later reports. Iodine absorbed from

TABLE 2.2. Materials Used in Leach Tests

Material	Surface Area, m^2/g		Form
	Iodine	BET	
Graphite	2.4		Graphite powder
GC-1000	6.4	58	Glassy carbon powder
GC-2600	9.6	38	Glassy carbon powder
PyC-SPC-5		0.1(a)	Supercalcine beads coated with PyC
PyC-1		0.036	Beads with outer coating of PyC
PyC-2		0.019	Beads with outer coating of PyC
SiC-1		0.012	Beads with outer coating of silicon carbide
SiC-2		0.012	Beads with outer coating of silicon carbide

(a) Estimate based on measurement of similar beads.

aqueous solution provided the basis for the iodine surface areas. These were used, where available, to calculate the reaction rates plotted in Figure 2.1; otherwise BET surface areas were used. It is apparent that iodine surface areas are smaller and result in a larger calculated reaction rate than BET surface areas do.

Inspection of Figure 2.1 shows that some of the materials have been tested so far only at 300°C. Work is continuing to fill gaps in the data. It is already apparent, however, that reaction rates for a rather wide variety of carbonaceous materials are falling within about an order of magnitude of one another and are far lower than for

FIGURE 2.1. Reaction Rate of Various Carbon Products in Deionized Water

many other types of materials.⁽⁴⁾ Since Gray has shown that the reaction being measured is with air rather than water,⁽⁴⁾ efforts are being made to measure reaction rates in an oxygen-free system.

PROCESS AND EQUIPMENT DEVELOPMENT

Ceramics – C. L. Timmerman, J. F. Nesbitt, and J. G. Carter

Installations of a disc pelletizer and a pin mixer agglomerator were completed. Pellets are formed in the disc pelletizer when small "seed" particles are wetted and tumble over dry powder, thereby increasing in size in a snowballing fashion. Pellets usually range in size from 4 to 16 mm. Small spherical granules are formed in the pin mixer agglomerator by the beating action of rapidly rotating pins. This beating action is apparently sufficient to overcome the surface tension of the liquid binding medium that allows fine particles to be wetted and compacted. Granules produced in this device average about 1 mm in diameter.

A series of tests were run using both devices. A mixture of simulated SRL calcine and frits was pelletized using a 5 wt% sodium hydroxide binder. Supercalcine powder that had been dry-mixed with 5 wt% cornstarch was also pelletized and granulated. The pelletized and granulated products contained 32 and 35 wt% binder water, respectively.

A third sintering run of pelletized supercalcine was performed. An Inconel canister containing internal heat transfer fins was filled with a mixture of ~100 kg of green supercalcine pellets and 170 kg of high-purity alumina. The alumina is used as a carrier to prevent the pellets' sintering together. The total heat-up and sintering cycle in an in-can melter furnace required

~23 hr to heat all pellets to 1200°C and hold them at that temperature for 2 hr. During the sintering, air was slowly purged into the canister for oxidation of the cornstarch binder and for removal of off gases. The pellets and carrier flowed easily from the can, indicating that the carrier did keep the pellets from sintering together. The pellets were very hard and tough but had a cream-colored coating. This coating has occurred in each run in which alumina carrier has been used, probably due to a reaction between the alumina and the supercalcine. Surface analyses of the sintered pellets indicated that only iron was slightly depleted.

Several tests were also conducted in a continuous, vertical sintering kiln. In these tests, a high-purity alumina carrier was mixed with supercalcine pellets before sintering at 1200°C for at least 2 hr in an Ar-4% H_2 atmosphere. The furnace exit jammed, and only about one-third of the pellets appeared to be adequately sintered.

Matrix Encapsulation – S. C. Slate, R. G. Nelson, and J. G. Carter

An engineering-scale process demonstration for encapsulating glass marbles in a lead matrix was completed. The product of this demonstration was a canister 40 cm dia by 213 cm long containing 300 kg of glass marbles encapsulated in 1400 kg of lead. In this process, glass is first melted in a conventional joule-heated melter. Molten glass is poured continuously into a marble-making device that consists of a series of thimble-shaped molds moving along a vibrated track. One marble is formed in each mold as the glob of molten glass in the mold rotates and freezes in the shape of a sphere. Acceptable marbles are added to a basket inside a

canister until the basket is nearly filled. Then the basket is capped to prevent the relatively lightweight marbles from floating when they are encapsulated in molten lead.

The marble-filled canister is then emplaced in a furnace (in-can melter) that heats the marbles to about 400°C. Heating of the marbles is enhanced by blowing hot air through the marble mass. When the marbles reach 400°C, lead shot is added to the canister. The lead falls between the walls of the canister and the marble basket and melts. When the canister is completely filled with molten lead, it is slowly cooled, starting at the bottom. This method of cooling permits molten lead to fill voids created when the lead densifies as it passes from its liquid state to its solid state. The process also provides for instantaneously starting and stopping the flow of molten glass and for recycling glass scrap.

In another matrix demonstration, supercal-cine pellets were successfully encapsulated in an aluminum-12 wt% silicon alloy. One canister 20 cm dia by 91 cm long was produced containing 33 kg of supercal-cine pellets and 46 kg of aluminum alloy. The canister and supercal-cine pellets were first heated to 500°C and placed under a vacuum of 760 mm Hg. Molten aluminum alloy at 730°C was then poured into the canister while maintaining the vacuum. After cooling, the canister was cut open, revealing no apparent porosity in the matrix.

Coatings - K. H. Oma and K. E. Eliason

Low-temperature PyC coatings have been successfully applied to irregularly shaped quartz particles (32 x 48 mesh) using the PNL low-temperature, fluidized-bed coater. The system consists of a gas distribution panel; catalyst bubbler; 27-mm-ID, fluidized-

bed reactor; off-gas filter; and oil trap. The run conditions used were based on previous parametric studies conducted at Battelle Columbus Laboratories and were as follows:

Bed temperature	430°C
C ₂ H ₂ concentration	1.5 mole%
Ni(CO) ₄ concentration	0.01 mole%
H ₂ concentration	Balance
Total flow	6.2 l/m
Bed weight	32.0 g

A micrograph of typical coated particles is shown in Figure 2.2. These particles were coated for 6 hr. The average coating thickness is about 10 µm. The coating shows no porosity and appears to be well-bonded to the quartz substrate. Coating discontinuities can be observed, however, where inclusions and depressions in particles exist.

Design of an engineering-scale large-particle coater system has been completed

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FIGURE 2.2. Low-Temperature PyC-Coated Quartz Particles.

except for the gas distribution system and the wiring for a gas control panel and an O₂ monitor. Two hoods for containing the coater system are on order, and the design for their installation has been completed. The coater, which is screw-agitated, will be supplied by BCL.

PAPERS AND REPORTS

A paper entitled "Leach Resistance of Alternative Waste Forms" was presented by J. M. Rusin and J. W. Shade at the Second Annual Argonne Workshop on Comparative Leaching Behavior of Radioactive Waste Forms on September 3, 1980.

The report PNL-3515, An Assessment of Glass Ceramic Waste Forms, has been cleared. The report concludes that the development of generic glass ceramics should not be pursued. Development should continue, however, in the area of basalt-based glass ceramics, which offer some promise because the crystalline phases would resemble those in a basalt repository. The volume fraction of the residual glass phase should be at a minimum and have a low alkali-metal content to improve overall glass ceramic durability.

REFERENCES

1. Rusin, J. M. et al. 1979. Multibarrier Waste Forms; Part I: Development. PNL-2668-1, Pacific Northwest Laboratory, Richland, Washington.
2. Weast, R. C., ed. 1969. Handbook of Chemistry and Physics, 50th edition, Chemical Rubber Company.
3. Cowan, R. T. 1966. Semi-Automatic Hot Pressing. LA-DC-7562, Los Alamos Scientific Laboratory, Los Alamos, New Mexico.
4. Gray, W. J. 1980. "Reaction of Graphite with Water and Its Implications for Radioactive Waste Storage." Radioactive Waste Management, 1:105.

The final report PNL-3477, Preliminary Evaluation of Alternative Waste Form Solidification Processes; Volume II Evaluation of the Processes, prepared under PNL's direction by E. R. Johnson and Associates, has received clearance and has gone to printing. Eleven alternative waste form processes were evaluated, including two reference glass processes. Glass, glass-ceramic, concrete, and encapsulated marbles ranked high in engineering practicality, whereas coated pellets, hot-isostatic pressed ceramics, titanate and cermet process ranked lower.

A draft report of PNL-3516, Comparative Waste Forms Study, by J. W. Wald, R. O. Lokken, J. W. Shade and J. M. Rusin was issued for comment. Ten waste form products were characterized by bulk properties, volatility, leach resistance and mechanical strength. Glass, glass-ceramic, and supercalcine waste forms ranked very close together and near the top in performance in all characterization tests. Sintered and hot-pressed calcine (without additives) waste forms were consistently lowest in performance.

3. NUCLEAR WASTE MATERIALS CHARACTERIZATION CENTER

R. D. Nelson - Program Manager

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

SUMMARY

State-of-the-art reviews of leaching and vaporization were drafted, and experiments were conducted on all waste-form test methods. The MCC-1 static leach test and supporting data were submitted to the MRB, and a round-robin test of MCC-1 was started. The MCC held two workshops and has completed plans for a third. One workshop concerned the effects of irradiation on the properties of nuclear waste forms and included a critique of the MCC-6 test for effects of alpha decay on waste solids. The second workshop dealt with the corrosion of engineered-barrier materials. A workshop on analytical methods has been planned for discussing support methods used in MCC characterization studies.

PROGRAM MANAGEMENT (1.1.1) - R. D. Nelson, W. A. Ross, and J. E. Mendel

The MCC has continued interfacing, communication, and coordination with other waste management programs, lead sites, and appropriate operations offices. The organization and purpose of the MCC have been publicized by presentations at the Argonne National Laboratory Workshop on Comparative Leaching Behavior of Radioactive Waste Forms and at

the TRU Program Update Meeting. The MCC also participated in the Interface Working Group (IWG) on High-Level, Waste-Form Selection Factors. Factors selected by the IWG correlate well with the test methods being developed by the MCC.

WASTE-FORM MATERIALS CHARACTERIZATION (1.3.1) - J. E. Mendel and D. M. Strachan

The MCC-1 static leach test and supporting data were submitted to the MRB for approval. The data included test series to show the capability and reproducibility of the method. A round-robin test of MCC-1 began with a planning meeting at DOE, Germantown; about 15 organizations indicated they will participate. Sample materials include a National Bureau of Standards reference glass and either a simulated waste glass or a basalt.

The MCC held a workshop concerning the effects of irradiation on the properties of nuclear waste forms. The purpose was to bring together technical experts from throughout the U.S. to examine issues of radiation damage to waste forms, particularly its effects on the long-term durability of the waste form and how to test the effects of irradiation. As part of the workshop, the experts reviewed and critiqued the procedure proposed by MCC for testing the

effects of alpha decay on waste solids (MCC-6). Although MCC-6 was supported, the need for fundamental studies on ionization damage, temperature and dose-rate dependence, and transmutations was stressed. In addition, it was the consensus of the workshop that MCC-6 would not be applicable to spent fuel.

An Analytical Methods Workshop has been planned for November 1980 to discuss support methods used in MCC characterization studies. These methods include ICP emission spectroscopy, atomic absorption, x-ray diffraction, x-ray fluorescence, metallography, SEM/EDX microprobe, and Auger/ESCA/SIMS, surface analyses.

Experimental work was conducted on all waste form leach test methods. This work included using the MCC-1 to determine the effect of the cutting fluid on the leach rate. In addition, a test matrix was established for MCC-3 to test such variables as temperature, leachant, particle size, and time. An all-Teflon[®] apparatus was obtained for use in the MCC-5 Soxhlet test to reduce the sorption of cesium, calcium, molybdenum, and strontium by the reboiler flask.

Other activities involved the drafting and review of the MCC-11 diametral compression test for waste forms. Soda-lime glass was tested according to this procedure, and specimens of PNL 76-68 glass and pelletized concrete (FUETAP) were procured for further mechanical testing.

Impact testing of a ceramic was done by Effects Technology to evaluate various options for the MCC-10 impact test. Procurement of a drop-tower impact machine was initiated for further onsite testing.

ENGINEERED BARRIER MATERIALS (1.4.1) - M. D. Merz

A workshop on corrosion of engineered-barrier materials was held to establish a basis for selecting test methods for further development. Important points identified at the workshop include the following:

- Uniform corrosion data can be obtained in nonaccelerated tests and used for extrapolation to 1000-yr service.
- Accelerated testing should be done to qualify extrapolation.
- Methods of accelerating tests by temperature and solution concentration will be considered for the MCC immersion test.
- Nonuniform attack will require statistical treatment of test data to predict service life.
- Survival possibly can be predicted at stresses below critical levels determined by cyclic loading tests in aggressive environments.
- Fracture toughness will be determined in such tests.

The first MCC test to be submitted to the MRB on corrosion of engineered-barrier materials will be an immersion test in static solution to give weight change. This test will address uniform attack and occurrence of pitting.

A subcontract with the University of Washington concluded. The resulting report, Assessment of Delayed Failure Modes in Titanium and Titanium Alloys, indicates that a test procedure will be required for delayed failures in barrier materials.

In other activities, construction continued on a gamma facility autoclave for corrosion testing of barrier materials in a radiation environment.

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4. TRU WASTE IMMOBILIZATION PROGRAM

C. R. Palmer - Project Manager

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

SUMMARY

This quarter's activities focused largely on development of basalt glass and glass ceramic waste forms. Products based upon blended process sludge and ash admixed with crushed basalt and with tailored additives were prepared, as well as a glass obtained by melting pure waste. Static leach tests showed all products to be quite durable, with significant improvement generally obtained upon crystallization.

Low- and high-melting glasses were also designed for blended wastes at about 50 wt% waste loadings. Screening leach tests indicate both formulations accommodate variations expected in the waste, and comparative static leach tests were started.

CRYSTALLINE PRODUCT DEVELOPMENT -

R. O. Lokken

Basalt Glass and Glass Ceramic

Several basalt-like waste forms for blended transuranic process sludges and incinerator ashes (TBW) were prepared by melting/recrystallization techniques. These forms were formulated to immobilize a reference blend of nonradioactive sludge and ash (TBW-R) from the Rocky Flats Plant having a chemical composition reported earlier.⁽¹⁾ Two products consisted of TBW-R blended with crushed basalt additions

(at 70 and 80 wt% basalt), one consisted of TBW-R with chemical additions to make the product composition approximate natural basalt, and one form was essentially 100% TBW-R. All samples were melted at 1300 to 1400°C and annealed at 550°C; recrystallization was achieved by heat treating for 1 hr at 670°C and 8 hr at 920°C.

Samples of each product were tested for chemical durability both before recrystallization (glass) and after (glass ceramic). Leaching was performed in static deionized water at 90°C for 14 days (ratio of solution volume to sample surface area was constant at 0.1 m). Leachates were analyzed for dissolved species by emission spectroscopy. Table 4.1 shows the results of the analyses for five elements. These data were calculated as the normalized elemental loss by the equation:

$$NL_i = \frac{m_i}{f_i \cdot SA}$$

where NL_i = the normalized mass of element i dissolved per unit surface area of sample, g/m^2

m_i = the mass of element i in the leachate, g

f_i = the mass fraction of element i in the unleached sample

SA = the surface area of the sample, m^2 .

TABLE 4.1. Normalized Elemental Losses, g/m², for Basalt-Based TRU Waste Forms Leached in Deionized Water at 90°C for 14 Days

Ion	BG-20 ^(a)	BGC-20 ^(b)	BG-30 ^(c)	BGC-30 ^(d)	SBG-18 ^(e)	SBGC-18 ^(f)	TBWG ^(g)
Ca	2.85	0.14	3.17	0.29	1.96	0.28	0.62
Mg	2.42	0.26	2.57	0.28	1.76	0.40	0.23
Na	1.95	--	2.74	1.60	1.48	2.96	3.45
Si	2.26	0.21	2.73	0.39	1.69	0.37	1.22
Fe	--	--	--	--	--	0.12	--

(a) Basalt glass with 20 wt% TBW-R, 80 wt% crushed basalt.

(b) Basalt glass ceramic with 20 wt% TBW-R, 80 wt% crushed basalt.

(c) Basalt glass with 30 wt% TBW-R, 70 wt% crushed basalt.

(d) Basalt glass ceramic with 30 wt% TBW-R, 70 wt% crushed basalt.

(e) Synthetic basalt glass with 18 wt% TBW-R, 82 wt% additives.

(f) Synthetic basalt glass ceramic with 18 wt% TBW-R, 82 wt% additives.

(g) TBW-R glass with no additives.

The chemical durability of the products with crushed basalt additions is improved about an order of magnitude by recrystallization, indicating the residual vitreous phase is quite leach-resistant. TBW-R tailored to a natural basalt composition and melted to form a glass (SBG-18) shows improved durability compared to the first two basalt glasses; SBGC-18, however, is slightly less durable compared to the other glass ceramics. Since all these products were heat-treated under identical conditions, different compositions and yields of crystalline phases are expected due to differences in viscosity at temperature for these formulations. TBW-R melted without additives exhibits relatively good retention of all ions except sodium in comparison to the other vitreous materials.

Comparative Study

In support of the waste form comparative study, four crystalline waste forms were prepared during the quarter:

- normal-cast hydraulic cement with 35 wt% TBW-R
- pressed hydraulic cement with 50 wt% TBW-R
- basalt glass ceramic with 30 wt% TBW-R
- crystalline ceramic with 33 wt% TBW-R.

The two cement products contained type II portland cement. The powders were mixed dry and then with water to result in a water-to-solids ratio of 0.35 and 0.5 for normal and pressed concrete, respectively. Pellets were pressed from the latter mixture at 172 MPa. Both products were cured at room temperature in sealed containers. Basalt glass ceramic samples were prepared by melting pomona basalt with 30 wt% TBW-R at 1300°C, followed by recrystallization according to the thermal schedule described above. The crystalline ceramic product was composed of laboratory-grade bentonite and 33 wt% TBW-R ball-milled for 5 hr. The resultant powder was dried at 400°C, pressed at 69 MPa, and sintered in air at 1000°C for 2 hr. These materials and the two glasses described below will be evaluated in static leach tests and mechanical properties tests during FY 1981.

VITREOUS PRODUCT DEVELOPMENT -

G. B. Mellinger, L. J. Ethridge,
C. A. Church, and R. E. Thornhill

Samples of a low-temperature borosilicate glass and a high-temperature aluminosilicate glass were prepared containing 50 wt% of the reference transuranic waste blend TBW-R. The glass compositions and compositional effects of expected TBW variations are shown in Tables 4.2 and 4.3. Melts of both glasses were prepared using ten waste variants within the ranges shown and subjected to Soxhlet and buffered acid screening leach tests. As expected, the poorest performance observed was with high alkali wastes, for which the borosilicate glass had a bulk acid leach rate of

10^{-4} g/cm²·day, and the aluminosilicate had a rate of 10^{-5} g/cm²·day. All other glass properties (e.g., viscosity and electrical resistivity at 1050 and 1300°C, respectively) met minimum criteria for every waste variant. Thus it was decided to initiate comparative static leach tests (90°C deionized water for up to 28 days) on the reference glasses. These tests will be completed and reported during the next quarter.

REFERENCE

1. Platt, A. M. and J. A. Powell, compilers. April 1980. Nuclear Waste Management Quarterly Progress Report October Through December 1979. PNL-3000-4, Pacific Northwest Laboratory, Richland, Washington.

TABLE 4.2. Chemical Composition of Borosilicate Glass Frit, Glass Containing Reference TBW, and Range of Glass Composition Due to Variation in TBW

Compound	Composition, wt%		
	Glass Frit 80-226	Glass 80-207 (50 wt% TBW-R)	Variation in Glass Due to TBW
Al ₂ O ₃	--	3.4	2-5
B ₂ O ₃	18.6	9.5	
CaO	12.9	10.1	8-12
CuO	4.6	2.3	
Fe ₂ O ₃	--	10.0	8-12
K ₂ O	3.7	1.9	
Li ₂ O	3.7	1.9	
MgO	3.0	3.8	2-5
Na ₂ O	7.4	6.8	5-8
P ₂ O ₅	--	2.5	1-4
SiO ₂	39.8	40.5	36-44
TiO ₂	2.4	5.0	3-7
ZrO ₂	4.6	2.3	
	100	100	

TABLE 4.3. Chemical Composition of Aluminosilicate Glass Frit, Glass Containing Reference TBW, and Range of Glass Composition Due to Variation in TBW

Compound	Composition, wt%		
	Glass Frit 80-227	Glass 80-208 (50 wt% TBW-R)	Variation in Glass Due to TBW
Al_2O_3	11.9	9.4	8-11
CaO	14.4	11.2	9-12
Fe_2O_3	--	10.0	8-12
K_2O	1.1	1.0	
MgO	2.8	3.8	2-5
Na_2O	5.8	5.9	5-7
P_2O_5	--	2.5	1-4
SiO_2	54.9	47.9	44-51
TiO_2	5.5	6.3	5-8
ZrO_2	<u>3.6</u>	<u>1.9</u>	
	100	100	

5. TRU WASTE DECONTAMINATION

R. P. Allen - Project Manager

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

SUMMARY

The process demonstration work continued with the processing of TRU-contaminated open-faced hood components, a HEPA filter housing, and 150 linear feet of 4-in.-dia pipe. The main emphasis was on identifying techniques to facilitate the handling of large components during their processing.

A portable, powered pipe-cutting machine capable of sectioning up to 2-in.-dia pipe was successfully tested using schedule 40 stainless steel pipe. This pipe cutter has the unique ability to cut pipe in situ, requiring only 1.5 in. of clearance.

A second public information meeting and tour, with over 60 in attendance, was held July 29-30 to update the information presented at the public information meeting on electropolishing held at Hanford in April of 1978.

A ³He neutron detector system was installed and demonstrated by Los Alamos Scientific Laboratory (LASL) personnel. The detector system is to be used for the criticality safety monitoring of the fissile material inventory in the decontamination facility.

Integrated operation of the decontamination and solution processing systems was demonstrated.

A feasibility study was completed on the use of in situ electropolishing techniques

for the decontamination of Savannah River Laboratory high-level waste canisters. This study included the construction and use of several in situ devices, evaluation of prospective electrolytes, and an investigation of the effects of the electrolytes on representative canister materials.

PROCESS DEMONSTRATION

Previous process demonstration work has indicated that more than 80% of the time required to convert TRU-contaminated components into non-TRU waste is currently spent on sectioning and materials handling.^(a) Several large TRU-contaminated components were processed this quarter to obtain a more detailed breakdown on the time required for each processing step. This work confirmed that the most time-consuming aspect of processing TRU waste is the materials-handling step.

The components processed during this evaluation included open-faced hood components, a high-efficiency particulate air filter and housing, and 150 linear feet of 4-in.-dia schedule 80 pipe. These components were disassembled and sectioned in

(a) Platt, A. M. and J. A. Powell, comps. 1980. Nuclear Waste Management Quarterly Progress Report April Through June 1980. USDOE Report PNL-3000-6, Pacific Northwest Laboratory, Richland, Washington.

preparation for decontamination, with particular attention to the man-hours required for these steps.

Both mechanical and plasma arc torch cutting techniques were used as part of the evaluation study. The mechanical techniques included reciprocating saws and shears. All of the sectioning techniques proved to be quick and effective. For example, cutting times for the 4-in. schedule 80 pipe were typically 2 min with a self-feeding reciprocating saw and 1 min with the plasma arc torch. However, the positioning of the pipe sections longer than 8 ft for sectioning proved difficult and time-consuming. For example, it took three men 20 min to position one long piece of the 4-in. pipe for sectioning. Typically it took two men 4 to 8 min to reposition lengths of the pipe that were longer than 8 ft and one man about 1 min for lengths 8 ft. Generally, as the length of the pipe was reduced the time required for repositioning was also reduced.

The plasma arc torch has been shown to be a very effective sectioning technique. However, complete capture of the smoke produced by its use is a problem that has eluded a completely satisfactory solution. An electrostatic precipitator was previously installed in the sectioning/pretreatment facility to collect the smoke and airborne debris from torch use. The effectiveness of this precipitator was enhanced by adding a flexible intake positioned immediately above the cutting area. This arrangement works well, except that the area effectively served by the flexible intake is relatively small. Sectioning large components, as in this segment of the process demonstration, requires that the intake be repositioned frequently; this drastically increases the time required for sectioning preparation when the plasma arc torch is used.

The feasibility of using the plasma arc torch in a chamber connected to the electrostatic precipitator is being examined. This chamber would be designed to permit easy handling of material while capturing any smoke produced by the plasma arc torch. In addition, it would provide protection from sparks and molten metal for other equipment located in the sectioning/pretreatment facility.

A hydraulic lift table was used to position the material for disassembly and sectioning, and an overhead bridge crane was used to transport material from one work location to another. The overhead crane proved very useful both for moving the large components and for moving the sectioned material in baskets. The lift table proved vastly superior to the fixed work tables previously employed. However, the lift table would be even more useful if it could be easily repositioned within the sectioning/pretreatment facility. Additional equipment is being considered to provide this capability.

This segment of the process demonstration shows that large components can be quickly sectioned if the component is properly positioned. However, positioning of large components is difficult and accounts for most of the time currently required for processing TRU waste. Significant man-hour savings could be realized by initially sectioning large components into several pieces that are easily handled before attempting to section the component into the ultimately desired size.

SECTIONING STUDIES

A portable, powered pipe-cutting device capable of cutting up to 2-in.-dia stainless steel pipe was successfully tested. This

5.3

device has a self-feeding pipe cutter that can be attached either to a motor-driven device or a hand-operated ratchet device as shown in Figure 5.1. Power is supplied to the motor drive with a portable drill motor, either electric or air.

This pipe-cutting device has the unique capability of cutting pipe in situ. In situ cutting is accomplished by inserting an end of the pipe to be sectioned into the opening in the power drive, attaching the pipe cutter, clamping the power drive device in place and starting the drill motor. If the pipe is continuous in the area where cutting is desired, the ratchet drive device can be installed around the pipe and used to cut out a section of pipe, permitting installation of the power drive. As little as 1.5 in. of clearance is required for the power drive. This permits cutting of pipes close to walls and other pipes such as in pipe galleries.

Typical cutting times are about 1.5 min for the power drive and 2 min for the ratchet drive.

PUBLIC INFORMATION MEETING

A public information meeting was held July 29-30 to update the information presented at the successful public information meeting on electropolishing held at Hanford in April of 1978. Topics discussed included an in-depth review of electropolishing and vibratory finishing decontamination techniques, sectioning methods, and contamination stabilizing coatings. Presentations were also given on Department of Energy-sponsored work at Rocky Flats on soil decontamination, on Savannah River Laboratory (SRL) plans for a pilot-scale facility for disassembly and decontamination of TRU-contaminated equipment, on Hanford alpha

8009993-9 A - Motor Drive

8009983-8cn B - Ratchet Drive

FIGURE 5.1. Portable Pipe-Cutting Device Which Can Be Used for the In Situ Sectioning of Pipe up to 2 in. in Diameter

decontamination experience in the decommissioning of the 233-S Building, and on Oak Ridge National Laboratory (ORNL) volume reduction of contaminated metal waste by melting. The meeting also included a tour of the 231-Z decontamination facility and a workshop session. The meeting was attended by more than 60 representatives of the DOE, DOE contractors, and the commercial nuclear industry.

CRITICALITY SAFETY/CONTAMINATION MEASUREMENT STUDIES

A ^3He neutron detector bank (Figure 5.2) was installed and calibrated by LASL personnel. This detector was designed to monitor the plutonium content of the electropolishing bath, and until other units can be obtained it will be used as a portable unit

8009993-10cn

FIGURE 5.2. ^3He Neutron Detector System

to monitor for plutonium hold-up throughout the decontamination facility. Consequently, several plutonium samples were used to obtain net count rates as a function of plutonium mass for source-to-detector distances of 0 in., 12 in., 24 in. and 30 in. These calibration curves will permit the detector to be used to monitor the sump and filters in the sectioning/pretreatment facility, the holding tanks and evaporator in the solution processing facility, and the compound recirculation tank associated with the vibratory finisher.

A multi-energy gamma assay system (MEGAS) is being prepared under the LASL subcontract which will screen low-density ($\rho \leq 0.1 \text{ g/cm}^3$), combustible TRU wastes at the 10 nCi/g level. The MEGAS uses a collimated NaI detector 5 in. in dia x 0.08 in. thick to scan a translating and rotating container of combustible waste. A complete pulse height spectrum, corrected for room background, is collected for the sample, and photon yields are computed and compared to a calibration curve to give the net activity of plutonium and americium in the waste.

LASL personnel are also investigating the feasibility of using a 10^7 neutron/sec $^{239}\text{PuBe}$ neutron source for on-line determination of the amount of stainless steel and phosphorous in phosphoric acid solutions by neutron activation analysis.

SOLUTION PROCESSING STUDIES

Integrated operation of the decontamination and solution processing systems was demonstrated. Forty gallons of TRU-contaminated electrolyte were transferred from the 400-gal electropolishing facility to the solution processing system using the liquid waste transfer system. In the solution processing facility, the contaminated

electrolyte was fed directly into, and processed by, the acid purification unit that had been permanently installed in this facility. This demonstrates the ability to directly and safely transfer and process TRU-contaminated electrolyte using permanently installed systems with minimal operator requirements.

RELATED PROJECTS

A feasibility study to evaluate in situ electrochemical techniques for the decontamination of selected areas of heavily-oxidized high-level waste (HLW) canisters was completed. Canister geometry, remote handling requirements and metal removal restrictions were considered for the design of the in situ devices. Four electrolyte systems were evaluated for their effectiveness in removing oxide from typical HLW material. The materials compatibility studies utilized both optical and scanning electron microscopy (SEM) to determine the effectiveness of the oxide removal process, detect any damage to materials, and reveal localized erosion problems.

Four types of in-situ devices were built for accommodating the varied geometries encountered on the canister. These devices

are described in Table 5.1 and shown in Figures 5.3 through 5.6.

Four electrolytes were tested for effectiveness of oxide removal at room temperature using preselected current densities of 3, 10 and 20 A/in.². The electrolytes were also tested for compatibility with the in situ devices. The electrolytes evaluated were 85% phosphoric acid, 50% phosphoric acid, a combination of 75% phosphoric and 25% sulfuric acid and sodium nitrate (5 lb/gal water). These tests indicated that 85% phosphoric acid operated at a current density of 10 A/in.² was the most suitable for the projected canister decontamination application.

The in situ electropolishing devices were tested using 85% phosphoric acid at 10 A/in.² on typical HLW canister material that had been deliberately oxidized. This oxide layer was completely removed in all cases. Moreover, no problems were encountered with erratic or isolated base metal erosion, and optical and SEM microscopy revealed no damage to materials.

The results show that the use of in situ electrochemical techniques for the decontamination of selected areas of HLW canisters is feasible. The use of 85% phosphoric acid as the electrolyte at room temperature in the devices described earlier should provide good

TABLE 5.1. In Situ Electropolishing Devices Evaluated for Decontamination of HLW Canisters

Type	Cleaning Area, in. ²	Use
Pumped stream	1.8	Spot decontamination
Pumped stream	0.13	Decontamination inside corners and grooves
Swab	3.1	Decontaminate curved or ridged areas
Contact	16.0	Decontaminate flat or uniform curved surfaces; electrolyte is contained within device

oxide removal without significant detrimental effects to the canister material. The sizing and adaptation of these types of in situ

electrochemical devices to the actual canister configuration and remote handling requirements are also quite feasible.

8009993-2cn

FIGURE 5.3. Pumped-Stream In Situ Electropolishing Device Used for Spot Decontamination

8009993-1cn

FIGURE 5.4. Pumped-Stream In Situ Electropolishing Device Used To Decontaminate Inside Corners and Grooves

8009993-4cn

FIGURE 5.5. Swab In Situ Electropolishing Device
Used To Decontaminate Flat, Curved or Ridged Areas

8009993-3cn

FIGURE 5.6. Contact In Situ Electropolishing Device Used To
Decontaminate Flat or Uniform Curved Surfaces. The electro-
lyte is contained within the process chamber of the device.

6. KRYPTON SOLIDIFICATION

G. L. Tingey - Project Manager

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

SUMMARY

Low-density silica (30% porosity) has been loaded with krypton as a function of pressure up to 140 MPa. Loadings of up to 15 cm³ of Kr(STP)/g of glass have been achieved at the highest pressures. Release of the krypton is very slow at temperatures below 1000°C. Extrapolation of long-term release rates shows a total release of 0.7% of the krypton after 10 yr at 420°C.

DISSOLUTION OR TRAPPING OF KRYPTON IN LOW-DENSITY VITREOUS SILICA - G. L. Tingey, J. M. Lytle, and K. R. Wheeler

One of the original goals of this program was to investigate the feasibility of dissolving krypton in an inorganic glass matrix. The glasses' stability to corrosion, chemical inertness, and insolubility in storage environments prompted us to consider them as candidates for storage of radioactive krypton. The initial results showed that krypton solubility in high-density glass or glass powders was too low to be of interest for our application.⁽¹⁾ We did find, however, that low-density silica could be loaded with up to 7 cm³ of Kr(STP)/g of glass if the loading was accomplished in krypton at about 35 MPa pressure. Furthermore, by sintering the glass while maintaining the krypton

pressure, the release rate is almost immeasurable below 400°C.

Recently we have measured the loadings of krypton in silica glass rods with about 30% porosity as a function of loading pressure up to about 140 MPa. Figure 6.1 shows the quantity of krypton contained in the rods as

FIGURE 6.1. Volume of Krypton at Standard Temperature and Pressure for Thirsty Vycor® Glass Loaded at Indicated Pressure and Held at 900°C for 1.5 hr or More

®Registered trade name of Corning Glass Works, Houghton Park, Corning, New York. The product is 96% SiO₂ with 28% porosity.

a function of loading pressure. The rods were heated in the krypton atmosphere to 900°C, the temperature being increased linearly in about 4 hr. They were then held for 1-1/2 hr or more at 900°C and cooled while maintaining the krypton pressure. All loadings at 55 MPa and below were conducted at our laboratory while those above that pressure were conducted by Exxon Nuclear Idaho Company for us. The scatter in the data at the high pressures appears to be due to variation in the sintering time. The data show that the krypton content does not increase linearly with pressure above 55 MPa, but loading in excess of 15 cm³/g of glass appears to be achievable at pressures of about 140 MPa.

Maximum loadings are achieved in the silica used in these tests (Thirsty Vycor) at temperatures as low as 850°C in about 4 hr at temperature. Measurements of the release rate of the krypton from the glass as a function of temperature show that the gas is, to a large extent, retained at temperatures up

to 1000°C. Long-term release does occur at a measurable rate, however, at lower temperatures. Figure 6.2 shows the fraction of krypton contained in the glass which is released as a function of square root of time at 420°C. The diffusion coefficient, written as D/r_0^2 , was determined from the equation

$$F = \left(\frac{36Dt}{\pi r_0^2} \right)^{1/2}$$

to be $8.66 \times 10^{-13} \text{ min}^{-1}$. For spheres of radius, r_0 , the fraction, F , of krypton released at any given time, t , is proportional to the diffusivity, D . This proportionality still holds with limited deviations from spherical if r_0 is defined appropriately. Extrapolation of these data yields a total release of 0.7% of the krypton after 10 yr at 420°C.

The results reported here show the potential of storing radioactive krypton in a glass matrix for long periods of time. The form of the krypton in the glass has not

FIGURE 6.2. Percent of Krypton Released Versus Square Root of Time for Thirsty Vycor Glass Loaded at 850°C and 35 MPa and Released at 420°C. The diffusion coefficient is written as $D/r_0^2 = 8.66 \times 10^{-13} \text{ min}^{-1}$.

been determined at present, nor is the mechanism of release clearly understood. Work is currently under way to investigate these points and to more carefully define the optimum conditions for loading and

sintering the glass. Lower temperature softening glasses have also been obtained to investigate the possibility of loading and sintering at temperatures below 800°C.

REFERENCES

1. Tingey, G. L., E. D. McClanahan, M. A. Bayne, and W. J. Gray. "Solid State Containment of Noble Gases in Sputter Deposited Metals and Low Density Glasses." Presented at the International Symposium on Management of Gaseous Wastes from Nuclear Facilities, Vienna, Austria, February 18-22, 1980.
2. Walker, P. L., Jr., L. G. Austin, and S. P. Nandi. 1966. "Activated Diffusion of Gases in Molecular-Sieve Materials." In Chemistry and Physics of Carbon, Vol. 2, p. 292, P. L. Walker, Jr. (ed), Marcel Dekker, Inc., New York, New York.

7. THERMAL OUTGASSING

L. L. Burger - Project Manager

The objectives of the Thermal Outgassing Program are to:

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

SUMMARY

Initial hot-cell tests using Shippingport UO_2 fuel were completed on schedule after modification of hot-cell facilities in the 325 Building. Experiments at 1500°C were completed using helium or $\text{He} + 6\% \text{H}_2$ as the sweep-gas. The release of xenon, krypton, and tritium was observed during the 6-hr heating cycle.

THERMAL OUTGASSING - L. A. Bray

Krypton, xenon, and tritium gas release rates were obtained during the thermal outgassing of Shippingport UO_2 fuel using sweep-gas techniques in the 325 Building Hot-Cells. (The use of DOE facilities with vacuum equipment already developed by HEDL for studying reactor transients has been delayed until FY 1981 because of unexpected building modifications.) The initial results show that greater than 93% krypton and 90% xenon were released during a 6-hr test at 1500°C using helium as the sweep-gas. When duplicate tests were completed with a sweep-gas containing $6\% \text{H}_2 + \text{He}$, 50 to 80% of the krypton was released with only 11 to 16% of the xenon. The difference in release rates

between xenon and krypton when hydrogen is present in the sweep-gas is now being verified. Residual ^3H values for the heated fuel are not yet available. The initial sweep-gas experiments using He or $6\% \text{H}_2 + \text{He}$ were completed using a 2-in. tube furnace, 1-g (1 or 2 pieces) samples of fuel, at a gas flow rate of 150 cc/min. The UO_2 was heated from 35°C to 1500°C during the first 2 hr, and hourly samples were taken for gas analysis during the 6-hr test. The exit gas was passed through a 400°C tube furnace containing copper oxide, and a series of ascarite and anhydrone traps before being separated in a charcoal U-trap cooled with liquid N_2 . The samples were analyzed using a gas chromatograph to obtain xenon and krypton results. Liquid-scintillation counting techniques were used to obtain the tritium results. The residual gas remaining in the fuel samples after outgassing was released from the fuel using a LECO Corporation, XK-10, inert gas fusion analytical furnace. Additional tests are being considered using other gas compositions and temperatures.

All major capital equipment requirements and appropriation requests have been identified and completed for FY 1980.

8. IODINE-129 FIXATION

L. L. Burger - Project Manager

The objective of this program is to develop technologies that will provide safe, effective removal and packaging of ^{129}I 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

Leaching studies of candidate fixation materials for ^{129}I and ^{14}C were continued. The results of these and previous studies suggest that the iodates of barium, strontium, and mercury and iodine-loaded silver sorbents in portland cement and iodine sodalite are acceptable fixation forms for ^{129}I and that the alkaline earth carbonates in cement are suitable for ^{14}C fixation. Based on leaching studies alone, the iodine-loaded silver sorbents may be satisfactory without further treatment. Firm decisions of acceptability cannot be made in the absence of storage or disposal criteria, and a report has been written suggesting factors useful in developing such criteria.

Thermal studies, differential scanning calorimetry (DSC), tend to support other studies in suggesting differences among the various iodine loadings of silver mordenite. Preliminary measurements using scanning electron microscopy (SEM), x-ray fluorescence, and electron spectroscopy for chemical analysis indicate that these techniques may be quite useful in characterizing the iodine sorption reactions.

LEACHING STUDIES - R. D. Scheele
and K. D. Wiemers

Current leaching studies are aimed at long-term behavior of selected iodine and

carbon fixation form candidates. The iodine-containing materials being examined are barium iodate, mercuric iodate, and iodine-loaded silver mordenite mixed with cement to an iodine-loading level of 0.8 mmol I/g dry cement, iodine-loaded silver sorbents--silver mordenite (AgZI), silver faujasite (AgXI), and AC6120 loaded to 70% silver use, and reduced silver mordenite loaded to 95% silver use (Ag^oZI)--and 20 wt% iodine sodalite. The carbon-containing material being studied is calcium carbonate in cement, 2.4 mmol C/g dry cement. The materials selected are potential end-products or suggested fixation forms for the various processes for trapping ^{129}I and ^{14}C .

Preliminary static leach test results obtained after 28 days of exposure to distilled water, Columbia River water, or sea water indicate the following:

- Within an order of magnitude no difference in the iodine fraction leached was observed for barium iodate-impregnated cement in river water or distilled water, mercuric iodate-impregnated cement in river water, sea water, or distilled water, or AgZI in cement in distilled water. The average fractions leached for cements with barium iodate, mercuric iodate, and iodine-loaded silver mordenite, normalized to a constant V/S, were 2.2×10^{-3} , 3.9×10^{-3} , and 1.0×10^{-3} , respectively. The amount leached for barium iodate was an order of magnitude

less than that reported by Oak Ridge National Laboratory (ORNL) using barium iodate-impregnated cement in an International Atomic Energy Agency (IAEA) leach test.⁽¹⁾ The iodine fraction leached for barium iodate-impregnated cement in sea water was an order of magnitude higher, 3.9×10^{-2} , similar to results obtained in earlier static leach tests for lead iodate-impregnated cements.

- The fraction of iodine leached from silver sorbents ranged from $<2.0 \times 10^{-7}$ to 2.0×10^{-5} , two to four orders of magnitude less than found for the same materials in cement. This surprising result may indicate that in the former case the apparent leach rate may be governed by the solubility of AgCl , Ag^+ being in excess and leachable. For the cement, samples in the leachate are higher and suggest that the silver is not available.
- The first iodine sodalite sample received from Rockwell Hanford Operations had a high iodine fraction leached, 5×10^{-2} , but was not considered to be a representative sample. Another iodine sodalite is being studied. Preliminary tests carried out by Rockwell on new samples showed very low leach rates.
- Calcium carbonate-impregnated cement specimens showed a carbon fraction leached in river water, distilled water, and sea water of 3.0×10^{-5} , 5.4×10^{-6} , and 7.3×10^{-7} , respectively. First tests showed the fraction of carbon leached from lead carbonate-impregnated cement to be an order of magnitude higher.

The IAEA type of leach test was used to examine the effect of adding sodium bentonite to calcium iodate-impregnated cement. Little effect was observed for samples prepared with a bentonite:cement weight ratio of 0.15:1 and 0.30:1. In these first tests the bentonite

content may have been too high to produce a good cement product.

At present, barium iodate, strontium iodate, mercuric iodate (and probably lead iodate),⁽²⁾ and the iodine-loaded silver sorbents, AgX, AgZ, AC6120 in a cement matrix, and probably sodalite, appear to be suitable storage forms for ^{129}I . The silver sorbents may also be used without cement; however, solidification in a matrix of some sort is probably desirable. Calcium, strontium,^(3,4) and barium carbonates in cement are probably suitable for storage of ^{14}C . Other materials, including several of the synthetic minerals, may still be considered for ^{129}I . The establishment of criteria for storage or disposal will ultimately indicate the goals for leach resistance.

SILVER SORBENT CHARACTERIZATION STUDIES

Thermal Analytical Characterization Studies - R. D. Scheele

Previous studies^(5,6) have shown a varied behavior of iodine-loaded silver sorbents with respect to iodine extractability with CCl_4 , and thermal behavior—loss of iodine, in the range of 200 to 900°C. Characterization studies are continuing using DSC and thermogravimetry. The normal temperature for sorption of iodine is 150°C. Figure 8.1 presents the DSCs for silver mordenite, AgZ, loaded at a higher temperature, 240°C, to 50, 100, 150, and 200 mg I/g AgZ (~25, 50, 75, and 95% Ag use, respectively). The 50 and 150 mg I/g AgZ samples have an endotherm occurring at ~250°C. This endotherm is missing in the DSCs for 100 and 200 mg I/g AgZ. A fraction of the 100 mg I/g AgZ was loaded to ~150 mg I/g AgZ. The DSC for this 150 mg I/g AgZ had a smaller and broader endotherm than that for the first 150 mg I/g AgZ. The DSCs for 50

FIGURE 8.1. Differential Scanning Calorimetry for Silver Mordenite Prepared at 240°C (A) 50 mg I/g AgZ, (B) 100 mg I/g AgZ, (C) 150 mg I/g AgZ, (D) 200 mg I/g AgZ

and 150 mg I/g AgZ prepared at 150°C instead of at 240°C do not have this endotherm. Potential iodine-containing compounds that might exist in iodine-loaded silver mordenite are iodine (mp 114°C; bp 184°C), silver iodine (crystal change 146°C; mp 556°C), silver iodate (decomposes 420°C), and silver periodate (decomposes 180°C). The 150°C endotherm could correspond to the AgI crystal change, but the endotherm expected for the melting point at 560°C was absent. Thermal transitions characteristic of pure compounds may not be expected in these sorbents, and previously prepared samples have not shown them to be present.

The materials prepared at 240°C varied among themselves also in their physical appearance. The 50 mg I/g AgZ was a light tan, and the 150 mg I/g AgZ was light green. The 100 and 200 mg I/g AgZ were red and purple red, respectively, and the 150 mg I/g AgZ prepared from the 100 mg I/g AgZ was brick red.

The variations in the physical and chemical characteristics of iodine-loaded silver mordenites continue to indicate the presence of different iodine species and different iodine-loading mechanisms dependent upon the experimental parameters. Further study of the nature of iodine-trapping on silver sorbents is desirable before these materials are used on a process scale for trapping or disposal of ^{129}I .

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

Preliminary studies using SEM and x-ray fluorescence were carried out on iodine-loaded and nonloaded silver sorbents. The sorbents studied were silver mordenite, AgZ; silver mordenite loaded to 100 mg I/g AgZ

(50% Ag use), AgZI; reduced silver mordenite Ag⁺Z; reduced silver mordenite loaded to 100 mg I/g AgZ (50% Ag use), Ag⁺ZI; silver faujasite, AgX; silver faujasite loaded to 100 and 200 mg I/g AgX (25 and 50% Ag use, respectively), AgXI. Also examined were samples of silver nitrate-coated Berl saddles and saddles loaded to 37.8 mg I/g. Micrographs and x-ray analyses were performed both on the original surface and on sectioned and polished particles. X-ray analysis does not detect elements with mass numbers less than sodium.

Some interesting differences were seen among the different materials. Figure 8.2 is a micrograph of Ag⁺ZI. The bright particles scattered randomly throughout the channels of the zeolite have an Ag to I ratio of about 1:1 and were probably AgI. In the areas where these bright particles do not exist, Ag:I ratio varies from 1:5 on the outside of the particle to 2:1 in the center.

21878

FIGURE 8.2. 1000X SEM of Ag⁺ZI (100 mg I/g AgZ)

In nonloaded $\text{Ag}^{\circ}\text{Z}$, particles containing only Ag are scattered randomly throughout the material, leaving areas of Ag depletion. These Ag particles are the precursor to the AgI found in $\text{Ag}^{\circ}\text{ZI}$. As can be seen in Figure 8.3, AgZI did not have these AgI particles; the Ag:I ratio was 2:1 distributed evenly throughout the material.

Figures 8.4 and 8.5 show 100X magnifications of polished sections of 50% silver-utilized mordenite and faujasite, AgZI (100 mg I/g) and AgXI (200 mg I/g). In AgXI there is a light-colored outer area and a darker inner core. The lighter colored area contains iodine and the darker area does not. The AgZI has iodine distributed uniformly throughout the material. Figure 8.6 is a micrograph of AgXI, 100 mg I/g AgX, 25% Ag use. Comparison of Figure 8.6 with 8.5 shows the deeper penetration of iodine into the faujasite with a higher iodine loading. Particles with a Ag:I ratio of $\sim 1:1$ were

scattered randomly over the surface of the iodine-loaded Berl saddles. There was no penetration of AgI or Ag into the ceramic material.

Surface Analysis Characterization -

M. T. Thomas and K. D. Wiemers

The Auger (MNN) peaks for ESCA silver spectra were taken on clean silver metal, silver iodide powder, silver faujasite (AgX), silver mordenite (AgZ), reduced silver mordenite ($\text{Ag}^{\circ}\text{Z}$), silver nitrate-impregnated silica (AC6120), and iodine-loaded forms of each of these silver sorbents. These samples exhibited clear differences in silver chemistry as determined by comparing peak position, separation, relative amplitude, and shape. Significantly, the silver-iodine bonds in the iodine-loaded sorbents were not identical to the silver iodide powder.

21875

FIGURE 8.3. 1000X SEM of AgZI
(100 mg I/g AgZ)

21872

FIGURE 8.4. 100X SEM of AgZI
(100 mg I/g AgZ)

21975

FIGURE 8.5. 100X SEM of AgXI
(200 mg I/g AgX)

21981

FIGURE 8.6. 100X SEM of AgXI
(100 mg I/g AgX)

CRITERIA FOR THE DISPOSAL OF ^{129}I - L. L. Burger

A report, Determining Criteria for the Disposal of Iodine-129, PNL-3496, has been written, which examines the quantity, distribution, and rate of movement of iodine on a global basis. The report considers ^{127}I (natural iodine), naturally produced ^{129}I , and anthropogenic ^{129}I . It is observed that the ^{129}I released as a result of nuclear activities over the past few decades is not uniformly dispersed, but that the possibility of much greater dispersion, and therefore of much greater dilution, exists. The potential for dilution with respect to either the ^{129}I concentration or the $^{129}\text{I}/^{127}\text{I}$ ratio far exceeds the minimum required for acceptable exposure to mankind.

A set of 14 basic items has been described which can be used to set criteria for storage and disposal of ^{129}I . It is suggested that preliminary standards be developed based on

these and perhaps other items to apply to
1) temporary storage and transportation,
2) disposal to a dry environment with a time limitation on calculated behavior, and 3) disposal to the deep ocean with complete release permitted in 10^3 yr. Early quantification of some of these items will permit better decisions on the research and development needed for iodine removal or control, fixation, and disposal.

Sodalite Studies - W. I. Winters,
Rockwell Hanford

Iodine sodalite products were prepared under 3000, 5000, and 7000 psi pressure and at 520, 820, and 1060°C temperature. Both bulk and apparent densities were determined for the samples. The iodine content was found to be between 15 and 20% as determined by x-ray fluorescence. The leachability of the products was determined by the American Nuclear Society procedure using distilled

water on a bulk sample. These studies showed that higher hot-pressing temperatures and pressures increased the density and reduced the porosity and leachability of the products. The effect of temperature was found to be more significant than pressure, with a superior waste form being produced at 1060°C. Products pressed at this temperature have apparent densities of 2.60 g/cm³ (99.5% of theoretical), porosities <0.05%, and cumula-

tive leach rates for 96 hr of $<1 \times 10^{-6}$ g/cm²/day. These tests continue to show promise for hot-pressed iodine sodalite as a long-term waste form for ¹²⁹I. The high-temperature product is hard and mechanically stable and has good leaching characteristics. Further work will examine the variables involved in the hydrothermal reaction, iodine losses during the process, and the structural and mechanical properties of the product.

REFERENCES

1. Clark, W. E. 1977. "The Isolation of Radioiodine with Portland Cement. Part I: Scoping Leach Studies." Nuc. Tech., 36:215.
2. Burger, L. L. 1979. In Nuclear Waste Management Quarterly Progress Report July Through September 1978. A. M. Platt and J. A. Powell, compilers. PNL-2378-3, Pacific Northwest Laboratory, Richland, Washington.
3. Burger, L. L. 1979. In Nuclear Waste Management Quarterly Progress Report July Through September 1979. A. M. Platt and J. A. Powell, compilers. PNL-3000-3, Pacific Northwest Laboratory, Richland, Washington.
4. Burger, L. L. 1980. In Nuclear Waste Management Quarterly Progress Report October Through December 1979. A. M. Platt and J. A. Powell, compilers. PNL-3000-4, Pacific Northwest Laboratory, Richland, Washington.
5. Burger, L. L. 1980. In Nuclear Waste Management Quarterly Progress Report January Through March 1980. A. M. Platt and J. A. Powell, compilers. PNL-3000-5, Pacific Northwest Laboratory, Richland, Washington.
6. Burger, L. L. 1980. In Nuclear Waste Management Quarterly Progress Report April Through June 1980. A. M. Platt and J. A. Powell, compilers. PNL-3000-6, Pacific Northwest Laboratory, Richland, Washington.

9. MONITORING AND PHYSICAL CHARACTERIZATION OF UNSATURATED ZONE TRANSPORT

T. L. Jones - Project Manager

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

SUMMARY

Analysis of radionuclide movement in laboratory columns was extended to modeling the movement of ^{85}Sr under changing salt loading conditions. A soil column was leached with a low-salt solution containing ^{85}Sr , with the result that the strontium was sorbed very well. The low-salt solution was then followed by an unspiked high-salt solution which caused the strontium to be released quickly from the soil. This is called the snowplow effect. The mobile-immobile water concept was used to describe this phenomenon. This same modeling approach was applied to tritium movement through a very large laboratory column. The effect on dispersion of increasing the scale of the experiment was seen in the shape of the breakthrough curve measured. Testing was started on a new procedure for measuring tritium from field soil samples. The technique ashes the entire sample and then condenses the tritium vapor for liquid-scintillation analysis.

PHYSICAL MODELING - G. W. Gee and T. L. Jones

Two major tracer experiments were analyzed this quarter: the movement of tritium through a large laboratory column (57 cm x 176 cm) and the movement of ^{85}Sr in small

laboratory columns under changing salt loading conditions.

Large Column

A sketch of the barrel used for the large-column study is shown in Figure 9.1. The column was layered by placing clean, coarse sand at a density of 1.38 g/cm^3 at 116 cm to simulate field stratification at a burial site. The total depth of the column was 176 cm, and the Rupert sand was packed to a density of 1.74 g/cm^3 . Tap water was applied until drainage occurred from the bottom of the column. Then tritium (^3H)-spiked water ($4.7 \text{ } \mu\text{Ci/l}$) was applied in daily pulses to the top of the column at a rate of 2.5 cm/day for 14 days. This resulted in 0.48 mCi total tritium being added to the column.

Breakthrough curves were analyzed for tritium using standard liquid-scintillation procedures.⁽¹⁾ Figure 9.2 compares the tritium breakthrough curve obtained from the large-column experiment and a representative breakthrough curve from a small-column experiment.⁽¹⁾ The small column was ~5.4 cm x 27.5 cm. Figure 9.2 shows an increase in the dispersion of the tritium through the large column over that through the small column. The flow velocity through the small column was 6.7 cm/day. The reduced flow velocity

FIGURE 9.1. Diagram of Large Laboratory Column

FIGURE 9.2. Comparison of Small-Column Tritium Breakthrough Curve with Large-Column

in the large column would reduce the dispersion over the small column; however, the increased dispersion due to the increased length of the column was dominant over the velocity effect.

Two approaches were used to model the breakthrough curve. The traditional two-parameter, convective-dispersive equation was used along with the four-parameter, mobile-immobile water equations of Van Genuchten and Wierenga.⁽²⁾ The best-fit curves using both approaches are shown in Figure 9.3. While the two curves are distinct, it would be difficult to say that one fits the data better than does the other.

Snowplow Effect

The salt concentrations in the bulk solution of a soil affects the sorption of certain radionuclides. Generally the higher

the salt concentration the lower the sorption due to increased competition for exchange sites from nonradionuclide species. Radionuclides that are sorbed under a low-salt concentration of the soil solution are released when the salt concentration is increased. Starr and Parlange⁽³⁾ have referred to this phenomenon as the snowplow effect.

The changing sorption of ^{85}Sr was illustrated by using the high-salt (H) and low-salt (L) solutions of Gee and Campbell.⁽¹⁾ Strontium was added to the low-salt solution and pulsed through a column. After 18 pore volumes of effluent, no strontium was measured in the column effluent. The high-salt solution was then added to the column, and the strontium was leached from the column within ten pore volumes. These data are shown in Figure 9.4. The mobile-immobile water model described in Van Genuchten and

FIGURE 9.3. Comparison of Two-Parameter, Convective-Dispersive Model with Four-Parameter, Mobile-Immobile Water Model Large-Column Tritium Breakthrough Curve

FIGURE 9.4. Snowplow Effect: Use of Mobile-Immobile Water Model To Describe Strontium Movement Under Conditions of Changing Salt Loading

Wierenga⁽⁴⁾ was used to describe the snowplow effect. The K_d values (taken from Gee and Campbell) were assumed to be 6 for the low-salt solution and 0.7 for the high-salt solution. The parameter f listed in Figure 9.4 describes the fraction of total sorption sites exposed to the mobile-water phase. Using data obtained from other small-column tritium and strontium columns, the best estimate of f is 0.7. Using f as 0.7 produces the dotted line in Figure 9.4. The match to experimental data is greatly improved by letting f equal 0.5.

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

A new procedure is being tested for analyzing tritium from field samples. Previously soil samples were leached to remove the tritium for liquid-scintillation analysis. The new procedure uses a sample oxidizer that ashes the entire sample and then recovers the tritium from the vapor phase and prepares it for liquid-scintillation counting. Preliminary work has shown it to be a quick technique, and work is continuing to allow comparison with the leaching procedure previously used.

REFERENCES

1. Gee, G. W. and A. C. Campbell. 1980. Monitoring and Physical Characterization of Unsaturated Zone Transport-Laboratory Analysis. PNL-3304, Pacific Northwest Laboratory, Richland, Washington.
2. Van Genuchten, M. Th. and P. J. Wierenga. 1976. "Mass Transfer Studies in Sorbing Porous Media. I. Analytical Solutions." Soil Sci. Soc. Am. J. 40:473-480.

3. Starr, J. L. and J. Y. Parlange. 1979. "Dispersion in Soil Columns: The Snow-plow Effect." Soil Sci. Soc. Am. J. 43: 448-450.
4. Van Genuchten, M. Th. and P. J. Wierenga. 1976. "Numerical Solution for Convective Dispersion with Intra-Aggregate Diffusion and Non-Linear Adsorption." In System Simulation in Water Resources, G. C. Vansteenkiste, ed., North Holland Publishing Company, Oxford and New York.

10. WELL-LOGGING INSTRUMENTATION DEVELOPMENT

R. L. Brodzinski - Project Manager

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

SUMMARY

Experiments on thermal neutron activation analysis of ^{90}Sr indicate that the reaction cross section is in the range of 0.3 - 0.6 mb. This is in marked contrast with the published literature value of 800 mb and seriously reduces the potential for successful application of this method to in situ ^{90}Sr analysis. Consequently, major emphasis on construction of a field system for analysis of ^{90}Sr is being shifted toward the bremsstrahlung technique.

Most of the components have been received for the in situ tritium logging system. Various subassemblies are described.

A synopsis of a paper entitled "In Situ Subterranean Determination of Actinides by High Resolution Gamma-Ray Spectrometry," by R. L. Brodzinski and H. L. Nielson, has been prepared for presentation at the IAEA International Symposium on Methods of Low Level Counting and Spectrometry, to be held in West Berlin, April 6-10, 1981.

Detailed field tests of the actinide photon detection technique have been completed, and the results are discussed. Six actinide isotopes can be measured simultaneously at concentrations less than 10 nCi g^{-1} in less than 7 min. Detection limits are given, and actual profiles in a field logging environment are shown. Interpretation of the data

is provided, and information obtainable with the technique is discussed and compared to that obtainable by other actinide well-logging techniques.

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

The experiments on thermal neutron activation analysis of ^{90}Sr have been successfully completed. Detailed data reduction will require some time to precisely define the capture cross section of ^{90}Sr and the sensitivity of this technique for in situ analysis. Preliminary examination of the data indicates that the cross section for the $^{90}\text{Sr}(n,\gamma)^{91}\text{Sr}$ reaction is in the range of 0.3 to 0.6 mb. This is in marked contrast with the published literature value of 800 mb⁽¹⁾ and seriously reduces the potential for successful application of this technique to in situ ^{90}Sr analysis. Consequently, major emphasis on construction of a field system is being shifted toward the bremsstrahlung technique developed earlier in this program.

The program plan has been completed for development of the software system for reduction of field ^{90}Sr bremsstrahlung analysis data. Conceptual plans have been formulated for construction of a calibration facility

necessary to obtain parametric data for the software system.

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

Efforts on the construction and application of the Nafion sampling and gas counter analysis technique tested earlier in this program are being greatly accelerated to provide a field operational analytical system at the earliest possible time. Machine shop work has been completed on the reduc-

tion furnace, the furnace sleeves of the canister, and the sampler and sampler guard. Design has been completed for the furnace temperature controller, the electrical leads and connectors for instrument components, the electrical leads, connectors, and switches for the control panel, the electrical cable attachments, and the preamplifiers. The sample flow path has been planned, and the physical layout of the instrument components has been determined. Most of the components have been received, and subassemblies, shown in Figures 10.1 through 10.6, have been fabricated wherever possible.

8008650-5

FIGURE 10.1. Tritium Logger Sampling Subassembly Showing Both Air and Water Sampling Ports

8008650-4

FIGURE 10.2. Tritium Logger Palladium Catalytic Oxidizer
Subassembly with Metering Valves

8008650-6

FIGURE 10.3. Tritium Logger Thermoelectric Cold Trap Subassembly and Bipolar Controller

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

A relatively high activity ^{57}Co isotopic excitation source has been ordered pursuant to investigation of x-ray fluorescence analysis techniques for in situ determination of actinides.

A synopsis of a paper entitled "In Situ Subterranean Determination of Actinides by High Resolution Gamma-Ray Spectrometry," by R. L. Brodzinski and H. L. Nielson, has been prepared for presentation at the IAEA International Symposium on Methods of Low Level

Counting and Spectrometry, to be held in West Berlin, April 6-10, 1981.

Detailed field tests of the photon detection technique for determination of actinides have been completed. This technology has been demonstrated capable of simultaneously measuring the concentration of six actinide isotopes, ^{235}U , ^{238}U , ^{237}Np , ^{239}Pu , ^{241}Pu , and ^{241}Am , in fission product free environments at concentrations less than 10 nCi g^{-1} in less than 7 min. The sensitivity of the technique is somewhat reduced in matrices containing large quantities of gamma-ray emitting fission product activities.

8008650-7

FIGURE 10.4. Exploded View of Thermoelectric Cold Trap Subassembly

In addition to the above actinides, primordial ^{40}K is also measured during each count and provides a check on the operation and reliability of the equipment as well as identifying changes in sediment configuration or composition, such as void areas, foreign cobble, or lithologic changes.

Although many gamma-rays can be observed in the spectra from the above isotopes, single photons have been chosen for each nuclide based on sensitivity and freedom from potential interferences. These photon energies are given in Table 10.1 along with the volume and range of sediments interrogated by 90% of the measured counts. Different ranges of interrogation are extremely important in interpreting data with respect to fine structure or inhomogeneous distribution of the activities. The listed interrogation volumes were

experimentally measured inside a 6-in., schedule 40 iron pipe and would be larger for wells cased with thinwall tubing or plastic pipe.

The 108 cm^3 intrinsic germanium diode gamma-ray detector used in these field tests was calibrated in the Rockwell Hanford Operations 4π plutonium calibration facility, a tank filled with Del Monte sand having a density of 1.36536 homogeneously spiked with plutonium and americium in two separate sectors approximately a factor of 10 apart in concentration. Although this facility has repeatedly been shown to be inadequate for calibrating neutron detection systems due to small size and nonrepresentative matrix material, it is large enough to represent an infinite volume for the detection of photons $\leq 414\text{ keV}$, and the matrix error introduced in

8008650-2

FIGURE 10.5. Tritium Logger Reduction Furnace Subassembly

calibrating the photon detection system is largely due to incorrect density as opposed to incorrect chemical composition, which so adversely affects the neutron detection techniques. The density of the sediments investigated in these field tests has been measured in the range 1.41 to 1.60. Efficiency factors obtained from the calibration facility are a complex function of both density and photon energy. However, calculations

indicate that calibration errors due to incorrect matrix density are probably less than 10%, and this is deemed insignificant when compared to the effects caused by inhomogeneous distribution of the actinides in the sediments. The concentrations of the plutonium and americium isotopes in both sectors of the calibration facility are given in Table 10.2.

8008650-1

FIGURE 10.6. Tritium Logger Oeschger-Type
Proportional Counter Subassembly

TABLE 10.1. Actinides (and ^{40}K) Measurable In Situ by High-Resolution Gamma-Ray Spectroscopy

Isotope	Gamma-Ray Observed, keV	Volume of Sediments Interrogated, ℓ	Range of Interrogation, cm
^{40}K	1461	1410	62
^{238}U ($^{234\text{m}}\text{Pa}$)	1001	720	48
^{239}Pu	414	72	19
^{237}Np (^{233}Pa)	312	26	12
^{241}Pu (^{237}U)	208	4.0	4.5
^{235}U	186	2.3	3.3
^{241}Am	60	<1	<2.0

TABLE 10.2. Concentrations of Plutonium and Americium Isotopes in the Rockwell 4π Plutonium Calibration Facility

Isotope	High Sector nCi g^{-1} on 9/12/80	Low Sector nCi g^{-1} on 9/16/80
^{238}Pu	6.639	0.6702
^{239}Pu	82.54	8.362
^{240}Pu	28.11	2.848
^{241}Pu	856.7	86.72
^{242}Pu	0.003422	0.003468
^{241}Am	13.74	1.395

Actual detection limits for each actinide based on field data taken from inside a 6-in., schedule 40 steel well casing are shown graphically in Figure 10.7 as a function of counting time. Except for ^{241}Pu , detection at the 10 nCi g^{-1} level is possible in less than 25 sec. This provides an economical method for real time in situ determination of actinide isotopes. Even greater sensitivity is possible for measurements made in boreholes or wells cased with thinwall tubing or plastic pipe.

Actual profiles of the ^{237}Np , ^{239}Pu , ^{241}Pu , and ^{241}Am concentrations around well 299-W18-159 in the 216-Z-1A crib are shown in Figure 10.8. All data shown represent a statistical uncertainty of less than 10%. The two plutonium isotope curves are

very similar, as would be expected. Although differences in the profiles might be expected due to different ages of the deposit, no such difference is readily apparent. This can be interpreted to mean that the plutonium has not migrated down through the sediments over a period of time, but that it has moved to a given depth relatively rapidly after introduction into the crib and then remained firmly fixed thereafter. This conclusion stems from the apparent similar age of plutonium at all depths. The significant difference in the plutonium profiles at a depth of 4 m is attributed to inhomogeneity in distribution exaggerated by the different range of interrogation for the two isotopes. Additional evidence for this conclusion will be presented later.

The americium profile shown in Figure 10.8 does not closely parallel the ^{241}Pu profile, indicating substantially different chemical interactions with the matrix and, therefore, different retention coefficients. Although all the americium present can be accounted for from decay of ^{241}Pu , the different profile demonstrates additional migration after formation.

The neptunium profile resembles neither the plutonium nor americium profiles and indicates substantially different soil

FIGURE 10.7. Detection Limits for In Situ Determination of Actinides in Subterranean Environments Using High-Resolution Gamma-Ray Spectroscopy

chemistry and enhanced mobility. The neptunium burden is too large, however, to be a product of the decay of ^{241}Pu and must be due to injection of neptunium-enriched wastes into the crib.

Profiles of ^{239}Pu , ^{241}Pu , and ^{241}Am taken from this same well utilizing a collimator which provided horizontal strata resolution every 1/2-in. are shown in Figure 10.9. The structure demonstrated by the ^{241}Pu profile is attributed to inhomogeneous distribution of the plutonium remote from the well. The relative smoothness of the ^{239}Pu curve is attributed to the larger range of interrogation, which tends to have an "averaging" effect on the concentration data and to the reduced effectiveness of the collimator for shielding the higher energy ^{239}Pu gamma-ray, leading to a certain amount of "cross-talk" between adjacent strata.

The marked structure and increased depth of the peak in the ^{241}Am concentration pro-

file reinforces the earlier conclusions regarding enhanced mobility of americium. Note that an order of magnitude change in plutonium concentration through a depth of only 12 cm is easily defined with this logging technique. Similar resolution utilizing neutron detection logging systems is not possible.

Data were also obtained at selected depths utilizing a collimator having a spatial resolution of 0.1 steradians to determine the radial distribution of the activities around the well. These data also indicate large inhomogeneities, particularly near the point of introduction. Similarly, use of peak-to-compton ratios, described elsewhere,⁽²⁾ show higher concentrations of activity remote from the well than adjacent to it.

Additional profiles have been obtained from well 299-W18-175 in this same crib, and these data along with additional discussions of the observations and technique will be

FIGURE 10.8. Actinide Concentration Profiles Measured from Well 299-W18-159 in the 216-Z-1A Crib

presented in more detail in a topical report and open literature publications on the subject.

Wells 299-W18-159 and 299-W18-175 have now been profiled to an estimated accuracy of $\pm 15\%$, and these wells can be used as a

secondary calibration facility for the in situ TRU monitoring systems that cannot be calibrated in the primary Rockwell Hanford Operations 4π facility: techniques such as those utilizing neutron interrogation and detection. An important caveat for this

FIGURE 10.9. Actinide Concentration Profiles Measured with a Thin Layer, High-Resolution Collimator from Well 299-W18-159 in the 216-Z-1A Crib

secondary calibration demands consideration of the interrogation volume for the various techniques, and those techniques that interrogate a much larger range will see an average concentration which may be substantially

different from that observed by the photon technique, particularly in areas demonstrating large inhomogeneities or rapid changes in concentration as a function of depth.

REFERENCES

1. Zeisel, G. 1966. "Reaktionsquerschnitte An ^{90}Sr Für Reaktorneutronen." Acta Phys. Austr. 23:223.
2. Nielson, H. L., N. A. Wogman, and R. L. Brodzinski. 1977. "In Situ Subterranean Gamma-Ray Spectroscopy." Nucl. Instrm. Methods, 143:385.

11. DETECTION AND CHARACTERIZATION OF MOBILE
ORGANIC COMPLEXES OF FISSION PRODUCTS

J. A. Franz - Project Manager

The objective of this project is to determine the important mobile or volatile organic complexes of fission and activation products found in storage of low-level wastes in shallow-land burial facilities.

SUMMARY

Europium-152-154 (III) desorption studies with EDTA have started this quarter. Large inconsistencies in soil results have been linked to the filtration medium. A different filtering medium has been selected.

The first draft of the report summarizing the technetium soil studies is being revised.

STUDY OF MOBILITY CHARACTERISTICS OF ORGANIC
COMPLEXES - L. Y. Martin and J. A. Franz

The desorption of $^{152-154}\text{Eu}$ (III) by EDTA has been examined. A problem has neces-

sitated repeating part of the experiment. Atypical behavior was being observed not only with the experimental samples but with the control samples as well. The difficulty has been traced to the filtration medium being used. The filters were sorbing much of the europium that was in solution, causing the inconsistencies in the data. Another filtering medium has been selected, and the filtrations will be repeated.

The first draft of the report summarizing the technetium soil studies has been completed and is presently being revised.

12. WASTE MANAGEMENT SYSTEM STUDIES

J. V. Robinson - Project Manager

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

SUMMARY

Two reports based on work PNL did for the International Nuclear Fuel Cycle Evaluation Working Group 7 (INFCE WG.7) were completed. One report on waste arisings has been published, and the other, which summarizes four release consequence analyses for geologic repositories, has been cleared for publication.

The Human Affairs Research Centers completed work on six of the seven FY 1980 tasks in this program. The sixth task was completed in an earlier quarter. Activity was heaviest this quarter in assisting in the design of a public participation program toward developing a National Plan for Radioactive Waste Management and in completing a draft report regarding social science research needs in nuclear waste management.

A draft report describing an alternative disposal concept for radioactive waste referred to as near-surface geologic disposal (NSGD) was completed. The report analyzes the viability of the concept in terms of mining technology, processing technology, economics, and long-term health and safety. It concludes that, although the NSGD requires further investigation, apparently the technology exists or is mostly available for this option.

An effort is under way to provide standardized sections and methodologies for use

in future Hanford EISs. Three reports on this task were submitted to the Department of Energy Richland Operations Office (DOE-RL) for clearance.

A draft report on technical aspects of waste management, written for interested laymen, was completed and sent to DOE-RL for comments.

The second in the series Commercial Nuclear Reactors and Waste: The Current Status was published. It shows a continuing sharp decline in the declared size of the commercial LWR nuclear industry.

Analysis of the types and amounts of defense wastes (expected to go into the first commercial repositories) has been done and a draft report prepared and sent to a peer review group for comment.

The Analytical Sciences Corporation submitted a draft interim report on a study defining and characterizing waste management containment systems. This study is to provide a basis for strategy in the selection of technologies.

To support DOE Headquarters' development of a National Plan for Radioactive Waste Management, PNL was requested to perform a scoping analysis of the scenarios, questions, and issues that should be addressed by an integrated systems studies program. A draft report describing PNL's analysis was completed and sent to DOE-RL in September for clearance.

Arrangements were made to provide staff support to the Division of Management Support of the Office of Nuclear Waste Management (ONWM) in connection with a health physics seminar planned at Headquarters the week of November 17, 1980.

INTERNATIONAL NUCLEAR FUEL CYCLE EVALUATION (INFCE)

Work continued on two PNL reports based on work we did on behalf of INFCE WG.7. One report entitled Wastes from Selected Activities in Two Light-Water Reactor Fuel Cycles, PNL-3425, was published in July. The second report, Summary of Four Release Consequence Analyses for Hypothetical Nuclear Waste Repositories in Salt and Granite, PNL-3548, was cleared for publication. Two of the four analyses were done for INFCE WG.7; the other two were done for the Office of Nuclear Waste Isolation (ONWI).

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

Battelle's Human Affairs Research Centers (HARC) continued work on six of the seven tasks they are performing under the FY 1980 program. The draft report regarding social science research needs in nuclear waste management, Task 1, was completed on schedule in September. The report analyzes research needs in the areas of belief and attitude research, multiattribute decisions making, public participation, social impacts, organizational analysis, legal and regulatory analysis, and implementation analysis. Five nuclear waste programmatic areas were considered, including high-level and transuranic waste, low-level waste,

away-from-reactor storage, remedial action programs, and nuclear materials transportation.

Task 2, the waste management survey research, was not completed this quarter due to delays in the approval process. All data were collected and coded, however, and key-punching was begun before the end of the quarter. Of the approximately 2025 questionnaires sent out, about 225 were returned because residents had moved. Of the remaining 1800 questionnaires, about 1000 were returned, and of these, about 750 contained usable data. The reports for this task will be written during the first quarter of FY 1981.

The final draft for Task 3, the analysis of factors leading to the preservation of information about waste repositories, was completed in September on schedule. Task 4, the analysis of remaining technical issues in nuclear waste management, was carried out last quarter. Stan Nealey attended a workshop, along with PNL staff, to discuss remaining technical and nontechnical issues in waste management. Of the technical issues listed, ten were chosen for further analysis for this task. These issues have been discussed with the technical experts to determine whether they might surface as social issues about waste management. No report was required for this small task, although a brief memo will be prepared during the first month of FY 1981 describing the outcome of the task.

Final work on task 5, the conflict mediation task, was done this past quarter. The draft report was read by consultants and HARC internal reviewers, and comments were collected and incorporated into the final report. The final draft of this report was completed in September and sent to PNL Program Office for review.

Task 6 was completed prior to last quarter. Work on Task 7, public participation input to the waste management plan being prepared by MITRE, was performed during this past quarter. A draft and a revised draft of the public participation plan were written. In addition, a planning memo was prepared for Headquarters describing how the plan should be implemented, e.g., regarding the setting up and timing of public meetings, and the processing of comments.

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

A draft report Near Surface Geologic Disposal of Radioactive Waste - An Initial Assessment, PNL-3580, was submitted to the PNL Program Office for review in September, prior to submission to DOE-RL for clearance next quarter.

The report describes an alternative disposal concept for radioactive waste referred to as near-surface geologic disposal (NSGD). The principle is to dilute and mix the radioactive waste evenly with a host geologic material. This material would then be buried in a pit similar to a large open-pit mine, covered, and reclaimed. The basic principle of the alternative is to blend the waste with sufficient amounts of earth so that in the final backfill configuration the waste meets or exceeds all long-term health and safety criteria.

The analysis presented does not constitute a feasibility study of the NSGD system. Rather, it identifies any major factors that might preclude the option and dismiss it from further consideration. The criteria evaluated in the study included mining technology,

processing technology, economics, and long-term health and safety (radiation exposure, criticality, thermal loading).

Several radionuclide inventories were evaluated, ranging from 54,700 MTHM of high-level spent fuel to the low-level waste inventory in a representative shallow-land burial site. Calculations with various configurations of the waste were also evaluated based on differing process techniques.

The technology necessary to mine and crush large volumes of rock ($>1 \times 10^9 \text{ yd}^3$) is in place and well documented. Current proven techniques would be used for this portion of the disposal system.

Receiving and preparing the spent fuel for blending into the soil matrix is also a straightforward engineering problem. Initial studies have shown that both demonstrated and previously researched reprocessing technologies would be employed for this phase. Using these technologies, various radionuclides could be removed for separate handling and disposal, especially ^{90}Sr and ^{137}Cs .

The report discusses the economics of the NSGD system and concludes the cost of the NSGD system is comparable to the deep geologic repository alternative and cheaper than most other disposal options being considered.

The most important criteria considered in this study were the long-term health and safety concerns. It was recognized that unless the disposal option could satisfy these criteria it would definitely be precluded from additional consideration. A wide range of disposal configurations was evaluated based on blending 54,700 MTHM into $1 \times 10^9 \text{ yd}^3$ of soil material. The soil materials considered were a poorly sorptive sandstone like that in existing uranium mines and a highly sorptive volcanic tuff like that found in the Great Basin of the Southwestern United States. The resulting

(a) For background information see PNL-300-6, the prior report in this series.

dose commitments from a worst-case human intrusion scenario were calculated. These doses were compared both to the radiation standards outlined in 10 CFR 20 (Code 1977) and the doses obtained at a natural uranium ore body for the same scenario. In general, the resulting doses at 100 yr for high-level waste blended in a tuff material with ^{90}Sr and ^{137}Cs removed were less than that from a natural uranium ore body. Additionally, if uranium and plutonium were also removed, the resulting doses would be comparable to those recommended in 10 CFR 20 (Code 1977).

The direct surface radiation of the blended material was also estimated assuming a minimum of 4 ft of soil cover. The calculated dose from once-through spent fuel was again very low at 1×10^{-3} rem/yr at 100 yr. The direct radiation from the uncovered waste material (once-through spent fuel with strontium and cesium present) was higher at 13×10^4 rem/yr. If the strontium and cesium were removed before disposal, the dose would be reduced to 7.7×10^2 rem/yr. This would mean that the backfilling operation would require remotely operated equipment.

Neither criticality nor thermal loading would prove particularly troublesome for the disposal option.

In general, none of the criteria evaluated appeared to preclude the disposal option from further consideration. While the system would require additional investigation, it appears that the technology either exists or is mostly available for this alternative.

SYSTEMS ANALYSIS SUPPORT TO DOE HEAD- QUARTERS^(a) - J. V. Robinson

A draft report entitled Issues and Scenarios for Nuclear Waste Management System

Analysis, PNL-3564, which records the results of the Nuclear Waste Management Strategy Workshop held in July, was sent to DOE-RL for clearance in September.

DEFENSE WASTES AND COMMERCIAL REPOSITO- RIES^(a) - R. Burns, consultant, J. H. Jarrett and J. V. Robinson

A draft report, Radioactive Waste Repository Needs, was prepared and in September was circulated to PNL and outside experts for peer review and comment.

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

A draft report entitled Standardized Input for Hanford Environmental Impact Statements, PNL-3509, was submitted to DOE-RL for clearance in September. Two other draft computer codes developed in support of PNL-3509 were also submitted in September to DOE-RL for clearance. They are HADOC - A Computer Code for Calculation of External Inhalation Doses from Acute Radionuclide Release (PNL-3503) and ALLDOS - A Computer Program for Calculation of Radiation Dose from Airborne and Waterborne Release (PNL-3524).

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

A draft comment report entitled Understanding Nuclear Waste Management, PNL-3570, was submitted to DOE-RL for comment. Its purpose is to provide information on technical aspects of waste management, written so as to be understandable to interested laymen. During the first quarter of FY 1981, PNL will recommend to DOE-RL means for disseminating the report information to the public.

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

WASTE FROM THE COMMERCIAL POWER INDUSTRY^(a) -
A. M. Platt and J. V. Robinson

A report, the second in a series, entitled Commercial U.S. Nuclear Reactors and Waste: The Current Status (PNL-3371-2), September 1980, was published. The report shows that the 165 power reactors presently declared (operating, being built, or planned) will peak at a capacity of 153 GWe in the year 2001, requiring as few as two "standard" repositories of 100,000 MTU capacity each. It also notes that since January 1, 1975, the industry size has dropped an amount equivalent in energy loss to about 10 years of the current rate of U.S. consumption of OPEC oil.

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

The objective of this study is to define and characterize containment systems for waste management operations in order to provide a basis for strategy for selecting technologies.

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

The Analytical Sciences Corporation (TASC) continued work on their contract to define and characterize alternative containment systems for waste management operations. TASC's draft interim report, Selection of Containment Systems for Commercial High-Level Waste Management, was submitted to PNL on September 15 and was still under review at the end of September. Preliminary project results reflected in the report are that 1) packaging of waste during predisposal operations should be minimal and 2) packaging for disposal should be done at the disposal site.

A final draft comment report is due to be submitted to PNL in December 1980.

WASTE MANAGEMENT HEALTH PHYSICS WORKSHOP -
C. M. Unruh

Arrangements were being made to provide staff assistance to Dr. W. J. Rowen, Planning and Analysis Branch, Division of Management Support, ONWM, in connection with the conduct of a health physics seminar planned at Headquarters for the week of November 17, 1980. Carl Unruh, who is coordinating this effort for PNL, met with Dr. Rowen in August to complete plans for the workshop. PNL submitted a work plan on the workshop to DOE-RL in September.

13. WASTE MANAGEMENT SAFETY STUDIES

P. J. Pelto - Project Manager

The objectives of this program are to aid in ensuring that waste management and its inherent safety function are given proper emphasis as various alternative fuel cycles become viable; develop assessment methods and identify portions of waste management systems that could benefit by safety design emphasis.

SUMMARY

A state-of-the-art survey of systems safety analysis methods was completed during this quarter. A series of issue papers on various waste management safety areas has been completed.

METHODS SURVEY

The survey of the state of the art of systems safety analysis methods was completed. Information was gathered in three basic areas: 1) safety assessment methods; 2) previous studies applying these methods to waste management systems; and 3) ongoing waste management safety programs. A draft report has been prepared summarizing the safety assessment methods portion of this survey. It is planned to combine this information with the large volume of materials gathered for the latter two portions of the survey into a single summary document early in FY 1981.

Many of the studies examined in the survey dealt with the long-term (post-closure) safety implications of a waste repository.

Another area of safety interest, waste repository operational safety, has received only minimal attention. The design, construction, licensing, and operation of a waste repository requires information on such areas as industrial accidents, occupational radiation exposure, and public radiation exposure during the operational phase. These areas may merit additional safety research and development.

ISSUE PAPERS

A series of issue papers on various waste management safety areas has been completed. These papers are informal and often preliminary examinations of areas that may require additional or more detailed safety research and development. Areas examined include ¹⁴C dispersion/accumulation tradeoffs, use of cost benefit analysis in waste management, acceptable risk criteria, use of safety indices to assist in setting waste management R&D priorities, and repository operational safety research needs.

14. ASSESSMENT OF EFFECTIVENESS OF GEOLOGIC ISOLATION SYSTEMS

F. H. Dove - Project Manager

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

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

SUMMARY

A report that describes the basic components of the AEGIS program, entitled "A Short Description of the AEGIS Approach" (PNL-3398) has been cleared and printed.

Multiple model runs of the repository release scenario model were made in full Monte Carlo mode for testing and debugging purposes. A manual describing the operation of this model was completed and submitted for clearance (DOE milestone).

Work continued on the study of fracture flow in a permeable medium and on the development of geohydrologic response functions as a means of evaluating the overall performance of a repository site.

Comments were received from ONWI (Office of Nuclear Waste Isolation) and Rockwell Hanford Operations reviewers on the working papers Basalt Conceptual Model and Mathematical Modeling Plan and Basalt Repository Release Scenarios. An unscheduled working paper entitled Aquifer Recharge Calculations was drafted and reviewed internally, and the working paper Regional and Local Flow

Modeling was started. These documents and the final working paper entitled Basalt Transport Modeling will provide a reviewed basis for the draft RSIA (reference site initial assessment) report scheduled for submission to ONWI and Rockwell on December 1.

Sensitivity studies with the RECHARGE code are complete, and the regional hydrologic model is complete. A presentation on the basalt hydrologic modeling was given for technical personnel from the Basalt Waste Isolation Program (BWIP) of Rockwell on August 26.

A working draft was sent to ONWI on August 28 that presents a preliminary comparison of four salt domes for ground-water transport and radionuclide retardation capacity in the strata overlying the domes.

PROJECT MANAGEMENT - F. H. Dove

Dr. Albin Brandstetter, AEGIS Project Manager, accepted a position as Project Manager, Safety Analysis, with the Licensing Department of ONWI, effective August 1. Dr. F. Harvey Dove, previously AEGIS

Assistant Project Manager for Site Applications, was named his successor, effective June 30.

An outline of the AEGIS Technology Program Plan (TPP) for FY 1981 was sent to ONWI on August 6. Project planning included a 3-day meeting of senior AEGIS and WRIT staff and PNL line managers to develop coordinated plans for two projects. The outline reflects a common objective for AEGIS and WRIT projects: to support the ONWI program in waste package and repository design, site selection, and licensing activities by providing and applying technology to evaluate the post-closure effectiveness of geologic isolation systems. Planned programmatic changes in accordance with this objective for the coming year include:

- emphasis in research and development aspects of hydrologic modeling in the AEGIS project
- relocation of all geochemical modeling to the WRIT project
- orientation of the release scenario model towards site applications in the AEGIS project
- development of repository release modeling in the WRIT project.

In addition to the traditional leach and sorption values, AEGIS will be dependent upon WRIT to provide geochemical support and repository release models for reference site initial assessments. Likewise, WRIT will be dependent upon AEGIS to provide hydrologic support and scenario translation for repository release modeling. The outline of the AEGIS TPP was discussed at ONWI on September 8. Both the work breakdown structure and the estimated costs were reviewed; as a result, however, of reduced funding for ONWI, the project funding level for FY 1981 was unresolved. Preparation of the final

TPP document is currently in progress and will be completed next quarter.

Corrective actions in response to the initial quality assurance (QA) audit conducted in May included a training session on the maintenance of QA records. Revision of quality assurance procedures AEGIS-1, entitled "Hand Calculations," and AEGIS-2, entitled "Development, Documentation, and Application of Computer Codes," was completed and approved. Revision of the AEGIS Quality Assurance Plan, PGM-2, continued, and a new procedure to standardize the DELPHI or expert opinion process for the development of release scenarios (AEGIS-3) will be prepared in FY 1981.

Information supplied by ONWI to date on the Environmental Protection Agency (EPA) risk assessment code was evaluated. A report was drafted and transmitted to ONWI assessing the adequacy of the available information and the need for additional information, and recommending detailed evaluations for a careful and defensible critique of the code, its assumptions, and its use in developing the proposed EPA criteria for waste isolation. A meeting in Washington, DC, on the emergency EPA radiation protection standards for waste repositories was attended by Dr. M. A. Harwell, an AEGIS consultant, and other representatives from ONWI, DOE (Department of Energy), and NRC (Nuclear Regulatory Commission). The methodology used in deriving the draft standards was discussed. It became clear to those attending the meeting that a detailed critique of the EPA standards derivation cannot be adequately made by AEGIS staff and consultants until the current EPA methodology documentation and EIS are available.

At the request of DOE/NV, Dr. Dove participated in an ONWI programmatic review of

radionuclide migration studies proposed by the Lawrence Livermore Laboratory and by the team of Los Alamos Scientific Laboratory, Sandia National Laboratories, and Argonne National Laboratories. The in situ experiments are to be performed at the Nevada Test Site in fractured granite and fractured tuff. AEGIS computer models will be used to predict the experimental results provided that the FY 1981 priorities for these calculations have ONWI concurrence.

The BWIP Site Characterization Plan (RHO-BWI-CD-51 Rev) was reviewed, and comments were forwarded to DOE/RL.

A written review of LBL-10500 (draft copy), Migration of Radionuclides Through Sorbing Media, Analytical Solution I by M. Harada et al., was completed and transmitted to ONWI on September 30. The review was requested by Dr. H. C. Burkholder and was conducted on a time-available basis by Dr. C. S. Simmons of the AEGIS staff.

In the fourth quarter, twelve reports, journal publications, and speeches were submitted for clearance. Nine reports, journal articles, and speeches were cleared, and seven reports were printed. Completion of DOE Milestone No. 9 was achieved with the submission of PNL-3542, Simulation Model for Release Scenario Analysis: A Hypothetical Site in Basalts of the Columbia Plateau. All nine DOE milestones for AEGIS in FY 1980 have been completed as scheduled.

METHODOLOGY DEVELOPMENT - D. J. Silveira
M. G. Foley, R. W. Nelson, and J. K. Soldat

Issues Analysis - D. J. Silveira

A Short Description of the AEGIS Approach (PNL-3398) was cleared and printed. A report (PNL-3414) was also prepared that discusses the potential influence of organic compounds

on the transport of radionuclides by ground water.

A technique for estimating the rate of change of porosity of an aquifer due to calcite precipitation has been formally established for input to the release scenario model. It has been shown that under the existing environmental conditions for the Pasco Basin aquifer, plugging due to calcite precipitation has no significant impact on porosity for a million-year time frame. Additional chemical plugging processes, however, such as clay formation, may be important in the flow through the regional aquifer systems.

Representative ground-water compositions have been compiled for several types of geologic media (basalt, granite, tuff, and bedded dome salt) under consideration as host rocks for a waste repository. This work was done to determine the amount of data available and to provide guidance for leaching and corrosion studies. These ground-water compositions were also used together with thermodynamic data to determine concentration limits due to solubility constraints on the elements uranium, plutonium, americium, neptunium, technetium, europium, and thorium.

Scenario Methodology Development

The logic for all submodels in the repository release scenario model was finalized, and all input variables were identified. Work continued on the statistical package and linkage of the submodels into the complete model. Test data were generated and entered into the computer. Multiple model runs were made in full Monte Carlo mode and are ready for testing and debugging.

A literature search was completed evaluating the resource potential of the Pasco

Basin. This information will be used to evaluate the potential for human disruption of a repository in basalt.

Transport Methodology Development

Research into uncertainty transport analysis indicated that the convective equation with uncertainty variations on the velocity parameter is the acceptable description of mass transport in a permeable medium. To permit use of this description, the velocity field and its variance must be determined. The individual parts, however, of the velocity--i.e., hydraulic conductivity, gradient of potential, effective porosity--and the variance of each of these variables are the only data generally available. This raises the problem of combining the individual means and variances so as to obtain the overall pore velocity mean and variance. Work is under way using geostatistically determined covariance components to obtain the combined pore velocity results.

The work on fracture flow in a permeable medium is continuing. An initial document (PNL-3547) has been completed containing the mathematics of fracture flow. The report contains the detailed mathematical description of viscous flow inside the fracture and of porous flow in the surrounding permeable material.

The main conclusion deduced from this program's research at PNL in FY 1980 is that a considerable restructuring of present transport analysis stochastically incorporating the velocity variation is required in order to properly describe dispersion effects over an entire ground-water system. Present results also indicate that selection between proposed analytical methods can be made only from application and testing with field-measured data sets.

Work continued on the development of geohydrologic response functions for evaluating overall performance of a repository site.

Next quarter, Methodology Development will be divided into two tasks: 1) Flow Methodology Development, which includes the current study of flow in porous materials and development of analytical capability for fracture systems, and 2) Transport Methodology Development, which includes geostatistical methods for studying flow and transport data, contaminant transport with uncertainty, dispersive effects analysis for columns, and field experimental data and geohydrologic response functions.

SITE APPLICATIONS - F. H. Dove, J. T. Zellmer, C. R. Cole, and J. K. Soldat

Salt Dome RSIA

The determination of radioisotopes in a repository over a one-million-year time period using the ORIGEN code is complete. The calculations considered both spent fuel and reprocessed high-level waste (HLW) inventories.

Reviewers' comments to PNL-2955 were further considered in the context of potential changes in the report before its issuance as a final document. Additional HLW calculations will not be included in the final report but will be the subject of a separate white paper in FY 1981.

Basalt RSIA

Comments have been received from ONWI and BWIP reviewers of the working papers Basalt Conceptual Model and Mathematical Plan and Basalt Repository Release Scenarios. An unscheduled working paper entitled Aquifer Recharge Calculations has been drafted and

reviewed internally, and the working paper Regional and Local Flow Modeling has been started. These documents and the final working paper Basalt Transport Modeling will provide a reviewed basis for the draft RSIA report scheduled for submission to ONWI and BWIP on December 1.

Sensitivity studies with the RECHARGE code are complete. The regional hydrologic model also is complete.

A presentation on the basalt hydrologic modeling to technical personnel from BWIP occurred August 26. The regional recharge calculations were presented in detail, and the regional and local hydrologic models were described from basic concepts through current status. The technical interchange was constructive.

The initial node map for the three-dimensional hydrologic model of Pasco Basin has been prepared. The map is based upon model boundaries selected for the local hydrologic system and includes consideration of the topography, unconfined water-table map, and two basalt structure maps.

The node maps for the local or Pasco Basin hydrologic model have been completed, and the computer subroutine to generate well logs has been completed and checked. All structure, potentiometric, and transmissivity maps for the Pasco Basin have been completed, and most of them have been digitized. A computer subroutine is being prepared to set elemental conductivities according to the transmissivity maps and structure maps.

Stratigraphic surface maps now in final form include Top of Saddle Mountain Basalt,

Top of the Grande Ronde Basalt, Top of the Wanapum Basalt (nearly complete). Potentiometric matrices now in the final form include Alluvial-Ringold composite and Saddle Mountains composite. Transmissivity maps (or matrices) now in final form include Saddle Mountain Basalt and Wanapum Basalt.

Stratigraphic, potential and transmissivity (thickness and hydraulic conductivity) distribution maps digitized in August are being checked. The repository release model and the selection of sorption coefficients for the transport simulation of radionuclides have been completed by staff of the WRIT project.

A first draft revision of the fourth working paper for the basalt RSIA, Regional and Local Flow Modeling, will be available for review in October.

The preparation of test data for the release scenario model as applied to the basalt RSIA is almost complete. The data include input variable requirements obtained from consultants and from AEGIS staff.

Salt Dome Site Evaluation

A working draft presenting a preliminary comparison of four salt domes for groundwater transport and radionuclide retardation capacity in the strata overlying the domes was sent to ONWI on August 28.

Next quarter, Site Applications will be divided into four tasks: 2) Scenario Analysis, 2) Hydrogeologic Analysis, 3) Transport Analysis, and 4) Dose Analysis.

15. WASTE/ROCK INTERACTIONS TECHNOLOGY

R. J. Serne - Project Manager

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

- 1. identify and 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. collect data, develop and evaluate the effectiveness (develop a perspective on applications/limitations of each model) of models that predict leaching, sorption, and release processes in the repository and surrounding media*
- 3. obtain, through verification studies and documentation, the most acceptable test methodologies for sorption, leaching, solubility limitations, and waste package-geomedia interaction studies*
- 4. support repository site characterization and licensing specifically through data generation analysis, and predictive model formulation*
- 5. support waste package design via waste package systems performance testing.*

SUMMARY

A workshop was held July 14-15 in Seattle to help the WRIT program assess its current status, rank future needs, and develop FY 1981 work plans.

Further efforts to quantify the sputter rate for 76-68 waste glass, needed to interpret elemental depth profiles, showed that sputter rates for the surface leached zone were about twice as fast as for the bulk glass.

Several series of waste-package interaction tests were conducted, and it was found that for some elements (such as cesium) granite and basalt markedly suppressed release to the solution. Experiments showed that possible geologic-repository anoxic conditions capable of supporting sulfides can immobilize TcO_4^- , presumably by reduction to TcO_2 . If sulfide minerals can be formed, they will be a relatively stable sink for technetium. Analyses using

Westerly granite have shown that the effective porosity of a rock column under flow conditions is not always the same as that measured by static methods.

Modeling efforts have developed a source term for a specific breach scenario, in a basalt environment, as support of licensing methodology demonstration.

PROGRAM MANAGEMENT - R. J. Serne

A workshop was held July 14-15 in Seattle to assess the current status of the WRIT program, prioritize future needs and develop specific work plans for FY 1981. It was attended by WRIT staff, Office of Nuclear Waste Isolation (ONWI) program managers, and principal investigators from each of the WRIT subcontractors. WRIT staff participated in several interactions with DOE waste management programs:

- The program on hydrothermal interactions at Pennsylvania State University (PSU) and PNL was reviewed.

- Work on spent fuel at Los Alamos Scientific Laboratory (LASL) and PNL was discussed.
- The MCC Workshop on Irradiation Effects on Nuclear Waste Forms, held in Seattle July 29-30, was attended.
- Peer review support was provided by WRIT during a meeting at Las Vegas August 18-19 discussing two field radionuclide migration experiments.
- A Nuclear Waste Technology Program Office informational meeting on alternative waste forms was attended.
- A draft Technical Program Plan (TPP) for FY 1981 work was prepared.

P. R. Partch joined WRIT in September as a full-time administrative assistant. She has worked out the remaining details of the quality assurance plan and is proceeding on its implementation.

WASTE-PACKAGE INTERACTIONS - NUCLIDE RELEASE STUDIES - D. J. Bradley

Waste Form-Solution Interactions

A technique for determining surface alpha emitter spectra versus depth has been used at Argonne National Laboratory (ANL) to measure alpha spectra from leached actinide doped glass. Alpha spectra have been obtained for PNL 76-68 glass beads containing ^{239}Pu and ^{237}Np and for similar beads that have been leached by anoxic water at 75°C for 2, 8, 16, 32, 106, and 341 days.

The very low leach rates of neptunium and plutonium and their dramatic declines with time of leaching is explained by the evidence for selective leaching of nonradioactive material and by its deposition as a coating on the simulated waste-glass surface. The plots for 106- and 341-day leached glass surfaces show that a layer of nonradioactive

material has formed between the concentrated radioactivity and the glass-liquid interface.

Waste-Package Interactions

Digestion Bomb Tests

A second series of waste package tests was completed in 125-ml digestion bombs using the same components as the first series of tests. The second series of salt packages was conducted at 150°C for 6 wk instead of 250°C for 4 wk. The second series of granite and basalt packages was conducted at 150°C for 4 wk.

The solution compositions from the salt packages were generally similar to the 250°C tests, suggesting that if a temperature effect occurs the longer test period compensates for it. Magnesium and boron were higher at 250°C than at 150°C, but cesium and strontium were about the same. Zinc concentrations were higher at 150°C than at 250°C, which suggests an analytical error. Table 15.1 summarizes some of these data.

The solution compositions from the granite and basalt packages showed trends similar to those of previous tests. The temperature effect of silica release seems to be greater for basalt than granite, but was about equal for boron release. Sodium and potassium seem to be only slightly affected by these two temperatures.

A polished cross section of the canister from the granite package test was examined by scanning electron microscopy (SEM) near the vertical slit simulating a rupture. A slight migration of uranium was observed from the glass into glass fracture regions and also in the rock powder next to the glass. Uranium was below detection limits in the solution.

TABLE 15.1. Solution Compositions from Salt Package Digestion Bomb Tests

Element	4 wk. at 250°C, μg/ml	6 wk. at 150°C, μg/ml
Mg	4048	2940
Cs	16	22
Sr	13	11
B	74	59
Mo	2	10
Zn	30	56

Direct Sampling Autoclave Tests

The final series of FY 1980 direct-sample autoclave tests (Series III) was completed in September, and the components are being analyzed. This series consisted of three tests using 1) a single minicanister and deionized water, 2) a granite package with granite-equilibrated water, and 3) a basalt package with basalt-equilibrated water. This test series was run with the packages submerged in the liquid, but the minicanister was not completely packed with crushed rock material and the open end was exposed directly to the liquid. The tests were run at 250°C, 2000 psig with argon overpressure for 8 wk, and the solutions were sampled periodically for both cation and anion analysis. One objective of this test was to obtain samples for study of corrosion effects at the glass-canister interface. In general, the same trends observed in previous package tests for cation concentrations are present. Some of the solution concentrations for samples collected at 5 wk are reported in Table 15.2.

Joint PNL-Sandia Package Tests

All components have been assembled for the joint PNL-Sandia 5-gal waste package systems

test. The test is scheduled to begin in the second week of October 1980. Some difficulty was experienced in preparing the UO₂-doped 76-68 glass semicylindrical canister. Thermal gradients resulted in partial cracking of the glass monolith at one end, but otherwise the monolith appeared satisfactory. Because some cracks will probably be present in real canisters, it was decided to use this half cylinder in the test. Another canister is currently being prepared for the second test.

Continuous Flow Test

All equipment, samples, and rocks were received during this reporting period. The assembly of the experimental enclosure, pump shelves, electrical wiring, and water manifolds were completed. The rock material was ground and sieved; the fraction 2.4 to 4.8 mm in size was placed into cleaned leach cells; and assembly of the experiment was begun.

TRU Leaching Studies

Modified IAEA leaching of portland cement, urea-formaldehyde and polyester-styrene waste forms in the five leachant solutions is ongoing along with static (25°C) leach testing of these waste forms. Static (25°C) leaching of urea-formaldehyde has been conducted with only the deionized water leachant since earlier data suggested a relatively rapid rate of plutonium release as compared to other waste forms. Static (70°C) leaching was started for portland cement and polyester-styrene waste forms in deionized water. Additional sets of portland cement and polyester-styrene waste forms were prepared for static (70°C) leaching in the remaining solutions.

TABLE 15.2. Solution Compositions of Series III Direct-Sample Autoclave Tests at Start of Run and After 5 Weeks, 250°C/2000 psi, µg/ml

Element	At P and T			5 Wk		
	Canister Only	Granite Pkg	Basalt Pkg	Canister Only	Granite Pkg	Basalt Pkg
Si	1.60	5.80	15.5	61.00	57.00	108.00
B	0.36	0.30	0.45	26.70	26.50	22.70
Mo	0.56	0.30	0.14	16.80	8.80	11.70
Cs	0.03	0.04	0.05	3.40	3.00	0.74
Na	1.92	3.17	3.78	58.30	49.30	45.10
K	0.21	4.03	1.94	0.29	4.06	6.26
Ca	0.29	0.77	0.59	0.06	0.09	0.03
pH				9.70	9.20	9.10

Surface Science Studies

Efforts were directed toward drawing more quantitative information from the results of ESCA (electron spectroscopy for chemical analysis) of leached 76-68 glass. Sputter-rate calibrations were performed on both leached and unleached specimens to obtain absolute depth scales for the sputter profiles. Elemental releases were calculated from the depth profiles and were compared to those obtained by inductively coupled plasma (ICP) solution analyses.

To produce a significant reaction layer for sputter calibration measurements, one group of polished 76-68 glass samples was leached for 14 days at 90°C in deionized water (DI), and another polished set was left unleached. These samples were then ion-milled with 5 keV argon ions rastered at $1 \times 1 \text{ mm}^2$ for various times followed by crater depth measurements using a surface profilometer. The sputtering rate in the leached zone of 76-68 glass was determined to be significantly different from that of bulk glass, while the measured rate in bulk glass was indistinguishable from that of SiO_2 . For the particular ion beam set-

tings used, the sputter rate of the first 1-3 µm of the reacted glass was $215 \pm 13 \text{ Å/min}$, that of bulk glass was $97 \pm 6 \text{ Å/min}$, and that of SiO_2 was $98 \pm 3 \text{ Å/min}$. Thus the sputtering rate in the leached zone was 2.2 ± 0.3 times greater than that of bulk glass.

The fastest sputter rates correlate to the region in which sodium has been depleted to its minimum concentration. Also depleted in the sodium-poor region were silicon, oxygen, calcium and molybdenum. In contrast, iron, zinc, titanium, nickel, zirconium, neodymium, and cerium were increased in the region. As the sodium concentration rose to that of the bulk glass, the sputter rate became consistent with that measured for bulk 76-68 glass.

From the integrated levels of depletion or increase of a particular element as compared to that measured for bulk glass, with corrections included for variations in the sputtering rate, elemental releases or buildups can be estimated from the ESCA depth profiles. The results of such calculations are shown in Figure 15.1 for 76-68 glass leached at 50°C in DI water. Actual releases for the same samples as measured by ICP analyses are given in Figure 15.2.

FIGURE 15.1. Normalized Elemental Release as Calculated from the ESCA Depth Profiles

FIGURE 15.2. Normalized Elemental Release from 76-68 Glass Leached at 50°C in DI Water as a Function of Leaching Time. Release values were determined by ICP solution analysis.

The magnitudes of the releases calculated from the ESCA results are considerably smaller than those determined directly by solution analysis for sodium, silicon, and calcium. Roughly one-third of the sodium release and roughly one-fourth of the silicon and calcium releases can be accounted for by the ESCA depth profiles. It must be concluded that under the experimental condition employed, 76-68 glass releases material into solution mainly by matrix dissolution rather than by selective element leaching. ESCA results are sensitive only

to releases (or buildup) that are in excess of that which occurs for the average matrix. Thus the differences between sodium and silicon (and calcium) releases in the ICP data of Figure 15.2 should about equal the differences determined by the ESCA analyses of Figure 15.1, as is the case.

In contrast to the results for 76-68 glass, similar measurements made on 79-150 glass, an aluminoborosilicate, resulted in relatively good agreement between ICP and ESCA analyses. Also of interest is the fact that aluminum builds up on the surface at

the same normalized rate that silicon, the main component, is released. (Titanium does not show this behavior.) It must be concluded that, at 90°C in DI water, 79-150 glass corrodes chiefly by leaching of selective elements. Matrix dissolution does not appear to be important.

The techniques of x-ray photoemission spectroscopy (XPS) and ion beam scattering (IBS) at ANL have been used to study the effects of leaching on several complex silicate glasses containing dissolved UO_3 , including PNL simulated waste glasses 76-68, 3008 and 76-101. Samples of 76-68, 3008 and 76-101 obtained from PNL were powdered, mixed with 1 mole % UO_2 powder, and remelted. The XPS and IBS spectra show pronounced effects on leaching and complement each other with respect to sample analysis depth information. With increasing glass complexity only the more prominent peaks are noted; however, similar behavior of common elements across the three glasses, especially uranium, was noted and is encouraging.

Spent Fuel Special Studies

A major goal of this work element has been to determine the mechanisms and kinetics of spent fuel leaching. This information is important for predicting long-term stability of spent fuel in geologic repository conditions via mathematical models. The complex structural, microstructural, compositional and thermal characteristics of spent fuel plus the lack of radiation-shielded analytical tools have necessitated a simpler systematic approach. This was achieved by using single-crystal UO_2 for the initial experiments, as being representative of the spent fuel matrix. Experiments for UO_2 oxidation and dissolution mechanism studies were designed to accommodate ready experimental

verification with spent fuel. It is necessary to determine the suitability of UO_2 behavior as a spent fuel stand-in before funds are expended in measuring detailed kinetics data on UO_2 leaching. The process report of the year's activities on UO_2 experimentation has been written and submitted for publication clearance.

The probable oxidation and dissolution mechanisms for single-crystal UO_2 surfaces, based on combined electrochemical and static dissolution tests, can be summarized as follows: A clean UO_2 surface exposed to solutions containing oxygen or other oxidizing chemical species will be rapidly oxidized. The initial surface oxidation may be in the form of:

The oxidized surface combined with the dissolved oxygen will rapidly dissolve to form uranyl ions or complex ions, depending on the solution chemistry.⁽¹⁾ For deionized water, the reaction will be

The dissolution of the UO_2 surface is strongly dependent on the available oxygen and the pH value. The dissolved uranyl ions or complex ions will then be hydrolyzed to form UO_3 hydrates or its complex compounds.⁽²⁾

Since both the dissolution of UO_2 surface and hydrolysis of UO_2^{+2} ions favor high temperatures, the oxidation and dissolution of UO_2 surfaces in oxidizing solutions may be considered as a phase transformation from the bulk UO_2 form into UO_3 hydrates as coatings and particle suspensions while the solution maintains a fixed amount of dissolved UO_2^{+2} ions. The UO_3 hydrate coatings will have some passivating effect to reduce the

dissolution rate, such as in the case of the brine solution. As the film thickness grows, however, it tends to crack and spall from the surface. The instability of the surface film and its tendency to crack and spall will create a major problem for investigating the long-term leaching behaviors for UO_2 and spent fuel.

The electrochemical experimental equipment was moved from the 231-Z Building to the 324 Building to make electrochemical leaching measurements on spent fuel. Electrical contact in the electrochemical cell was made by clamping the spent-fuel sample between the tips of a passivated titanium tweezer. Blank tests have shown that the titanium tweezer holding the single-crystal UO_2 sample gives experimental results similar to those where the electrical contact is made with a copper wire cemented with conducting epoxy. During the electrochemical tests, the solution was not stirred or deoxygenated.

Measurements of the open-circuit potential values (E_0) obtained from single-crystal UO_2 surfaces to the E_0 values of the spent fuel in the same solution were nearly 0.5 V higher. The high E_0 for as-received spent-fuel fragments may be due to the oxidation of the surface during the 3 yr of storage in an uncooled container of fuel. After 1 hr of accelerated leaching at a potential nearly 0.5 V above E_0 , there was no increase in the E_0 value, indicating that the surface was heavily oxidized. An attempt was made to polish the spent-fuel surface with 600-grit paper; however, only about one-fourth of the surface area became shiny, indicating a polished surface. This polished surface gave a much lower E_0 value, but not as low as the UO_2 case. We concluded that the spent-fuel surface was covered with oxides or hydrates in the as-received stored conditions.

The preliminary data from electrochemical leaching of spent fuel indicate that the initial leaching and dissolution of spent fuel matrix material was similar to that of the UO_2 surface. Further experiments are needed to correlate the electrochemical methods to the standard spent-fuel leach tests for better understanding of the dissolution and leaching kinetics and mechanisms of spent fuel. The electrochemical methods require further improvements in instrumentation and work procedure. However, the potential for the electrochemical methods may be realized by their demonstrated rapid response and the kinds of information obtainable during the leach tests.

GEOLOGIC MEDIA-NUCLIDE INTERACTION -

J. F. Relyea

Evaluation of Experimental Methodology

Analyses of tritium spikes passing through columns of crushed Westerly granite at PNL have shown that the effective porosity of a column under flow conditions is not always the same as the porosity measured by static methods. Porosity measurements made with noninteracting solutes such as tritium, iodide or chloride tracers are often used to characterize columns of soil, sand, crushed rock and intact rock cores. A small volume of tracer, the spike, is eluted through the column, and the volume needed to obtain the peak concentration is taken as the pore or void volume. Table 15.3 shows the ratios of dynamically determined pore volumes to static volumes for three such columns at several flow rates. Dynamic pore volumes tend to decrease with increasing flow rate, which indicates that the effective porosity of a porous media also decreases as the average

TABLE 15.3. Ratio of Dynamic to Static Pore Volume For Three Westerly Granite Columns (Crushed Rock)

Flow Rate, m/yr	(Dynamic Pore Volume)/ (Static Pore Volume)		
	Column		
	A	B	C
102	0.87-0.96	-	-
133	-	-	0.96-0.98
204	0.87-0.93	0.80-0.88	-
408	-	0.72-0.86	-
533	-	-	0.96-0.98
1330	-	-	0.92-0.94
2670	-	-	0.90-0.92

water velocity increases. Investigators at LLL have also observed differences between static and dynamic pore volumes using intact sandstone cores. In the sandstones, however, dynamic porosities were on the order of one-half to one-fourth of the static porosities. This, of course, directly affects the modeling of radionuclide migration in porous media. The effective porosity and effective surface area available for radionuclide retardation are reduced compared to those parameters commonly measured in the laboratory by static methods. Thus radionuclide breakthrough can occur much earlier than predicted by static experiments.

Results from laboratory column experiments should include information about the flow rate and static and dynamic porosities. Static porosities at PNL have been determined using the relationship

$$\epsilon = 1 - \frac{\rho_b}{\rho_p}$$

where ϵ is the porosity, ρ_b is the bulk density of the rock, and ρ_p is the rock particle density. For consolidated material or intact rock cores the method used at LASL may be simpler for intact cores. A solution containing a noninteracting tracer of known concentration (such as ^3H or ^{36}Cl) is used

to fill an evacuated core. The tracer is then eluted and analyzed. Because the total tracer activity is proportional to the original solution volume, the porosity of the core can then be found.

Intact core studies at LASL with strontium on tuff have shown that results from columns of crushed rock and intact rock cores may agree better with each other than the results of either one with the corresponding batch experiments. However, the batch tests do not always yield higher sorption values than do column tests with crushed rock. Several "peakless" elutions have been observed by LASL researchers, mostly with cesium. A sorption K_d calculated using the volume in which 50% of the total cumulative activity is eluted usually yields a column K_d which is larger than the batch K_d values. The very slow "peakless" elution indicates that some mechanism other than simple sorption-desorption is responsible for radionuclide retardation, possibly the formation of a cesium mineral from products released by alteration of fresh rock surfaces.

In an effort to determine the reason for differences often observed between batch and column sorption tests, researchers at LASL have begun a hybrid batch/column test consisting of columns of crushed rock through

which spiked ground water can be recirculated (instead of a once-through column test). A blank is also being run (without rock) to determine the sorptive characteristics of the pump, tubing, and column holder.

Mechanism Studies

Sorption studies with altered basalt and some of the secondary minerals found in basalt are being conducted at Rockwell with a different ground-water type than that used previously (pH ~10 compared to ~8 previously and F^- $\sim 10^{-3}M$ in new formulation). Neptunium sorption is still found to decrease with increasing neptunium solution concentration, and precipitation of neptunium is indicated in experiments with the secondary minerals (between 10^{-6} and $10^{-5}M$ Np). Neptunium precipitation was not observed, however, in the experiments with altered basalt up to about $2 \times 10^{-5}M$ neptunium. Americium was also found to be more soluble in the new ground water than in the previous lower pH solution, and sorption of americium on both materials was relatively constant: K_d ~500 ml/g on secondary minerals from $10^{-12}M$ to $10^{-10}M$ Am and K_d ~100 on altered basalt from $12^{-12}M$ to $10^{-9}M$ Am. Precipitation of strontium is indicated by an increasing K_d layered basalt over the range of $10^{-9}M$ to $10^{-6}M$ Sr in solution.

Uranium sorption studies on montmorillonite and powdered SiO_2 at LBL have shown that ion exchange is likely to be the adsorption mechanism at pH = 5.0. K_d values tend to decrease with increasing NaCl concentration and increase with decreasing uranium concentrations. At higher pH values (pH = 7.0 and 9.0) these trends are no longer consistently observed. In fact, K_d values for uranium at the higher pH tend to increase with increasing NaCl and uranium concentrations, a

complete reversal of behavior at pH 5.0. Comparisons with the geochemical-sorption model MINEQL predictions are reported under "Methodology Application Studies."

At Oak Ridge National Laboratory (ORNL) the nonideal behavior of mixed mineral sorbents Al_2O_3 -Illite was investigated. Analysis of solutions equilibrated with Al_2O_3 reveals about $10^{-4}M$ Al(III) in solution, which apparently occupied many of the sorption sites on illite and reduced strontium K_d values. Again the chemical composition of the ground water is a major factor in determining sorption K_d values and retardation coefficients and should not be overlooked in the laboratory or in the field.

In studies of europium sorption on illite at ORNL, ion exchange is the retardation mechanism responsible for lowering europium concentrations at pH values <7.0. It should be noted that these experiments were carried out at tracer levels below those expected to precipitate $Eu(OH)_3$.

The migration of americium through intact and crushed basalt was investigated at ANL. Ground water was spiked to provide a solution of $\sim 10^{-10}M$ Am at pH = 8.0. The americium concentration was found to vary with time, and after 21 days the americium concentration was about $5 \times 10^{-11}M$. The solution was pumped through a column of crushed basalt at a rate of 250 m/yr, and the americium concentration was found to level off at around 40% after 130 pore volumes had passed through the column. Subsequent filtration of the eluted solution showed that about 80% of the americium in solution after passing through the column could be filtered out by a 0.015- μm filter. More filtration experiments showed that significant amounts of the americium could be removed from the ground-water feed solution. It appears that the column acted as a filter to remove the americium.

particulates (~60%) $>0.4\ \mu\text{m}$ in size and the rest passed through. The nature of the americium particulates is unknown at present; they may be americium hydroxide precipitates or americium adsorbed onto other particles formed in the ground water. They were certainly formed or introduced to solution after addition of americium to the ground water, because it was prefiltered through another $0.4\text{-}\mu\text{m}$ filter after the addition of americium.

Site-Specific Data Generation

No work is reported this period.

Methodology Application Studies

As mentioned previously, uranium sorption work at LBL is being used as an experimental check for the predictions of a geochemical-sorption model, MINEQL. Similar experiments were conducted to determine the sorption of cesium on powdered SiO_2 . Previous sorption results for cesium on montmorillonite agreed very well with the model predictions. Because the model worked so well for cesium on the clay, an attempt was also made this quarter to model uranium sorption on the clay. Preliminary results, assuming sorption of only the UO_2^{+2} species, predict much higher final uranium concentrations than were observed experimentally in neutral and higher pH solutions. These results indicate that adsorption of more complex species than UO_2^{+2} must be considered as well as the possibility of solid precipitates other than the simple $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$. It is hoped that experience gained from the modeling of uranium behavior under environmental conditions can be used to develop the techniques needed for predicting the behavior of other multivalent radionu-

clides for which very little or no thermodynamic data now exist.

Isotope Generation

The last shipment of ^{237}Pu was shipped to those WRIT subcontractors expressing a need for it. The last shipment of $^{95\text{m}}\text{Tc}$ will be sent in late September or early October 1980. Because of reduced funding and the resulting loss of several subcontractors on WRIT Task 3, no generation of special isotopes will be possible in FY 1981.

NUCLIDE SOLUTION CHEMISTRY - D. Rai

Ground-Water Chemistry

The main objective of this subtask is to determine or predict the ground-water compositions expected at potential repository sites. Work in this microtask was transferred to AEGIS earlier this year.

Nuclide Solution Chemistry

The influence of $\text{S}^=$ and Fe^{2+} on the loss of $^{99}\text{TcO}_4^-$ from solution was investigated using both brine (WIPP formula without $\text{Fe}_2(\text{SO}_4)_3$) and demineralized water, each containing varying concentrations of Na_2S and FeSO_4^- , and adjusted to specific pH values. After a designated period, the solutions were filtered through $0.22\text{-}\mu\text{m}$ membrane filters, and the $^{99}\text{TcO}_4^-$ remaining in solution was determined by liquid-scintillation counting. In the water solutions containing both Fe^{2+} and $\text{S}^=$, a black precipitate was observed. Within 24 hr of equilibration the black precipitate had turned brown. Brine solution containing both Fe^{2+} and $\text{S}^=$ took about 3 days for such changes. These changes reflect

changes in the types of iron solids. In the demineralized water system the loss of TcO_4^- with increasing initial amounts of Fe^{2+} is evident (Table 15.4). The relationship of TcO_4^- to the $\text{S}^{=}$ concentration is not as obvious and will require further study. The results from the brine solutions indicate that 1) the sulfide alone can remove TcO_4^- from solution; 2) the iron (II) can remove TcO_4^- more efficiently than the sulfide can under the same pH conditions; 3) the removal of TcO_4^- by iron (II) is pH-dependent; and 4) the loss of TcO_4^- from solution was greater after 3 days equilibration than 5 days equilibration, possibly caused by coprecipitation with the amorphous FeS .

The experimental results have two significant implications. First the anoxic conditions of a deep geologic repository that can support sulfides (H_2S , HS^- , $\text{S}^{=}$ or iron (II) species (Fe^{2+} , $\text{Fe}(\text{OH})^+$) can immobilize TcO_4^- presumably by reduction to insoluble TcO_2 . There may be a pH dependence on such reactions, however, such that solutions with $\text{pH} > 7$ may be required. Second, if geologic conditions permit formation of the sulfide minerals that incorporate the technetium,

the relatively insoluble iron sulfide minerals will be a stable sink for technetium.

Solubilities of Compounds

Laboratory studies on the dissolution of ($^{243}\text{Am}/^{233}\text{U}$)-doped glass beads were initiated. The experimental techniques are similar to those described earlier except that the americium/uranium studies were conducted under unbuffered oxic conditions. Samplings of the various solutions indicate that from pH 3 to pH 8, americium concentrations range from $5 \times 10^{-8}\text{M}$ to $7 \times 10^{-10}\text{M}$ and uranium concentrations range from $1 \times 10^{-5}\text{M}$ to $5 \times 10^{-8}\text{M}$. Oxidation-state analysis indicates that U(VI) and Am(III) are the dominant oxidation states, as expected. Further study is needed to determine the degree of carbonate complexing, especially with U(VI). Previous alpha counting of samples was done on surface barrier detectors, but liquid-scintillation counting is being implemented because of the large number of samples.

Because literature data suggest that the specific activity of plutonium oxide may be important in controlling plutonium solubility and that the solubilities of oxides of different plutonium isotopes may differ, solubility experiments were performed on $^{238}\text{PuO}_2$, $^{240}\text{PuO}_2$, and $^{242}\text{PuO}_2$ in addition to continuing studies of $^{239}\text{PuO}_2$ solubility. Rai, Strickert and Ryan⁽³⁾ have shown that alpha radiolysis produces nitric acid from dissolved air in solution and that the rate of nitric acid production is approximately proportional to the hydrogen ion concentration.

In the current experiments, the different plutonium oxides were suspended in quinhydrone-buffered solutions adjusted to a pH range of 3 to 8. Preliminary results show that the solubility lines are similar to

TABLE 15.4. Percent 99Tc Activity(a)
Remaining in Demineralized Water Containing
Various Amounts of Sulfide and Ferrous Iron
After 1 Day of Equilibration

Initial Sulfide Concentration, $\mu\text{g/ml}$	Initial Fe(II) Concentration, $\mu\text{g/ml}$ (b)			
	0	6	24	48
0	100	100	69	47
6	99	99	77	37
24	99	98	56	20
48	98	96	92	29

(a) Starting 99Tc concentration 10^{-5}M .

Starting pH = 9.5 ± 0.5 .

(b) $1 \mu\text{g/ml} = 1.7 \times 10^{-5}\text{M}$.

that previously reported⁽⁴⁾ for $\text{PuO}_2(\text{c})$ except for $^{238}\text{PuO}_2$, which followed a solubility line about two orders of magnitude higher [around the solubility of $\text{Pu}(\text{OH})_4$]. Phase changes due to alpha radiolysis of the 88-yr half-life plutonium isotope may be the cause. Experimental monitoring of solution parameters is continuing.

Continuing studies of NpO_2 solubility have shown that the concentration relationship does not follow what would be predicted from a simple $\text{NpO}_2(\text{c}) \rightarrow \text{NpO}_2 + \text{e}^-$ reaction. X-ray diffraction indicates that the solid phase is predominantly $\text{NpO}_2(\text{c})$, and oxidation state analysis has shown that $\text{Np}(\text{V})$ is the only oxidation state in solution. Because it was possible that other minor neptunium phases were controlling the concentration, solubility studies were initiated using neptunium (V) hydroxide $\text{NpO}_2\text{OH}(\text{Am})$ under oxic conditions. Oxidation state analysis, pH, and concentration measurements will be performed on the pH-adjusted solutions contacting $\text{NpO}_2\text{OH}(\text{Am})$.

Solubility and Eh-pH

Determination of the solubility of redox-sensitive elements requires the knowledge of the redox potential of the solution. Use of platinum electrodes in measuring the solution potential has been hampered by low exchange currents and has resulted in mixed potentials that are not meaningful in determining the oxidation state distribution of a particular nuclide.⁽⁵⁾ One way of creating a redox potential that is maintained throughout the solution is by using an Eh-buffer. A research effort is being made to obtain various Eh-buffers over a range of redox potentials. The requirements for an Eh-buffer are as follows:

- $0.2 \text{ V} \leq \text{formal potential} \leq 0.9 \text{ V}$
- stable to decomposition in the pH 2-9 range
- rapid redox reaction kinetics
- no significant precipitation or complexation reactions with the nuclide of interest
- reversible redox reaction.

Quinhydrone has been used previously with good and consistent results. Other organic and inorganic compounds have been suggested and will need to be tested. Those compounds with low potentials will need to be used in an anoxic chamber to prevent reacting with atmospheric oxygen.

PREDICTIVE MODEL DEVELOPMENT - W. L. Kuhn

A source term has been developed for a specific breach scenario, in support of licensing methodology demonstration. For this study, it is assumed that a geologic fault intersects a repository and shears those waste packages it intercepts. The resulting ground-water flow is assumed to be upward along the fault plane, and so release would be from the ends of sheared waste packages to water flowing in the fault plane. Ground-water flow through unbreached portions of the repository is assumed to be comparatively negligible.

To determine the source term in terms of ground-water flow rate, the bounding case of solubility-controlled release is calculated. This requires three things: solubilities as a function of temperature and chemical environment, temperature as a function of time, and the volumetric flow rate available to any given portion of the waste inventory. To facilitate calculations it is assumed that radionuclides release proportionately to uranium (congruent leaching), although

experiments⁽⁶⁾ show this is correct only within an order of magnitude. Then the source term becomes the uranium solubility times a flow rate times the various radio-nuclide fractions in the spent fuel. The repository release is assumed to be directly from waste packages.

The solubility of uranium to be estimated is that in the ground water leaving the waste package, since that determines the release rate. The solubility depends on pH, redox potential, ligand concentrations, and the assumed solubility controlling solid phase. For this study, only phases resulting from reactions among UO_2 , O_2 , and H_2O were considered. The redox potential in deep basalt ground water is extremely low, characterized by oxygen fugacities on the order of 10^{-50} atm or less,⁽⁷⁾ which would keep uranium in the +4 valence state. However, because radiolysis occurs at an unknown rate, it is assumed that the uranium oxidizes according to

It is felt that dominance of a ground-water redox potential cannot be presumed since the rate of transport of reducing agents (e.g., Fe^{++}) into the waste package might be much less than the oxidation rate due to radiolysis. Using available thermodynamic data,⁽¹⁾ it is found that the dominant contribution to soluble uranium is calculated to be from

It is believed that the ground water would be saturated with silica due to vitreous phases in the basalt. Given empirical relationships⁽⁷⁾ for the equilibrium pH

of basalt ground water as a function of temperature, the silicate ion concentration entering the waste package can be estimated, and is found to buffer the pH such that the release of uranium is controlled by

The effective solubility is then limited to

$$\text{U}(\text{kg}/\text{m}^3) = 0.141 + 0.00228 (T, ^\circ\text{C}). \quad (4)$$

Approximate waste packaging temperature calculations were made for an initial heat loading of $13 \text{ W}/\text{m}^2$ ($53 \text{ kW}/\text{acre}$). They ranged from 150°C at 100 yr to 80°C at 50,000 yr.

The time required to leach the inventory from an entire waste package depends primarily on the water velocity in the fault. For this study a water flow between 0.1 and $1 \text{ m}^3/\text{yr}(\text{m-width})$ is estimated. In the plane of the fault, the end of the waste package is a region of high permeability, and potential flow theory can be used to estimate the flow that enters it. The ground water inside waste packages is assumed to be well mixed by natural convection.

The uranium mass per waste package is 1315 kg. Considering the flow and the temperature history, and using the effective solubility, the time to release the uranium is estimated to be 5000 to 50,000 yr. For waste packages sheared in half, the release would last half as long. Actual release times would potentially be orders of magnitude greater due to poor mixing. Katayama⁽⁶⁾ reports uranium release rates from spent fuel down to $10^{-5} \text{ kg}/\text{m}^2\text{-day}$ at 25°C and a typical spent fuel surface area of $0.2 \text{ m}^2/\text{kg}$. Based

on this, the release duration would not exceed 1400 yr. Hence the release would not be kinetically limited. Although the scenario is hypothetical, it illustrates the difficulty of using experimentally determined leach rates directly in licensing calculations. In this particular study, only experimental information regarding leaching congruency has been utilized.

Contrary to the assumption of congruency, it seems likely that a $\text{UO}_2(\text{OH})_2$ layer forming on UO_2 might be permeable and permit relatively soluble radionuclides, such as cesium, iodine, and anionic technetium, to release to ground water. Then for these the release rate will depend on the rate of oxidation/hydration of UO_2 . Presumably radiolysis would supply the oxidant, and its rate could limit the radionuclides' release. Also, the rate of water permeation into the $\text{UO}_2(\text{OH})_2$ might be limiting. The solubilities of the actinides, or their tendency to sorb in $\text{UO}_2(\text{OH})_2$, might control their release.

It is concluded that licensing methodology would be well served by leach studies that:

- quantify the effect of radiolysis on oxidation of spent fuel
- quantify the permeability of a protective layer to water and soluble nuclides
- quantify the sorption/precipitation of actinides and other radionuclides in a protective layer
- develop thermodynamic data on the speciation/solubility of pH/redox-sensitive radionuclides.

REFERENCES

1. Lemire, R. J. and P. R. Tremaine. 1980. Uranium and Plutonium Equilibria in Aqueous Solutions to 200°C. AECL-6655, Atomic Energy of Canada Research Company, Whiteshell Nuclear Research Establishment, Pinawa, Manitoba, Canada.
2. Holland, H. D., and L. H. Brush. 1979. "Uranium Oxides in Ores and Spent Fuels." Proceedings of the Conference on High-Level Radioactive Solid Waste Forms, December 19-21, 1978, Denver, Colorado. NUREG/CP-0005.
3. Rai, Dhanpat, R. G. Strickert, and J. L. Ryan. "Alpha Radiation Induced Production of HNO_3 During Dissolution of Pu Compounds." PNL-SA-8751, Pacific Northwest Laboratory, Richland, Washington.
4. Rai, Dhanpat, R. J. Serne and D. A. Moore. 1980. "Solubility of Plutonium Compounds and Their Behavior in Soils." Soil Science Society of America Journal, 44:490-495.
5. Strickert, R. G. 1980. Sorption of Redox-Sensitive Elements--Critical Analysis. PNL-3432, Pacific Northwest Laboratory, Richland, Washington.
6. Katayama, Y. B., D. J. Bradley, and C. O. Harvey. 1980. Status Report on LWR Spent Fuel IAEA Leach Tests. PNL-3173, Pacific Northwest Laboratory, Richland, Washington.
7. Wood, M. I. 1980. BWIP Data Package for Reference Data of Groundwater Chemistry. RSD-BWI-DP-007, Rockwell Hanford Operations, Richland, Washington.

16. SYSTEMS STUDY ON ENGINEERED BARRIERS

M. O. Cloninger

The objectives of the Systems Study on Engineered Barriers Program are:

1. *to determine what incentives exist for providing highly durable, effective engineered barriers for isolating radioactive waste in a deep geologic repository (based on what effect, if any, the engineered barrier may have on the ultimate potential dose to humans) and to indicate the degree of effectiveness that may be required for maximum benefit*
2. *based on present barrier concepts and knowledge, to determine whether current technology and barrier concepts meet the requirements implied by the successful completion of the first objective and to perform a cost/benefit analysis for those concepts that show promise.*

SUMMARY

The reference salt site analysis document was revised and completed except for printing and distribution. The document should be issued in December. The calculations for the combined reference basalt, granite and shale sites analysis were completed, and documentation of the work will be completed next quarter. The final report should be issued in January 1981. The "BARRIER" engineered barriers performance model document and the Barriers Performance Assessment Task final document were issued.

CONSEQUENCE ANALYSIS

All calculations were completed for the assessment of barriers performance versus consequences in four reference repository geologies. The results will be documented in two separate reports during the next two quarters. Summary conclusions from the overall analysis are as follows:

- In nearly all cases, the regional geology is the most effective barrier to the release of radionuclides to the biosphere; however, for long-lived isotopes of

carbon, technetium and iodine, which are poorly sorbed on the geologic media, the geology is not very effective once a leach incident begins.

- While the need for, and the effectiveness of, a release rate-limiting barrier function is somewhat dependent on the sorption properties of the geologic media, generally a release rate of $<10^{-3} \text{ yr}^{-1}$ (fractional) is necessary to reduce the potential dose from ^{14}C , ^{99}Tc and ^{129}I to a baseline level below that of the actinides. Beyond that, a rate of $<10^{-5} \text{ yr}^{-1}$ is required before the potential dose from the actinide chains can be further lowered by this mechanism (Figure 16.1, lower two lines). This is because the distribution of actinide chain members in time and space--due to their different sorption properties and the characteristics of the ground-water flow field--has the same effect as a release rate reduction of 10^{-5} to 10^{-6} yr^{-1} . Only in extreme cases of the intrusion water well scenario (upper line, Figure 16.1) is there a direct relationship between release rate from the repository and release to the biosphere.

FIGURE 16.1. General Effect of Rate-Limiting Barrier Function

- Generally, the delay in leach incident initiation that an engineered delay function (container, sealant backfill, etc.) might provide, 10^4 years or less, is insufficient to accomplish any reduction in the maximum potential dose. Only the delay provided by a dry, stable geology, 10^5 years or more can accomplish this (bottom two lines, Figure 16.2). However, in the extreme and very unlikely case of the water well scenario (upper line, Figure 16.2), the maximum potential dose is optimally reduced by a containment function lasting about 400 yr. If the containment should last beyond

1000 yr, the maximum potential dose can actually be increased due to ^{226}Ra accumulation (from uranium decay) in the repository confines.

Specific nuclides of concern, in no particular order, are ^{99}Tc , ^{129}I , ^{14}C , ^{226}Ra + daughters (U), ^{237}Np (Am), ^{229}Th (Am, Np), ^{234}U , and, for the extreme case of well scenario, ^{90}Sr .

BARRIERS PERFORMANCE ANALYSIS

This task was completed during this quarter.

FIGURE 16.2. General Effect of Barrier Delay Function

A performance assessment model for multiple barrier packages containing unprocessed spent fuel has been modified and applied to several package designs. The new version contains a refined and expanded corrosion rate data base that includes pitting, crack growth, and graphitization as well as bulk corrosion. Corrosion rates for oxic and anoxic conditions at each of two temperature ranges are supplied. Other improvements include a rigorous treatment of radionuclide release after package failure; this includes resistance of damaged barriers and backfill, refined temperature calculations that account for convection and radiation, a

subroutine to calculate nuclear gamma radiation field at each barrier surface, refined stress calculations with reduced conservatism and various coding improvements to improve running time and core usage.

Barrier performance is determined in terms of two main parameters: time of initial release of radionuclides to the geosphere (leach initiation) and duration of radionuclide release at constant rate. Time is measured from a zero time scenario when the repository is sealed and assumed saturated with water. The performance model treats a barrier package as a series of layers, each consisting of a solid wall(s) filler

16.4

(or backfill) and of a gap between barriers. Materials and designs for barrier packages are chosen to give a range of cost and performance. The key concern is to identify where additional barrier cost yields little increased benefit.

The model was used to assess post-repository closure performance for several designs that were all variations of basic designs from the Spent Unreprocessed Fuel (SURF) program. Many designs were found to delay the onset of leaching by more than 1000 yr, and in some cases over 10,000 yr, in salt and hard-rock geologies with oxic or anoxic ground water.

Furthermore, judicious use of backfills to sorb radionuclides and/or exclude water

can greatly reduce radionuclide release after barrier failure as well as greatly delay the onset of radionuclide release. Results indicate that a few inches of backfill provide sufficient barrier to radionuclide release. Large backfill thicknesses yield little advantage as long as sufficient sleeve thicknesses and/or a cast stabilizer are used. The backfill's stress defense is questionable as it contributes very little and never contributes to stress application if a very "soft" material is used. The key question with regard to backfills remains whether the backfill material will retain its properties or geometry over long periods (over 1000 yr).

17. DEVELOPMENT OF BACKFILL MATERIAL

E. J. Wheelwright - Project Manager

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

SUMMARY^(a)

A preliminary prioritized list of desired attributes (performance criteria) of a multi-component backfill has been prepared. Candidate backfill materials have been reviewed, and those which best match the attributes have been selected for the first laboratory evaluation. A plan is given for the laboratory testing of backfill materials.

DEFINITION AND PRIORITIZATION OF BACKFILL REQUIREMENTS

Numerous possible backfill attributes were generated from literature review, interaction with DBM consultants, and internal brainstorming. A preliminary unprioritized list of attributes was distributed to PNL and project consultants for review and comment on content, organization, and priority.^(a) The proposed attributes were developed as descriptors of performance criteria, not necessarily as fundamental or as directly measurable properties. Fundamental properties represent supporting quantities used to describe the attribute. For instance, the water exclusion attribute is supported by such properties as swelling pressure,

permeability, porosity, bulk density, and water viscosity in the pores.

Early review indicated a need for much reorganization of the list because of repetition and interrelationships of attributes. This was done; then subjective, iterative analysis was used to select and rank the most important attributes. The selected, ranked backfill attributes are:

1. Exclude ground water from the waste canister.
2. Retard (immobilize) selected ions.
3. Self-seal minor cracks or fractures in backfill and interfacing geology.
4. Retain performance criteria at all repository temperatures.
5. Control ground water pH and Eh.
6. Resist faulting.
7. Retain performance criteria during and after radiation in repository.
8. Maintain mechanical stability - provide resistance to mechanical forces.
9. Provide adequate thermal conductivity.
10. Be compatible with geology and other barriers.

Note that attributes cannot be completely separated as most of them are interdependent. For instance, thermal stability is necessary to maintain most of the other attributes. A material that is compatible with the geology and with other barriers may have no other useful barrier attribute, but a material that is absolutely impermeable to ground

(a) For background information on this project, see Section 23 of PNL-3000-6, the prior report in this series.

water would have no value as a barrier if it is incompatible with the intended geology and other barriers.

Details developed regarding the status of testing in support of the attributes are given in a Science Applications, Inc., draft report. These include defining fundamental properties that could be measured and their defining equations or methods of analysis used to relate tests to the fundamental properties.

SCREENING OF POTENTIAL BACKFILL MATERIALS

Several backfill materials have been proposed for initial study. Where possible, these were ranked in terms of attributes.

The proposed backfills are:

1. 10% bentonite in quartz sand
2. >10% bentonite/quartz blends
3. natural and synthetic zeolites
4. powdered metal or graphite.

The individual attributes of these materials are discussed in the following sections. During FY 1981, laboratory tests will be conducted on compacts of the individual materials and on compacts of homogeneous mixtures of two or more materials.

Bentonite/Quartz Mixtures

In the bentonite/quartz blends each material brings certain advantages and disadvantages

to the blend, as summarized in Table 17.1.

The bentonite proposed for backfill materials is sodium bentonite (Volclay MX 80), size distribution 0.07 to 0.80 mm. The sand is pure quartz sand (98% SiO₂), sized 0.063 - 2 mm, with a sintering point of 1400°C. To possess good bearing capacity, thermal conductivity, and low permeability, the quartz-bentonite fractions should be mixed in portions to provide a good particle size distribution.

Increasing the bentonite mix tends to lower the permeability, decrease the friction, and increase the cohesion. High bentonite content in buffer material is favorable in upper portions of tunnels to fill voids by swelling.

The sand/bentonite backfill material can also act as a pH buffer for the ground water system, with a stabilized pH 8 to 9 at the repository temperatures expected. The buffer acts to modify the ground-water chemistry of the waste repository by acting as a pH, Eh control, to decrease corrosion of the canister.

Powdered Metals and Graphite

Candidate buffer materials must be specifically tailored to the canister and overpack and to the repository geology. An iron-based canister in a basalt geology would use

TABLE 17.1. Main Advantages (+) and Disadvantages (-) of Bentonite/Quartz Material

	<u>Quartz Material</u>	<u>Bentonite</u>
Long-time stability	+	+
Bearing capacity	+	-
Plasticity	-	+
Permeability	-	+
Swelling properties	-	+
Heat conductivity	+	-
Ion exchange capacity	-	+

candidate buffer materials such as graphite or powdered iron, aluminum, and titanium.

Graphite is a useful buffer material to choose for the moderation of oxygen fugacity in the repository. It has good thermal conductivity qualities and aids in the transport of heat outside of the waste package.

Aluminum, like graphite, is a good thermal conductor. As a buffer material, aluminum aids in moderating the ground-water pH, much the same as do other candidate buffer substances such as lime and the carbonates. Swelling clays and aluminum are both possible buffer materials to consider when the ability to inhibit ground-water intrusion is required in a waste repository.

In selecting a tailored barrier material, one needs to consider the environment that the barrier will be subjected to. The expected repository temperature, ground-water chemistry, and other repository conditions need to be evaluated first to permit selection of a barrier material tailored to site-specific parameters.

Synthetic and Natural Zeolites

The primary incentive for using these zeolites is their ion-exchange capacity and

potential selective sorption of "high-hazard" radionuclides that are not sorbed by other materials. These zeolites display a low permeability but do not have the sealing capabilities that the swelling clays have. Zeolites might be used as an inner backfill layer with a swelling clay on the outside. Several natural and synthetic zeolites have been studied in Sweden such as K^+ zeolites, mordenite, phillipsite, Chabonite, Clinoptilolite, erionite, Onalene, and "13X."⁽¹⁾ U.S. studies have included work with Clinoptilolite and mordenite.⁽²⁾

Ranking of Materials

An overall ranking of the above materials for different attributes is given in Table 17.2. This ranking is very preliminary, based as it is on available data and engineering judgments.

LABORATORY EVALUATION OF SELECTED BACKFILL MATERIALS

The objective of this task is to experimentally measure the performance characteristics of the selected backfill materials and to evaluate the experimental results in terms

TABLE 17.2. Ranking of Backfill Materials
(1 = high, 4 = low)

Attribute	10% Bentonite/ Quartz	>10% Bentonite/ Quartz	Zeolites	Powdered Metal or Graphite
Water exclusion	2	1	3	4
Ion retardation	3	2	1	4
Self-sealing	2	1	3	4
Thermal stability	3	2	4	1
Chemical buffering	2	1	4	3
Fault resistance	3	4	2	1
Radiation stability	?	?	?	?
Mechanical stability	2	1	3	4
Thermal conductivity	3	2	4	4
Compatibility with geology and other barriers	?	?	?	?

of the attributes defined in the activity "Definition and Prioritization of Backfill Requirements."

A plan has been formed for FY 1981, with experiments in four categories: 1) water migration, 2) radionuclide migration, 3) physical property measurements, and 4) chemical stability. The experiments and results in these categories, however, are not independent of each other. Early screening tests will consist of simplified experiments to measure relative differences in the rates for water and radionuclide migration in the initial group of potential backfill materials. The purpose of these tests is to reduce the number of backfill materials to a more manageable group for exhaustive experimental evaluation.

Water Migration

For water-migration experiments, a rigid-volume flow cell will be used for permeability measurements from 25 to -150°C. Because the permeability measurements are strongly dependent on the density of compaction, it is important that the flow-cell have provisions for "in-place" compaction of the backfill barrier material. The permeameter system will consist of a rigid-volume flow-cell, a fluid reservoir, a constant-temperature bath or oven, a pressure intensifier, and fluid-sample collectors. Two suitable designs have been identified for the rigid-volume flow cell. Each flow-cell consists of a stainless steel cylinder and two pistons. The steel cylinder provides lateral confinement for the sample. The two pistons allow for "in-place" compaction of the sample within the cylinder, as well as for an axial load during fluid injection into the sample. For sample compaction, material is placed between the pistons, and

a controlled pressure is applied to the two pistons by a hydraulic press. When the desired compaction is achieved, the pistons are secured in position by two threaded end-caps or two basal support plates that are bolted together. A group of one or more cells will be fabricated to allow simultaneous, multicell permeability measurements.

The permeameter system will be used to measure the water-migration rates through the potential backfill materials as a function of 1) composition of the backfill material, 2) compaction density, 3) composition of ground water, 4) thermal treatment, and 5) radiation treatment. Test variables for these initial experiments will consist of:

1. two fluid pressures sufficient to obtain a measurable flow rate through the compacted material
2. two compaction densities--1.0 and 2.0 ton/m³
3. three fluid compositions--Hanford ground water, a granite ground water, and a WIPP-site brine
4. three temperatures--25, 60, and 120°C.

Backfill materials will also be exposed to thermal and gamma-radiation treatments prior to compaction and the water-migration experiments. The purpose of these treatments is to determine their effects on the water migration rates in the compacted samples. The thermal treatments will consist of dry heating in an oven and hydrothermal "cooking" in an autoclave for at least 1 month at 250°C. The hydrothermal fluids will consist of the same compositions as those used in the water migration tests. At the end of the thermal treatments, the solid phases will be inspected by petrographic microscope, x-ray diffraction, and scanning electron microscope techniques for changes in chemistry, morphology, and crystallinity. The chemistry of the final aqueous fluids will be

analyzed for major cations, anions, pH, and Eh. The radiation treatment will consist of irradiating backfill materials in dry and aqueous environments with a ^{60}Co source. The effects on the solids by the gamma radiation and radiolysis products in the aqueous phase will be measured. The final solid phases and aqueous solutions will be analyzed with the same techniques used for the thermally treated samples.

The final permeability measurements will be completed on a high-temperature ($>100^\circ\text{C}$) stress/strain flow system. This system will have provisions for controlling and monitoring the sample volume during a long-term flow and permeability experiment. The stress/strain flow system will provide sufficient data from the permeability measurements to monitor the physical and chemical responses of a backfill material to a realistic simulation of a repository environment. The water-migration experiments on the stress/strain flow facility will be completed at a confining pressure of 250 bars, three temperatures (120, 200, and 250°C), as well as the flow rates, fluid compositions, and compaction pressures used in the measurements in the rigid-volume flow-cell. These experiments on this flow system shall include measurements of sample deformation, changes of fluid pressure and flow rates caused by the swelling and chemical instability of the sample, and chemical changes in the exiting effluents.

Radionuclide Migration

The initial experiments to measure the rates of radionuclide migration will be identical to the permeability measurements with the rigid-volume flow-cell. The rates for radionuclide migration through compacted backfill materials at 25 to 150°C will use the same experimental equipment, test vari-

ables, and techniques for phase characterization. The only difference is that the ground-water solutions will be spiked with appropriate radionuclides. For these experiments ^{129}I , ^{99}Tc , and ^{239}Np will be three of the nuclides considered for the spiked solutions. The compacted samples in the flow-cell will be saturated with clean ground water prior to injecting the radionuclides into the effluent stream near the inlet of the flow-cell.

Physical Property Measurements

The physical property measurements necessary to characterize the selected barrier materials should minimally include thermal conductivity, specific heat, swelling pressure, bearing capacity, and stress/strain relations. All these properties must be measured as a function of composition, compaction density, and temperature (25 to 250°C). Swelling pressure, bearing capacity, and the stress/strain relations of a backfill material can be measured simultaneously with the water permeability measurements by means of the stress/strain flow system. Because this instrumentation can cycle temperature during a single experimental run, these properties can be measured over the entire temperature range during one experiment. Thermal conductivity measurements can be obtained with a microprocessor-controlled, cut-bar thermal conductivity apparatus. The specific heat of a backfill sample can be determined by high-temperature drop calorimetry and/or differential scanning calorimetry.

Chemical Stability

Chemical data, collected in the water and radionuclide migration experiments, will provide a large data base for interpreting

the chemical stability of potential backfill barrier materials. Data from the high-temperature ($>150^{\circ}\text{C}$) permeability measurements will be particularly important because the chemical data are collected in situ for the effluent from the stress/strain flow system. High-temperature, pressurized autoclaves will be used for long-term, hydrothermal stability studies of backfill materials. This instrumentation has the capabilities for fluid sampling during the duration of the experiment. The test parameters will include time (1 to 12 months), temperature (60 to 250°C), confining pressure (300 bars),

barrier composition, and ground-water composition. Due to the sluggish kinetics of silicate dissolution, the initial autoclave experiments should be restricted to a minimum temperature of ~ 120 to 150°C . The autoclave experiments will be coupled with accurate fluid analyses that should include the major cations, anions, pH, and Eh, and with high-resolution characterization of the reacted solid materials by petrographic microscope, x-ray diffraction, scanning electron microscope, electron probe analysis, and bulk-chemical analysis techniques.

REFERENCES

1. Neretnieks, I. 1977. Retardation of Escaping Nuclides from a Final Depository. KBS Report No. 130, Stockholm, Sweden.
2. Nowak, E. G. 1980. Radionuclide Sorption and Migration Studies of Getters for Backfill Barriers. SAND79-1110, Sandia National Laboratories, Albuquerque, New Mexico.

18. CRITERIA FOR DEFINING WASTE ISOLATION

R. D. Widrig - Project Manager

The objective of this project is to provide technical support for the Office of Nuclear Waste Isolation's (ONWI) efforts to prepare waste management criteria, with particular emphasis on criticality and spent fuel isolation criteria.

SUMMARY

Work continued in two areas: 1) identifying the conditions under which spent fuel in geologic media could achieve criticality and 2) comparing the radiological consequences of natural uranium ore deposits with those of spent fuel geologic repositories.

In the criticality work, analyses indicated plutonium concentrations in dry geologic settings must exceed 10^{-3} g/cm³ for criticality to be possible. Furthermore, the plutonium must be relatively free of uranium. This concentration does not appear realistic under the reducing conditions expected of most deep geologic regimes. But, if oxidizing conditions exist, such concentrations appear theoretically possible. Other factors, however, still could preclude a criticality condition.

The comparative analysis of uranium ore deposits versus repositories was completed. Repositories are quite comparable to many natural deposits and, in some cases, present less radiological hazard than their natural counterparts.

NUCLEAR CRITICALITY SAFETY OF SPENT FUEL DISPOSAL - B. F. Gore

Calculations performed during the preceding quarter have shown that for criticality

to be possible in a dry geologic setting concentrations of plutonium exceeding 10^{-3} g/cm³ are required. Furthermore, the plutonium must be relatively free of uranium since criticality cannot occur in such a setting when $^{238}\text{U}/^{239}\text{Pu} = 9$ over the range of concentrations from 0.001 to 0.1 g Pu/cm³.

During the present quarter, studies have addressed the possibility of such conditions resulting from leaching and aqueous transport of spent fuel constituents. The solubilities of uranium and plutonium compounds have been calculated for ground waters characteristic of the following geologic regimes: Columbia Plateau basalt (Hanford, Washington), Jackass Flats tuff (Nevada Test Site), Climax Stock granite (Nevada Test Site), domed salt (East Texas Gulf Coast), and bedded salt (WIPP site, New Mexico). Because solubilities are sensitive to both Eh and pH conditions, solubilities were calculated for both oxidizing and reducing conditions for each of these media.

The solubility defines the highest concentration of dissolved solids possible in solution. The product of the solubility times the distribution coefficient K_d gives the maximum concentration that can be adsorbed on geologic materials in equilibrium with a saturated solution. This adsorbed concentration limit was determined using best-estimate values of K_d obtained from the literature.

Under reducing conditions (those most likely in deep geologic regimes) and at normal temperatures this maximum adsorbed concentration limit for plutonium is less than 10^{-4} g Pu/cm³ in the salt media and orders of magnitude lower in rock. Consequently, under reducing conditions adsorption will not yield fissile concentrations high enough to be of criticality concern.

Under oxidizing conditions at normal temperatures, the maximum concentration limit for adsorbed plutonium was found to be about 10^{-3} g Pu/cm³. This limit was obtained using best-estimate values of K_d selected from a range of published values. If subsequent studies result in higher K_d values, then the adsorbed concentration limit would increase above the 10^{-3} g Pu/cm³ limit required for criticality. Nevertheless, it might still be possible to dismiss concern for criticality with plutonium adsorbed on rock by including the effects of admixed uranium and/or the failure of ground water to transport plutonium at solubility limits.

COMPARATIVE CONSEQUENCES ANALYSIS - URANIUM DEPOSITS VERSUS NUCLEAR WASTE REPOSITORIES -
M. O. Cloninger and O. J. Wick

The comparative analysis was completed during this quarter. The reference spent-fuel repositories were compared to natural uranium ore deposits in terms of 1) intrinsic characteristics such as radionuclide inventory, depth, proximity to aquifers, and regional distribution and 2) the actual and potential radiological consequences that are occurring from some ore deposits and that may eventually occur from repositories and other ore deposits. The results show the repositories to be quite comparable to the natural ore deposits and, in some cases, to

present less radiological hazard than their natural counterparts.

On the basis of the first comparison, placing spent fuel in a deep geologic repository apparently reduces the hazard from natural radioactive materials occurring in the earth's crust by locating the waste in impermeable strata without access to oxidizing conditions. Under such conditions, even in the event of containment failure, the limited solubility of material exposed to limited quantities of water permeating through geologic materials with high adsorptive capacities would restrict migration of most isotopes to less than the 0.1 to 1.4 cm/yr, the estimated migration rate for natural uranium deposits under conditions of oxygen-saturated ground water and permeable strata.

On the basis of the second comparison, a repository constructed within reasonable constraints presents no greater hazard than a large ore deposit. Even without such constraints, however, the natural hazard due to some observed radioactive releases to the biosphere in the U.S. far exceeds any hazard that could reasonably be expected (or accepted) from a spent-fuel repository. Therefore, while it is, at first intuition, reasonable to use natural ore deposits as a basis for criteria for nuclear waste repositories, the variability in the natural system is so great that it does not allow a specific criterion to be stated in absolute terms.

It is suggested that if the naturally radioactive environment is to be used as a basis for a criterion regarding repositories, then this criterion must be carefully constructed. The criterion should be based on the radiological quality of the waters in the immediate region of a specific repository and should be in terms of an acceptable

18.3

potential increase in the radiological content of those waters due to the existence of the repository. This criterion could then be used as a basis for developing, through experimentation and modeling, specific cri-

teria for a repository system design that is reasonably assured of meeting the environmental criteria.

Detailed documentation of the analysis should be issued in December 1980.

19. 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

PNL has been active in several areas of study on spent fuel pools. In addition to providing testimony at licensing hearings, the work has included consulting on an international spent fuel storage handbook, examination of spent fuel pool components, and corrosion mechanism studies.

Fuel rods from Shippingport and Connecticut Yankee have been examined, and the data are being evaluated. Some of the Zircaloy-clad fuel has been in storage for extensive periods and shows no substantial change in properties.

Possible mechanisms of failure are being examined in simulated storage pool conditions. Emphasis is on an examination of pipe which cracked by intergranular stress corrosion cracking from a spent fuel pool system. Four papers are being prepared for presentation at CORROSION 81 in Toronto, Canada, next April.

PROGRAM MANAGEMENT - A. B. Johnson, Jr.

PNL participated in the preparation of the Nuclear Regulatory Commission (NRC) Confidence Hearing testimony on Storage and Disposal of Spent Fuel. The testimony was issued as DOE/NE-007, April 15, for public

comment. About 25 written responses were received, some supporting, some opposing the Department of Energy's (DOE) position. Responding to the public responses, DOE prepared a Cross Statement which was issued on September 5 as DOE/NE-007 Suppl. 1.

During FY 1980, the program produced the following publications, in addition to the two hearing statements:

- Draft Report: Investigation of the Condition of Metallic Spent Fuel Components, PNL-3537.
- Interim Report: Three Mile Island No. 1 Spent Fuel Pool System Pipe Cracking Analysis, PNL-3102, November 1979.
- Annual Report - FY 1979: Spent Fuel and Fuel Pool Component Integrity, PNL-3171, May 1980.
- Draft Report: Summarizing the World Survey of Spent Fuel Storage Experience. Currently undergoing editing by the IAEA/NEA Consultant Group.
- Two foreign travel reports were issued: April 23, 1980 and July 31, 1980.
- Four quarterly reports were issued.

INTERNATIONAL - A. B. Johnson, Jr.

A. B. Johnson was invited by the International Atomic Energy Agency (IAEA) to consult with the Nuclear Materials and Fuel

Cycle Section in Vienna regarding the report World Survey of Spent Fuel Storage Experience. He also will comment on IAEA plans for a spent fuel storage handbook. The trip will occur during October 1980.

The schedule for the World Survey Report calls for a comment draft by 1980 and public release of the report by March 1981.

SPENT FUEL ACQUISITION AND EXAMINATION -

W. J. Bailey, E. R. Bradley, and
D. C. Langstaff

The examination of eight Shippingport fuel rods (four from each of the two fuel bundles), scoped for FY 1980, was completed in September. For four rods from each bundle the detailed examination included visual inspection, gamma scanning, eddy-current testing, leak testing, and fission gas release measurements. For two rods from each bundle, the detailed examination included profilometry, burst testing, metallography on four sections, and analysis of four samples of cladding for hydrogen. One rod from each bundle was also analyzed for burnup. Examination results are being evaluated. The preliminary assessment suggests that none of the cladding properties have changed substantially during storage of the Zircaloy-clad fuel in water for periods up to nearly 21 yr.

The nondestructive examination of Connecticut Yankee Fuel Assembly S004 included visual inspection and sipping. The nondestructive examination of the stainless steel-clad fuel rods included visual inspection, profilometry, gamma scanning, eddy-current testing, and weighing. The destructive examinations on two fuel rods involve fission gas analysis, cladding metallography, determination of the cladding's mechanical properties, and fuel studies (e.g., burnup

analyses, density determinations, ceramography, leaching rates). The metallographic examination, including scanning electron microscopy, is in progress. Mechanical properties tests, burnup analyses, ceramography, density determinations, and leaching rate measurements remain to be done. The results to date from the visual inspections, eddy-current tests, and metallographic examinations have not shown evidence of cracks in the cladding of S004 fuel rods.

The draft of a paper, "Spent Fuel Behavior in Water Pools," is undergoing final editing before clearance is started. That paper is to be presented at CORROSION 81, the symposium to be held by the National Association of Corrosion Engineers in Toronto in April 1981.

A draft of a paper, "Significance of Shippingport and Connecticut Yankee Fuel examinations to Extended Water Storage of LWR Fuel," is being prepared for presentation at an IAEA meeting on spent fuel storage at Las Vegas, November 17-21, 1980.

SPENT FUEL POOL COMPONENT EXAMINATIONS

Examinations have been completed on stainless steel specimens from the Yankee Rowe, Point Beach and Three Mile Island Unit 1 spent fuel pool components. All three reactors are pressurized water reactors. A draft report summarizing the examinations has been written (PNL-3537). Arrangements have been completed to obtain component specimens from a Savannah River Pool (receiving basin for offsite fuel), from La Crosse (boiling water reactor) and from Zion (pressurized water reactor). A decision is pending on whether to add results of the other three examinations to PNL-3537.

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

Pipe Cracking Study

Constant extension rate tests (CERT) are being conducted on samples removed from a pipe/elbow joint of the Three Mile Island No. 1 spent fuel pool system to identify the cause of the intergranular stress corrosion cracks observed during operation. As reported previously,⁽¹⁾ intergranular stress corrosion fracture was observed only in a test conducted in a solution of 13,000 ppm H_3BO_3 + 15 ppm Cl^- using a sample removed from the pipe/elbow joint with the original inner diameter (ID) surface intact. Ductile fracture was observed when a sample with the ID surface removed was tested in the same solution. Strain to failure values of 53 to 67% and reduction of area values of 41 to 69% were obtained.

Brookhaven National Laboratory (BNL) performed CERT tests on samples from a welded joint removed from the Three Mile Island No. 1 spent fuel pool system. The PNL and BNL samples came from the same heat (#334165). BNL reported strain to failure values of 15 and 50% when tested in boric acid and air, respectively. In the boric acid test, BNL claims to have 100% intergranular fracture while in the air test they claim to have 50% intergranular and 50% ductile fracture.

In an effort to clarify the discrepancy between the PNL and BNL results, a BNL CERT sample was tested at PNL. This test was conducted in solution of 13,000 ppm H_3BO_3 at 32°C and at a strain rate of $7 \times 10^{-7} \text{ sec}^{-1}$, corresponding to a crosshead rate of $2.1 \times 10^{-3} \text{ mm/min}$ ($1.4 \times 10^{-6} \text{ in./sec}$). This sample had a yield strength of 260 MPa (38,170 psi) and an ultimate tensile strength

of 607 MPa (89,200 psi). Ultimate tensile stresses ranging from 614 to 657 MPa were observed for the PNL pipe/elbow samples while an average ultimate stress of 616 MPa was observed for three furnace-sensitized pipe CERT samples. The ultimate strengths of the BNL CERT sample and the PNL pipe and pipe/elbow samples are therefore very similar.

A strain to failure of about 30% and a reduction of area of 60% were obtained for the BNL CERT sample tested at PNL. The reduction of area value is consistent with values obtained from the pipe/elbow CERT samples; the strain to failure is about half that obtained with the pipe/elbow CERT samples. This difference in strain to failure is probably due to the fracture morphology. The BNL CERT sample failed predominantly by ductile (microvoid coalescence), with considerable shear or tensile separation along longitudinal surfaces (Figure 19.1). Some of these interfaces could be intergranular as their dimensions are similar to the grain size. However, these shear or tensile separations are secondary cracks and probably formed after the ultimate load had been exceeded. This could explain the similarity in the reduction of area where the necking process was not affected by these separations while the nonuniform component of the total strain was affected by these separations. The primary fracture was ductile microvoid coalescence and does not appear to show any signs of stress-corrosion cracking.

General Corrosion Studies

Overall, there have been very few materials problems in spent fuel pools. The component materials are generally corrosion-resistant in the relatively low temperatures and benign coolants. Current projections suggest that spent fuel pools will be an

FIGURE 19.1. Scanning Electron Micrographs of the BNL CERT Sample Fracture Surface After Test in Boric Acid, A) Inner Diameter of Pipe and B) Near Center of the Pipe. Note the difference in scale between the tensile and shear separations, which are consistent with the grain size difference between inner diameter and interior of pipe.

important link in the management of spent fuel for the next several decades. There is prudence in an improved definition of the behavior of materials in the spent fuel pool environments to:

- confirm operator experience which suggests that very little significant corrosion occurs on spent fuel pool materials, and
 - further define the few cases where significant corrosion has been observed.
- Observations that have been made about the various spent fuel pools are:
- Corrosion - No significant problems in deionized water systems.^(2,3) Cracking observed in pool piping in boric acid systems.⁽⁴⁾

● Materials^(a)

- Liners - 304 stainless steel, epoxy, fiberglass
- Racks - 304 stainless steel or 6061-T6 aluminum
- Canister - 304 stainless steel or 5083/5086/6063 aluminum
- Misc. - Mostly 304 stainless steel with some 316 stainless steel.

● Temperature - 25-35°C

- Chemistry - Deionized water - pH 4.4 - 9, normally about 6 - 7; Cl^- <0.1 ppm
- Boric acid - pH 4.4 - 7, normally 4.8 - 5.3; Cl^- <0.01 ppm

- Volume (pool) - 900 to 5000 m^3 (0.25 to 1.3 Mgal)

(a) Preponderant materials; a few pools use materials other than those shown for components.

A series of ten tests have been set up to simulate the above pool characteristics as well as to provide a controlled departure from these operating conditions. Five test chambers have been set up to simulate de-ionized water pool storage and five for boric acid pool storage.

Each test chamber consists of a 304 stainless steel tank, 43 by 58 by 30 cm tall, inside an insulated polypropylene tank and is equipped with a stainless steel lid. Inside the stainless steel tank are the electrically insulated (with PTFE) coupon racks, the stainless steel heater, stainless steel-clad thermocouples, and the conductivity probe. The pH and chloride electrodes are located in the tank of the high-chloride solutions but in the water cleanup line of the low chloride baths.

The test coupons consist of 304 stainless steel (of several different carbon levels ranging from 0.1 to 0.9%) and 6061 aluminum. The metals are inserted as weight loss coupons (to be used as base line comparisons), galvanic couples, crevice corrosion specimens (including crevices between as-received and heat-sensitized specimens), and stress corrosion cracking specimens (U-bends will be used for comparative studies).

Ten sets of samples will be prepared for installation in the various test conditions. These conditions will consist of five tests set up using temperatures to be selected between 30 and 80°C and chloride levels between 0 and 100 ppm.

Each tank is equipped with an individual water cleanup system consisting of a recirculation pump and a mixed-bed ion-exchange column followed by a stainless steel filter. The water cleanup system is controlled by a microcomputer-based automatic control column (Figure 19.2).

FIGURE 19.2. Microcomputer System for Data Collection and Process Control for Simulated Spent Fuel Pools

The microcomputer-based monitoring and control system was purchased to provide automatic data collection and to control the water chemistry. It monitors and records temperatures, chloride concentration, pH, and conductivity. The computer is also used to control the water quality by switching in the ion-exchange unit or adding make-up water. The temperature is controlled by a separate control system.

A paper, "Overview of Spent Fuel Pool Materials Studies at Pacific Northwest Laboratory," will be presented at CORROSION 81.

SPENT FUEL STORAGE - A. B. Johnson, Jr.

Negotiations are under way with two spent fuel pools for placement of DOE surveillance fuel assemblies.

REFERENCES

1. Johnson, A. B., Jr. 1980. "Spent Fuel and Fuel Pool Component Integrity Program." In Nuclear Waste Management Quarterly April Through June, 1980. PNL-3000-6, Pacific Northwest Laboratory, Richland, Washington.
2. Johnson, A. B., Jr. 1977. Behavior of Spent Nuclear Fuel in Water Pool Storage. BNWL-2256, Pacific Northwest Laboratory, Richland, Washington.
3. Johnson, A. B., Jr., W. J. Bailey, R. E. Schreiber and F. M. Kustas. 1980. Annual Report--FY 1979, Spent Fuel and Fuel Pool Component Integrity. PNL-3171, Pacific Northwest Laboratory, Richland, Washington.
4. "Pipe Cracks in Stagnant Borated Water Systems at PWR Plants." NRC IE Bulletin 79-17, July 26, 1979.

20. ANALYSIS OF SPENT FUEL POLICY IMPLEMENTATION

M. K. White - Project Manager

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

SUMMARY

Project activities have consisted of updating the spent fuel storage and disposal fee calculations and modifying the computer models used to reflect changes in the reference methodology. The storage and disposal

fees have been updated because of changes in the program assumptions for facility startup for the management of spent fuel and because of changes in estimated program costs. The calculational methodology has been modified to incorporate recent changes in the fee prepayment assumptions.

21. 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

Several scenarios that could result in criticality have been postulated, and two have been identified for further analysis. Computational capabilities are being implemented which will be used to model the postulated criticality events.

POSTULATED SCENARIOS

Postulated scenarios have been reviewed with the sponsor, and two particular scenarios have been selected for further analysis. All scenarios that have been identified consist of particular events believed to be highly unlikely. The particular scenarios identified for further analysis represent reasonable extremes with respect to the magnitude and rate of reactivity insertions.

MODEL DEVELOPMENT

The objectives of this program require the capability to model the time-dependent neutronic and thermal-hydraulic behavior of a system comprised of an array of spent fuel in a nonpressurized water environment. The two-dimensional, time-dependent neutronics program TWIGL⁽¹⁾ and the thermal-hydraulic

analysis code COBRA⁽²⁾ were selected for use in the analysis. The two codes have been modified and combined into one. The resulting computer program will provide adequate modeling capabilities. The new program is currently being tested.

CRITICALITY ANALYSIS

Preliminary calculations have been performed to determine the excess reactivity available as a result of incidents associated with selected scenarios. Neutronic and thermal-hydraulic parameters required for dynamic analysis are currently being developed. The dynamics of reactivity excursions associated with selected scenarios will be analyzed during the next two quarters.

REFERENCES

1. Yasinsky, J. B., M. Natelson, and L. A. Hageman. 1968. TWIGL: A Program to Solve the Two-Dimensional, Two-Group, Space-Time Neutron Diffusion Equations with Temperature Feedback. WAPD-TM-743. Bettis Atomic Power Laboratory, Pittsburgh, Pennsylvania.
2. Stewart, C. W. et al. 1977. COBRA-IV: The Model and the Method. BNWL-2214, Pacific Northwest Laboratory, Richland, Washington.

22. ASPHALT EMULSION SEALING OF URANIUM TAILINGS

J. N. Hartley - Project Manager

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

SUMMARY

Studies of asphalt emulsion sealants during the quarter have shown these sealants to be effective in containing radon and other potentially hazardous material within uranium tailings. Results of laboratory and field studies indicate that radon exhalation from uranium tailings piles can be reduced by >99% to less than background levels. Field tests at the tailings pile in Grand Junction, Colorado, demonstrated the effectiveness of an 8-cm admix cationic asphalt emulsion seal containing 22 wt% asphalt applied with a cold mix paver. Other techniques successfully tested included a soil stabilizer and a hot, rubberized asphalt seal applied with a distributor truck. After the seals were applied and compacted, overburden was applied over the seal to protect it from ultraviolet degradation.

LABORATORY STUDIES

Tailings Characterization - M. R. Elmore

The Vitro, Durango, and Shiprock tailings sites were sampled, and selected samples were sent to DOE-sponsored researchers. Sampling of Canonsburg has been delayed due to legal restrictions.

Grand Junction tailings samples were physically and chemically characterized to determine the potential effect of the tailings on the seal to be applied during the field test. Also included in the characterization was the concrete sand to be used for the admix seals.

Seal Formulation - P. L. Koehmstedt

Samples of concrete sand from the two Grand Junction sources were tested for bonding characteristics. Two cationic asphalt emulsions being considered for application in the forthcoming field test were used. The United Concrete sand was more anionic than the Whitewater material and, therefore, was preferred.

Using United Concrete sand, Armak cationic asphalt emulsions with 92, 78, 56, and 54 mV positive zeta potential were compared at ambient (68°F) and expected field temperatures up to 130°F. The 92 mV emulsion reacts too fast at either temperature to be of practical application. The 78, 56, and 54 mV emulsions all reacted similarly and would provide what is believed to be the best admixture consistency for paver placement at 68°F. At the expected field temperatures (80-100°F) and emulsion arrival temperatures (100-130°F) the reaction rates of the

78 mV emulsion are rapid, but the admixture consistency is believed to be the best achievable for paver operation.

Five +18-mV (Armak type 4868) emulsion systems with different asphalt bases were tested using both local blow sand and concrete sand at 100°F and 68°F mixing conditions. The five emulsions were as follows:

1. Eddington, CA Untreated
2. Lyon (Smackover Chemically treated
Crude) AK
3. Lyon (Smackover Untreated
Crude) AK
4. Oklahoma City, OK Chemically treated
5. Oklahoma City, OK Untreated

Seal specimens prepared with local blow sand and emulsions 2, 3, 4, and 5 at both temperatures were radon-tight. All specimens prepared from emulsion 1 failed the helium low-pressure test. These tests point out the need to match asphalt source, emulsifier, and aggregate as a system for optimum radon sealing.

The asphalt emulsions selected for the Grand Junction field test include Armak CSS (+18 mV) emulsion to be used with the soil stabilizer and Armak CMS (+78 mV) emulsion to be used with the cold mix paver, pug mill/paver, and concrete truck/paver.

Radon Diffusion Measurement - H. D. Freeman

No radon diffusion measurements were made on seals during the fourth quarter. All effort was directed toward the Grand Junction field test. Nine radon measurement systems were calibrated using Grand Junction tailings. The radon flux measured by each of the systems was within $\pm 12\%$.

Seal Stability - R. L. Clark

We performed several preliminary leaching experiments on different types of asphalt

seals and tested methods of chemically characterizing the asphalt. The results have yielded insight into the design of experiments to determine long-term asphalt-emulsion admix seal stability. The combined results of our literature search and experimental work indicate that asphalt auto-oxidation, ground-water leaching, and microbial attack are the most likely mechanisms to degrade asphalt. We also think that cracking due to freeze-thaw stress and subgrade settling might be a generic problem to all the proposed seal technologies.

In the first leaching experiment, simulated tailings ground water was dripped onto five poured-on, asphalt-emulsion fog seals. Five emulsions were used, each made from a different asphalt. Three of the five seals failed due to asphalt dissolution into the brine, while two showed no change. After an examination of possible differences in the asphalt emulsions, we concluded that the three fog seal failures were caused by insufficient curing. This experiment indicated that proper curing is an important factor in determining asphalt resistance to stripping.

A slightly different experimental design was used to test this inadequate curing hypothesis. The cationic emulsion that gave the worst performance in the first experiment was selected, and fog seals were made by pouring 40 ml of emulsion into each of five 250-ml Erlenmeyer flasks. Air was blown over the seals for 3 days; then the flasks were stored in a vacuum drying oven for 2 days at 100°C, removed, and allowed to cool to room temperature. Approximately 100 ml of the simulated ground water was poured into each flask, and the stoppered flasks were mechanically shaken for 15 days. After 5 days, the liquid began to change from clear to murky dark brown, and the previously smooth seal surface began to pucker. Filtration through a medium-porosity,

sintered-glass funnel removed the suspended asphalt solids and produced a clear, slightly yellow filtrate. The residual asphalt seal was also much softer after the leaching. The pH of the brine did not change during the experiment, and the color change was probably due to oxidation of ferrous iron in the brine. Some water uptake into the seal probably occurred, causing the asphalt to soften. Since the asphalt did not dissolve, the observed stripping was probably caused by the brine's abrasive action on the seal during agitation. This experiment indicated that both the level of curing and the water flow conditions are important factors in asphalt stability.

Because asphalt emulsions are designed for use with aggregate as an admix, a third experiment was performed to determine the stabilizing effect of the aggregate. Two asphalt-emulsion admix seals were prepared and were then drip-leached with simulated tailings ground water as in the first experiments. After 30 days, no identifiable change had occurred and the experiment is still continuing. These three experiments indicate that simple variations in the asphalt system can produce different outcomes in stability experiments. Our preliminary results underscore the importance of exactly duplicating the admix-overburden seal system in future stability determinations.

We also analyzed six different types of asphalts using gel permeation chromatography (GPC), proton nuclear magnetic resonance spectroscopy (^1H NMR), infrared spectroscopy (IR), and carbon-hydrogen-nitrogen (CHN) elemental analysis. The CHN analyses indicated that the asphalts were highly aliphatic (average $\pm$ standard deviation), i.e., 0.3 ± 0.5 nitrogen, 86.2 ± 3.2 carbon, and 11.2 ± 0.7 hydrogen. No carbonyl peaks

that would indicate the presence of oxygen were found in the IR studies. The NMR work corroborated this and showed that the asphalts were primarily aliphatic but with a minor aromatic component. The GPC studies indicated a bimodal molecular weight distribution with peak maxima occurring at ~ 6000 and ~ 2000 Daltons. (A Dalton is equal to one atomic mass unit.) We found that GPC can detect changes in the asphalt caused by auto-oxidation. GPC of dilute asphalt solutions in tetrahydrofuran allowed to auto-oxidize for 3 days indicated that ~ 6000 -Dalton peak increased at the expense of the ~ 2000 -Dalton peak. In these studies we developed the analytical capability for detecting oxidation-induced changes in the chemical composition of asphalt.

FIELD STUDIES

Field Test (Grand Junction) - J. N. Hartley, D. J. Esterl, and J. L. Buelte

The 1980 field test was carried out at the Grand Junction, Colorado, uranium mill tailings pile. Four basic application techniques were tested; these included 1) soil stabilizer, 2) cold-mix paver, 3) continuous pug mill and paver, and 4) concrete truck mixer. Two other techniques also were tested: 1) chip sealer and distributor truck and 2) distributor truck applying a rubberized asphalt seal.

Based on the ease of application, the Midland Cold-Mix Paver showed the most promise in applying an admix seal consisting of concrete sand and a +73 mV cationic medium set asphalt emulsion (CMS). Seals with depths of 7.6 to 15.2 cm (3 to 6 in.) were applied in widths 3 to 3.7 m (10 to 12 ft) to cover an area totaling 0.85 acres. The residual asphalt content of the seals averaged 22 wt%.

The BOMAG Soil Stabilizer was able to mix +18 mV cationic slow-set asphalt emulsion (CSS) directly with the tailings to form an admix about 10.6 cm (4 in.) deep covering about 0.2 acres. Some difficulties were encountered, however, in obtaining a uniform mix with the soil stabilizer. The Calenco Continuous Pug Mill was able to successfully mix the CMS emulsion with concrete sand, forming a good admix. Three asphalt emulsions were tested with this technique, i.e., 1) +73 mV CMS, 2) +50 mV CSS-1h/CMS mix, and 3) +18 mV CSS-1h. None of these emulsions worked very well for this particular technique because of problems in transporting the admix to the paver. (The admix would settle in the dump truck and would not flow into the paver.) For this reason we abandoned the technique. Preliminary tests with the concrete truck mixer were unsuccessful because of poor mix control; therefore this technique was not tested further. The use of a chip sealer to apply concrete sand followed by a distributor truck to spray on asphalt emulsion was partially successful. It is difficult, however, to obtain a uniform admix by this multipass technique.

After all the admixes were applied, they were allowed to dehydrate for several days before being rolled with a vibratory and

static steel roller to form the final 7.6-cm (3 in.) seal.

After the admix seals were completed, a hot rubberized asphalt seal was applied to an area of tailings 167 m² (200 yd²). A mat 3 to 6 mm (1/8- to 1/4-in.) thick was applied using a distributor truck. Since the material is a homogeneous asphalt rubber phase instead of the usual two-phase (ground-tire asphalt) mixture, it showed promise as a radon seal.

After all seal applications tests were completed, the test area was sampled and radon flux measurements were made. A biological barrier was applied to part of the test area followed by overburden application. Revegetation of the test site was then started.

Radon Field Measurements - H. D. Freeman

Field radon measurements of the Grand Junction tailings pile before and after sealing were compared. The results are shown in Table 22.1. Further Radon flux data will be obtained in the overburden over the Grand Junction test site after time is allowed for radon equilibrium in the overburden. In-depth analyses of current radon flux data is under way.

TABLE 22.1. Radon Flux Reductions Obtained at Grand Junction Test Site

<u>Sealing Technique</u>	<u>Flux Range, pCi/m² -sec</u>	<u>Average Flux Reduction, %</u>
Bare tailings (control)	86-1149 (409 avg.)	--
Midland Cold-mix Paver Seal	0-0.6	99.9
Fog seal	0.3-344	95.7
Chip seal	1.4-4.3	99.6
BOMAG MPH100		
Hydrostatic stabilizer seal	0.6-178	96.5
Hot rubberized asphalt seal	0.5-12.9	99.3

23. LINER EVALUATION FOR URANIUM MILL TAILINGS

J. L. Buelt - Project Manager

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

SUMMARY

Since initiating the liner program in mid-July, efforts have been directed primarily towards installing two prospective liners at the Grand Junction mill tailings site for field evaluation. The liners, a catalytic, airblown asphalt and a bentonite, gravel, and sand mixture, were installed and covered with tailings in a trench 0.75 m deep at the tailings site. Also, tailings samples from sites at Salt Lake City, Durango, and Shiprock have been obtained and partially analyzed for the characterization study.

FIELD STUDIES

The trench in which the liners were installed was 12 by 76 m, with a maximum depth of 0.75 m. It was first stabilized with a roadbase material and covered with a layer of soil. The catalytic asphalt membrane and clay liners were installed at opposite ends of the trench, separated by a clay dam for an independent assessment. The trench was then refilled with tailings and water and covered to eliminate significant evaporation.

The liners were instrumented to determine exposure conditions and moisture transport. The clay liner can also be monitored for

transport of hazardous chemicals and radionuclides. After 2 to 3 years' exposure the liners will be re-excavated and destructively analyzed to help correlate the results from accelerated laboratory tests.

CHARACTERIZATION STUDY

To help define liner exposure conditions in the laboratory, tailings samples have been obtained from three of the four priority sites considered for reclamation. Samples from the tailings pile at Salt Lake City have already been analyzed by ICP (inductively coupled argon plasma emission spectroscopy). Analyses of leachant samples from six different locations show acidity ranges from pH = 2.8 to neutral. Interestingly, calcium concentrations in the samples were at maximum solubility in the leachant as determined by the solubility product for calcium sulphate. This high-calcium concentration may be cause for concern for clay liners because of calcium's capacity to exchange with the sodium ions in some types of bentonite clay. Bentonites that are resistant to calcium ion exchange are now being evaluated.

DIRECTION

Besides monitoring the liners in the field and completing the characterization study, near-term future objectives are to evaluate

and select the most promising liner materials for laboratory testing. These tests will be carried out under conditions representative of a thousand-year exposure.

24. 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

Several laboratory and field tests of multilayer soil covers for radon control were started. Soils were tested for properties that could be used in an engineering design to control radon exhalation rates from uranium tailings. The key material properties were determined to be water content, bulk density, and radium content. The literature was surveyed and found lacking in data that fully describes radon transport through cover materials. In the past, key material properties of soil covers have not been measured routinely; this has necessitated tests to better describe the radon diffusion through soils.

A new approach to the determination of radon diffusion in soils and earth materials was developed. The bulk diffusion coefficient was determined in such a way that it included the effects of water content on radon diffusion directly. A power function relationship was developed between the effective diffusion coefficient and the air-filled porosity. It was found that radon diffusion is significantly reduced only when the air-filled porosity is <0.1 .

Prototype multilayer systems, including a clay/rock layer and a capillary barrier, were field-tested at Hanford to determine compaction and moisture-holding characteristics and were found to be suitable for more exten-

sive testing. Engineered cover systems were installed at Grand Junction, Colorado, and tested for radon control. Initial measurements of radon flux before and after cover placement generally agreed well with values calculated from our diffusion model. Continued measurements at the field site are planned to compare long-term diffusion effects on flux rates and to verify the effectiveness of thin cover systems that incorporate engineered moisture retention properties. Cover materials from several inactive sites have been collected, and radon diffusion tests are being run to verify model predictions of optimum cover thickness requirements.

MATERIAL TESTS AND MODELING - R. W. Nelson,
G. W. Gee, C. Oster and A. C. Campbell

Radon movement has traditionally been treated as a diffusion process, a description generally viewed as a realistic characterization of the actual mechanisms at work. The bulk radon diffusion coefficient is strongly dependent upon both the moisture content and the density or degree of compaction of the porous material. Both moisture content and compaction affect the air-filled pore space of the material through which the radon diffuses. Accordingly, consideration of the moisture movement and the density effects should yield a better description of

the radon diffusion process. A new approach for assessing radon diffusion was developed for this study that considers both density and moisture.

Radon diffusion tests were completed on laboratory columns. These tests were conducted on compacted clay/rock mixes at the radon diffusion test facility used by the Asphalt Emulsion Project at Hanford. Results of these tests confirm that air-filled porosity is the critical factor in determining the radon diffusion through porous materials. The bulk diffusion coefficients computed for the tested clay/rock mixes were found to vary from 1.7×10^{-6} to 2.3×10^{-5} cm^2/sec for air-filled porosities varying from 0.01 to 0.03 cm^3/cm^3 . Utilizing available data from these tests and the literature resulted in development of the power function relationship:

$$De'/Da^0 = a (P-\theta)^B$$

where

De' is an effective radon diffusivity in the porous media

Da^0 is the radon diffusivity in air

$P-\theta$ is the air-filled porosity

a, B are empirical constants.

Values for a and B were found to be 0.74 and 2.16, respectively.

We used this relationship to model radon diffusion through multilayer cover materials that had differing water contents and densities.

Characteristics are shown in Table 24.1 for a test case where radon diffusion was modeled in a multilayer system. The cover over the tailings consisted of soil materials that had the indicated physical properties and thicknesses. The layers are listed in sequence beginning at the soil surface.

When no cover was placed on the tailings, the calculated radon flux was 1179 $\text{pCi m}^{-2} \text{sec}^{-1}$ from the soil surface.

Table 24.2 reports computed surface radon fluxes of the multilayer described in Table 24.1 for a range of air-filled porosities in layer 3 (clay/rock). The data illustrate that a relatively thin (15 cm) layer of wet clay/rock material can effectively reduce the radon gas flux from the cover provided the

TABLE 24.1. Initial Characteristics of Multilayer Radon Cover System

Layer	Thickness, m	Material	Porosity, cm^3/cm^3	Density, g/cm^3	Radium, pCi/g
1	1.0	Overburden (clay soil)	0.47	1.37	0
2	0.3	Rock fill (≤ 3.8 cm dia)	0.32	1.80	0
3	0.15	Clay/rock mix	0.27	1.94	0
4	6.18	Tailings	0.46	1.47	1600

TABLE 24.2. Computed Radon Flux Attenuation, Through Table 24.1 Soil Cover, as a Function of Air-Filled Porosity ($P-\theta$) of Layer 3 (clay/rock)

Layer	Material	$P-\theta, \text{cm}^3/\text{cm}^3$	Radon Flux, $\text{pCi m}^{-2} \text{sec}^{-1}$
3	Clay/rock (15 cm thick)	0.25	283
		0.10	135
		0.00	0.78

layer has an air-filled porosity near zero. Field data at Grand Junction, Colorado, further support these observations. No attempt was made to characterize the cover material except through its physical properties, i.e., density and moisture content. This approach permits rapid testing of a wide variety of cases to determine optimum cover thickness without regard to specific cover type or detailed physical and chemical characterization.

FIELD TESTS - B. E. Opitz, D. R. Sherwood, and G. W. Gee

Radon Requirements

A field test was conducted at the uranium tailings site in Grand Junction, Colorado. A test site was prepared by removing the overburden material and leveling and compacting the tailings surface prior to application of cover material. Based on preliminary measurements at Hanford, a cover similar to that listed in Table 24.1, consisting of a wet clay/rock layer, capped by clean gravel and covered by overburden, was constructed at the test site. Four types of clay/rock mixes were used, varying in density and composition of rock, soil and clay. The average thickness of the clay/rock layers was 20 ± 5 cm for the test area.

Radon flux measurements of the test area, 76.2×30.5 m (250×100 ft), at Grand Junction were taken before and after the multilayer clay system was applied. The multilayer system test area was divided into 40 test areas with dimensions 7.6×7.6 m (25×25 ft) and then regrouped into test points 15.2×15.2 m (50×50 ft). Test points, labeled for future identification, were used both before and after the seal was applied to the tailings pile to directly com-

pare the radon fluxes before and after sealing. Radon measurements were made using a flow-through tent system described in the Asphalt Emulsion Project (this report).

Figure 24.1(a) shows the initial radon fluxes from the bare tailings before the multilayer clay seal was applied to the tailings pile. The values in that figure show that the flux was much lower in the northwest area of the plot than in the remainder of the test plot. This was due to a very high sand size tailings content (sands are defined as 74 to 2000 μ , and slimes are <74 μ) and a lower radium concentration (Table 24.3). Radon fluxes in the northwest area of the plot ranged from 50 to 550 $\text{pCi m}^{-2} \text{sec}^{-1}$ compared to radon fluxes as high as 1911 $\text{pCi m}^{-2} \text{sec}^{-1}$ in the slimes area of the test plot.

Table 24.3 shows the radium concentration, water content, and density for each quadrant of the test plot prior to cover placement. The smaller particles in the slimes area account for the higher radium concentration due to a much higher surface area than the sands. The moisture retentivity of the slimes is also evident from the analysis of the moisture content throughout the test plot. The water contents in the area of the sand size particles are in the range of 3 to 7 wt% compared to values ranging from 12 to 20 wt% in the slime area.

Radon flux rates through our seal after the tailings had been covered for 8 to 10 days are also shown in Figure 24.1(b). The cover dimensions were similar to those shown in Table 24.1 with layer 3, clay/rock mix, densities varying as shown in Figure 24.1(b). Results show radon flux substantially reduced: values of 96% to >99.5% reduction of radon gas from the tailings were achieved with the multilayer clay seal. From the results of these measurements it is apparent that

FIGURE 24.1. Measured Radon Flux Rates in pCi m⁻² sec⁻¹ for the Grand Junction Uranium Tailings Experimental Plots

thin, wet soil/rock layers can be used as effective radon barriers. The longevity of this effectiveness is the subject of additional research.

BIOBARRIER TESTS - B. E. Opitz, J. F. Cline, and K. A. Gano

For the multilayer clay system to attenuate the radon gas flux, the seal of the clay material over the tailings must be kept wet and intact. If the seal is broken, the break will act as a vent for radon gas to escape to the atmosphere. One problem associated with application of the cover at Grand Junction is penetration of the seal by ground burrowing animals as they dig their pathways and bur-

rows underground. Another is root penetration into the wet clay layer. Field studies were initiated in June at the Arid Lands Ecology (ALE) reserve operated for DOE by PNL. The purpose was to see if a natural material barrier could be designed so that it would prevent any burrowing animals or plant roots from intruding through our system and at the same time be feasible to place over the multilayer clay cover.

Animal Intrusion Tests

Four sites were selected at the ALE facility to do the animal intrusion studies. Each site consisted of an excavated hole containing a plywood box, 1.2 by 1.2 by 1.2 m, open

TABLE 24.3. Grand Junction Tailings Characteristics

Plot	Sample	Radium Content, pCi/g	Water Content, g/g	Air-Filled Porosity, cm ³ /cm ³	Bulk Density, g/cm ³
1	1	1711	0.199	0.40	1.07
	2	1680	0.172	0.35	1.20
	3	1585	0.184	0.29	1.29
	4	1099	0.141	0.25	1.48
	5	1675	0.148	0.37	1.23
	6	1689	0.165	0.36	1.20
	7	1720	0.170	0.34	1.23
	8	1764	0.171	0.39	1.14
2	1	427	0.035	0.44	1.38
	2	1639	0.166	0.40	1.12
	3	1450	0.158	0.29	1.36
	4	545	0.054	0.36	1.52
	5	1689	0.137	0.41	1.17
	6	1725	0.149	0.37	1.22
	7	1626	0.193	0.33	1.20
	8	1342	0.137	0.35	1.28
3	1	860	0.116	0.24	1.58
	2	1346	0.121	0.35	1.32
	3	2103	0.167	0.38	1.16
	4	1234	0.116	0.32	1.41
	5	1873	0.151	0.35	1.24
	6	1495	0.164	0.32	1.29
	7	1454	0.161	0.32	1.29
	8	1698	0.157	0.35	1.24
4	1	1878	0.170	0.43	1.07
	2	1738	0.169	0.34	1.23
	3	1540	0.142	0.36	1.25
	4	1968	0.196	0.40	1.06
	5	1729	0.165	0.36	1.20
	6	1716	0.134	0.39	1.23
	7	1396	0.123	0.36	1.31
	8	1693	0.164	0.36	1.21
5	1	1635	0.204	0.32	1.20
	2	2283	0.240	0.39	1.00
	3	1809	0.204	0.35	1.13
	4	1540	0.137	0.38	1.23
	5	1630	0.165	0.35	1.23
	6	1509	0.135	0.40	1.19
	7	2058	0.243	0.34	1.08
	8	1738	0.201	0.37	1.11

only at the top. Inside the box was a small-scale version of the multilayer cover that we planned to use at Grand Junction. The clay layer was laid over the mortar sand (to represent tailings) and compacted to form a 6-in. layer with the same inner dimensions of the plywood box. Over the compacted clay layer was the proposed barrier to be tested,

consisting of a 15-cm layer of ~3.8-cm crushed, washed river rock. A very thin layer of pea gravel was then spread over the crushed rock to fill voids and act as a base for the overburden to sit on instead of sifting through the larger size rock. The rest of the box was filled with overburden to the level of the surrounding area.

Ground Squirrel Intrusion Tests

A large wire screen cage was situated over two of the four test plots so that the test box was in one corner of the 3 by 4.5-m cage. A wire screen was placed over the floor of the cage except where the test box was, with a 2 to 5-cm layer of overburden covering the screen. This was done to ensure that the only place the animal could burrow deeper than 5 cm was in our test box.

Two ground squirrels were placed in each of the two cages in August, near the time they normally begin hibernation. Within 2 days the squirrels had tunneled in the section with the test plot and started their burrow. Each box had two or three entry or exit holes into the test box. It was evident that the ground squirrels had reached the barrier by the small amounts of pea gravel that had been pushed to the surface from on top of the crushed rock.

Plans are under way to keep the squirrels in the cage until they become active again in the spring. Future plans for spring and summer include excavating the two test boxes to learn how deep the tunnels are and whether the clay cover has been penetrated. Observations made in September showed a few pieces of the larger crushed rock on the surface, but at that time not enough was evident for the squirrels to have gone through the rock.

Ant Intrusion Tests

The other two test boxes made were for an intrusion study on penetration of the clay layer by ants. The boxes were designed and filled the same as the ground squirrel boxes were, but, to indicate how deeply the ants tunneled, zinc sulfide was sprinkled over the clay layer in one box and over the pea gravel layer in the other box. Zinc sulfide

was used because it is fluorescent in ultraviolet light. Shining an ultraviolet light over the ants' tunnel will enable us to see sulfide on the surface of the plot if the ants have reached the pea gravel in the one box or have gone through the crushed rock layer and reached the clay layer in the other box.

The ants were relocated onto our plot in August also, and had started the tunnel system within days. At the last inspection period there was no evidence of zinc sulfide on the surface of either box, and the exact depth of the tunnels was unknown.

No water loss has been detected to date from the clay layers in any of the test boxes.

Plant Intrusion Tests

In August, two plant intrusion studies boxes were built in the same fashion as the animal intrusion boxes but were only 0.6 by 0.6 by 1.2 m and were portable. The same sequence of sand, clay, rock and overburden was used to fill the small boxes as that used in the animal intrusion studies. Added to the clay layer as the top inch was being applied was 50 ppm cobalt chloride (CoCl_2); and added to the layer of overburden that initially covered the pea gravel layer was a 50-ppm concentration of lithium chloride (LiCl_2). These were added to indicate root depth and penetration in the box. In the event of root penetration of the rock layer, the LiCl_2 in the soil next to the rock will be readily absorbed by the roots and transported throughout the plant. The lithium can then be analyzed by atomic absorption spectroscopy. The same principle applies for root penetration of the clay layer. When the roots reach the moist clay layer, the CoCl_2 spike in the top 2 cm

of the cover will also be absorbed by the root and determined by atomic absorption. Vegetation was planted in the boxes in late September, and initial measurements are currently under way.

COMPOSITE COVER OPTIMIZATION MODELING -
Rogers and Associates

A general n-layer steady-state radon diffusion model has been developed to permit analysis of radon transport in multilayered systems and in the presence of moisture gradients. The multilayer model is being verified experimentally by means of layered soil

test columns containing uranium-tailings sources and site-specific cover materials that have been collected for this project. The source characterizations are nearly complete. Related time-dependent diffusion measurements for individual materials are being planned, and related quality control experiments with test materials are in progress. Field moisture probes have been emplaced and grab samples collected at five inactive tailings sites to characterize vertical moisture distributions during various seasons. Theoretical and experimental plans have also been made for accelerated testing of cover materials.

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

J. F. Cline - Project Manager

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

SUMMARY

Eight different polymers were combined with trifluralin in PCD systems. Trifluralin release rates were determined for each PCD system. The first pelletized PCD system was developed, the release rate determined, and the system placed into greenhouse experiment as the first step in field testing.

Trifluralin as a liquid (short term) was placed over the asphalt emulsion and multi-layer clay seals at the Grand Junction uranium tailings site. A stone layer also was installed over the same seals to test its effectiveness as a barrier to animal intrusions.

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

Trifluralin was studied with various organic matrices. These included not only homogeneous mixtures of trifluralin with the polymer, but also polymer/chemical reservoirs surrounded by a polymer coating that controls the diffusion rate of the trifluralin from the reservoir. Results of these preliminary studies indicate several good candidates in further studies that should lead to a bio-barrier for uranium mill tailings. Both the polyethylenes and the polypropylenes provided

very stable, readily available, and low cost polymers with low phytotoxin release rates. Based on these observations, polypropylene/trifluralin pellets were produced to be used in laboratory-scale lysimeters and greenhouse studies. The combination of greenhouse, lysimeter and flow system measurements will establish the density of pellets and the pellet release rate needed for field applications.

DETERMINE HERBICIDE RELEASE RATES FROM PCD SYSTEMS - F. G. Burton

Analysis using a continuous flow system was used to determine the release rates of trifluralin from PCD systems. Controlled release rates of selected PCD systems are shown in Table 25.1. These results indicate that there are a number of good polymer candidates for use in further studies leading to a biobarrier for uranium tailings. Polypropylene/trifluralin pellets will be run in a continuous flow system to determine the release rates in vitro.

PHYTOTOXICITY AND DEGRADATION STUDIES - D. A. Cataldo

The rate of trifluralin loss in soils resulting from microbial degradation and chemical decomposition will require that

TABLE 25.1. Release Rates of Trifluralin from Polymers

Polymer Type ^(a)	Release Rate, μg/cm ² /day ± SD	
Polyurethane (Estane 5714-F)	3.42	0.95
Dow Corning Silastic 382 (10% loading)	2.7	0.9
Polyester Hytrel 5525	7.32	1.70
Shell 520 polypropylene	4.23	0.45
Microthene F	~11	
USI Microthene MN 710-20 polyethylene	~10	
Microthene MN 710-20	~27	

(a) Contains 10% trifluralin in herbicide portion unless otherwise stated.

minimum effective levels for trifluralin be increased proportionally. Since we are concerned with potential long-term effects, degradation effects become important. In anticipation of these efforts, preliminary studies of trifluralin effects on glucose transport and metabolism (mineralization of carbon in glucose to CO₂). These studies have demonstrated no significant effect of trifluralin (1, 10, and 100 ppm) on either process in short-term experiments. In addition, ring-labeled (¹⁴C) trifluralin has been procured and experimental protocols developed for detailed evaluation of the decomposition and degradation of trifluralin.

GREENHOUSE AND FIELD STUDIES - J. F. Cline

Ten plant growth containers, 2 x 2 x 3 ft, were constructed and loaded as follows for testing of the first prepared pelletized PCD system. Two asphalt emulsion seals and two multilayer clay seals were placed 2 ft below the soil surface of the containers. Pellets were placed directly onto the seals and then covered with top soil. Four containers without seals were treated by placing the pellets in a thin layer 2 ft below the soil surface,

and the remaining two containers were controls without seals or pellets. All containers were irrigated and planted to barley.

Trifluralin was applied to the soil profiles to prevent plant root intrusion of the newly installed asphalt emulsion and multilayer clay seals at the Grand Junction site. Also a 1-ft layer of stones was placed over parts of the two seals to determine their effectiveness as a barrier to animal intrusion of the seals.

ANIMAL INTRUSION STUDY - K. A. Gano

The animal enclosures were completed, and Townsend ground squirrels were introduced. Four additional burrow boxes were installed and harvester ant colonies established in each to test asphalt and multilayer earth barriers.

A letter report on burrowing depths and habitat preferences of rodents and ants was issued during August 1980. In September, a site visit to the Grand Junction tailings pile was made and a rock barrier installed over a portion of the asphalt test area. This 25-ft² area will be used to test the barrier against prairie dogs in the spring of 1981.

26. REVEGETATION OF INACTIVE URANIUM TAILINGS SITES

L. L. Cadwell - Project Manager

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

SUMMARY

Test plot studies begun at the Grand Junction, Colorado, site will be used to evaluate the interaction between remedial action cover technologies and selected revegetation strategies. Under investigation are the relationship between vegetation and each of the methods being evaluated for sealing radon in the tailings, interaction of plants with herbicide barriers for preventing root intrusion, and plant requirements for soil depth.

Data on the characteristics of the individual sites were acquired. These included engineering reports on each site and soil data for areas surrounding most of the sites. A data retrieval system was set up to handle organization and recall of the information, and the use of the Plant Information Network (PIN) data base was begun. PIN, developed by Colorado State University for the Fish and Wildlife Service, contains information on vascular plant species in Colorado, Wyoming, South Dakota, and Montana. Through PIN, we obtained a preliminary list of plant species with possible revegetation potential in Colorado, South Dakota, and Wyoming.

TEST PLOTS - J. R. Skalski and R. H. Sauer (PNL) and M. A. Simonds (Century West Engineering Corp.)

Test plot studies were initiated at Grand Junction, Colorado, to evaluate the interaction between remedial action cover technologies and selected revegetation strategies. Results from additional test plots will also be used to compare and evaluate the relative effectiveness of revegetation methods selected to stabilize the surface of inactive uranium mill tailings piles.

The inactive mill tailings pile located at Grand Junction, Colorado, has been chosen for testing radon sealants as well as biological barriers for preventing plant root and animal intrusions into the sealants. Liners for minimizing the below-ground migration of hazardous components of uranium tailings are also being tested. Revegetation studies on the Grand Junction site will permit examination of relationships between vegetation and technologies for containing radon in the tailings. Asphalt emulsions and saturated clays will be examined as well as herbicide barriers that will limit plant root penetrations into sealant systems. Soil depth treatments over asphalt are also being investigated to determine minimum plant requirements.

The general accomplishments of this task have been to complete the experimental design for the test plot, to place contracts for constructing and planting the plot, and to start the earthmoving activities required for test plot construction. Soil amendments and seed were obtained for planting the test plot, and the laboratory calibrations of instruments for use at the test site are well under way.

PLANT SPECIES SELECTION - M. C. McShane and N. R. Hinds

During FY-1980, the primary activity of the Plant Species Selection Task was data acquisition. Because many types of data will be required in order to make well informed decisions concerning revegetation, a computerized data retrieval system was set up to provide efficient storage and retrieval of information available. Entries into the system are bibliographic and can be retrieved through the use of subject, author or genus keywords, dates of publication or entry on the system, reference type (for example, report, map, or article) or unique identification number. This system allows

- rapid updates of material on hand
- efficient sorting and recall of all data related to the uranium tailings sites
- immediate access to the amount and types of information available for each site.

Basic information on revegetation in general, on the uranium tailings sites themselves, and on soils surrounding the areas has now been obtained. Contacts established with State Soil Conservation Service Offices in the vicinity of uranium tailings sites provided us with soil maps as well as a list of counties for which information is presently unavailable. We are now in the process of acquiring additional sources for soils

information and obtaining climatic data for the areas surrounding uranium tailings sites.

One of the most useful sources of information on plant species with revegetation potential for uranium tailings sites in Colorado, Wyoming, and South Dakota has been in a data base called the Plant Information Network (PIN). PIN was developed for the Western Energy and Land Use Team of the U.S. Fish and Wildlife Service by Colorado State University. It contains information on all vascular plant species, native or naturalized, in Colorado, Wyoming, South Dakota, and Montana. For many plant species, information on their geographic, taxonomic, biologic, economic and ecologic attributes has also been cataloged.

To use PIN it was necessary to collect certain site-specific information. The Ford, Bacon and Davis engineering reports prepared for all the uranium tailings sites provided data on exact county locations and elevations for each site. PIN used this information to generate a preliminary list of plant species that may have revegetation potential for the uranium tailings sites in Colorado, South Dakota and Wyoming. Since plant communities do not follow state boundaries, it may also be possible to use PIN to assist in choosing plants for revegetation at uranium tailings sites located in other states but near areas covered by PIN.

Data on climate and soils also are very important parameters to consider in choosing plant species for revegetation. The Ford, Bacon and Davis engineering reports prepared for all the sites were reviewed for specific climatic and soils data pertaining to each site. These reports describe the radiological and physical characteristics of each inactive uranium tailings site and summarize the engineering alternatives available for compliance with Public Law 95-604.

Although they give useful preliminary information, they are probably inadequate to characterize the inactive mill tailings sites for a specific planting selection.

Climatic and soils data will be used together with PIN to select individual species or groups of species for revegetation trials

at uranium tailings sites. At sites where PIN cannot be used, these data will be supplemented with information from available literature. At sites where existing data are minimal, field sampling will be employed as necessary prior to species selection.

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