**Nuclear Waste Management
Quarterly Progress Report
January Through March
1981**

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

June 1981

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

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

June 1981

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Richland, Washington 99352

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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 October Through December 1980, PNL-3000-8.

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1. HIGH-LEVEL WASTE PROCESS DEVELOPMENT

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

The objective of the High-Level Process Development Program is threefold: 1) to process small volumes of nonradioactive and radioactive liquid wastes (commercial and defense) in laboratory-scale process equipment to define process effluent composition; to develop decontamination methods for the process effluents; and to evaluate the waste solidification processes and products; to develop the basic technical information for the design of waste containers, emphasizing the reference canisters for waste glass and including conceptual designs and material data for canisters for alternative waste forms and for barrier canisters; and 3) to analyze and document PNL-developed waste vitrification technology and the condition of the dismantled liquid-fed ceramic melter.

SUMMARY

The analysis of the technetium and iodine run in the Remote Laboratory Scale Waste Treatment Facility (RLSWTF) has been completed, and a document summarizing the results has been written. Analytical results for the samples taken during the December run at Savannah River Laboratory (SRL) have been received. A RLSWTF run was completed with simulated radioactive West Valley wastes. The NO_x destructor system was installed for nonradioactive tests.

The examination of samples removed from the original liquid-fed ceramic melter (LFCM) was completed. The primary interest areas this quarter included the corrosion of the metallic melter materials, the slag deposited on the floor of the melter, and completion of the static modeling of the melter refractory stresses.

For container development, PNL glass 77-260 was established as the reference commercial waste glass. The waste has a modified PW-7c composition. Full-scale and bench-scale glass canisters were filled and cross-sectioned to measure cracking levels.

A topical report, Decontamination of High-Level Waste Canisters, was issued.

RADIOACTIVE PROCESS DEVELOPMENT - C. A. Knox

During the calcination of simulated commercial wastes spiked with ⁹⁹Tc and ¹³¹I, 0.15% of the technetium and 31% of the iodine was volatilized. Most of the volatilized technetium was removed from the off-gas in the venturi scrubber, the first cleanup device in the process off-gas system. Approximately one-half of the volatilized iodine was removed in the venturi scrubber; 25%, however, of it reached the building stacks. A solid adsorbent was not used for this run but would be needed for the calcination of any wastes that have iodine present. Analytical results have been received for the feed, scrubber and off-gas samples which were taken during the December run with a SRL simulated waste composition. A run was completed with simulated radioactive West Valley Wastes in the RLSWTF. Numerous off-gas samples were taken. About 25 % of feed was processed to the spray calciner in-can melter, and two canisters of

glass were produced. A NO_x destructor has been installed for nonradioactive tests. A Safe Operating Procedure has been written and a safety review completed.

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

The examination of samples removed from the original LCFM was completed. The primary interest areas this quarter included the determination of the mechanisms of corrosion in the metallic melter materials, examination of the slag deposited on the floor of the melter, and completion of the static modeling of the melter refractory stresses.

Several different corrosion mechanisms were detected in the examination of the melter off-gas piping, the ionic booster electrodes, the Inconel plate installed above the melting cavity drain, and the melter pouring tip. A section of the melter off-gas piping, removed from near the melter, and the flexible metal bellows used to seal the ionic booster system exhibited similar corrosion patterns. Each component had been fabricated from 304L stainless steel and exposed to both the internal melter environment and ambient conditions. Sulfur compounds (sodium sulfate, sulfite compounds, and elemental sulfur) along with chlorine ions were detected in the materials, and the base alloys were found to be of depleted nickel. These components were found to be devoid of nickel at points where the metal had failed. These results indicate that some volatile nickel compound is forming in the temperature regime at which these metals are exposed and indicate the need to use a different alloy, more resistant to this specific degradation mechanism.

The ionic booster electrode, also made from 304L stainless steel, was shown to contain the proper nickel/iron, and nickel/chrome ratios for this alloy. The failure mode for this system was found to be formation of chrome carbide ("sensitization") at the weld zones and to a lesser extent at the grain boundaries. This sensitization results in eventual brittle failure of the affected metals. Chlorine and sulfur compounds were detected in only trace quantities.

The plate installed in the riser region of the melter was constructed of Inconel 690. This material was chrome-deficient in the base metal near the exposed surfaces. The riser plate contained numerous voids to a depth of ~ 0.1 cm at the exposed surfaces. A chromium-rich phase, present in some of the voids, indicated that chromium is migrating to the surface and forming pockets of a chrome-rich material and then a volatile chromium species that creates the voids. The composition of the chrome-rich phase has not been determined, but because this phase is not confined solely to the grain boundaries, chrome carbide is not indicated.

The melter pouring tip was fabricated from Inconel 690, but it exhibits different corrosion characteristics than the other metallic components. In this case, a multi-layered reaction zone exists. Nearest the glass a chromium-iron-nickel-manganese alloy has formed. Behind this layer is a band of chrome oxide, and behind this is a chromium-deficient layer of the base alloy.

The examination of the slag samples removed from the melter floor was completed, and the slag was found to be a complex mixture of phases including Cr-Fe-Mn-Ni spinels, Cr-Fe-Zn crystals, CeO_2 deposits, Al_2O_3 nodules, Ru-containing phases, a metallic Ni alloy, a variety of glass compositions, and

trace sulfur compounds. Also the slag concentrations of Ce, Cr, and Zn were shown to vary inversely to the concentrations of Fe, Mn, and Ni. These relative concentrations identify the glass formulation being processed when the slag phases precipitated.

The details of the original LFCM refractory design were coded for computer-simulated stress analysis. The stresses were simulated for three locations in the refractory: along the centerline; within the riser block, but not including the pouring channel; and in the melter sidewall, away from the riser block. These locations in the refractory were simulated using boundary conditions representative of both liquid feeding and idling modes of melter operation. The results of this analysis indicate that local stresses are present in the refractory that exceed the published rupture strength of Monofrax K-3.[®] These results support the theory that the cracks form due to the tensile stresses present at the back of the refractory wall and propagate toward the glass as determined by the principal stresses at the crack tip. A transient calculation is presently being performed to indicate the magnitude of the stress fields at the initiation of liquid feeding.

The major implications of the melter examination to date are that future melter designs must include input from thermal stress calculations to ensure that the melter will resist the stresses induced by the variety of thermal expansions exhibited by the materials of construction and by the thermal gradients present in the materials. Also, due to the variety of compounds condensing and volatilizing at different locations in the melter system, particular alloys must be selected to resist the specific cor-

rosion mechanism inherent to the application rather than relying on a few alloys to fill all of the melter applications.

VITRIFICATION TECHNOLOGY ANALYSIS AND DOCUMENTATION

As part of the technology documentation effort, two documents were issued:

- Annual Report on the Development and Characterization of Solidified Forms for Nuclear Wastes, 1979 (PNL-3465)
- Investigation of Foaming During Nuclear Defense Waste Solidification by Electric Melting (PNL-3552).

HIGH-LEVEL WASTE CONTAINER DEVELOPMENT - S. C. Slate

Work is proceeding on a document defining a reference commercial high-level waste composition and a reference canister design. PNL glass 77-260 was selected as the reference waste glass after an extensive review of commercial waste literature. New ORIGEN 2 runs were made to update data on the activity levels of the waste, a modified PW-7c. The waste and glass have been described by Ross (1978). This document will be issued as a topical report in the fourth quarter of FY 1981 (a major milestone).

Work has continued on developing crack-reduction techniques for filling and cooling canisters of glass. Seven full-scale canisters (24 in. dia by 10 ft long) have been cross sectioned to measure the cracking levels as a function of filling and cooling conditions. The glass surface area in these canisters has been found to be about 20 times the monolithic surface area. Two bench-scale canisters (6 in. dia by 3 ft long) have been filled. The first bench-scale test reproduced cracking levels similar to those found

[®]Registered trademark of the Carborundum Company, Niagara Falls, New York

in full-scale canisters. In the second test the canister was carefully insulated with 5 cm of insulation ($0.06 \text{ w/m-}^\circ\text{K}$) and was slow-cooled after filling. Cracking was reduced by about a factor of 10. Additional bench-scale tests and computer modeling will precede the full-scale confirmation test.

A new topical report, Decontamination of High-Level Waste Canisters by J. F. Nesbitt, S. C. Slate, and L. K. Fetrow, was issued this quarter. This report describes PNL

experience with decontamination of high-level waste canisters and details a conceptual design for an electropolishing decontamination system.

REFERENCE

Ross, W. A. et al. 1978. Annual Report on the Characterization of High Level Waste Glasses. PNL-2625, Pacific Northwest Laboratory, Richland, Washington.

2. ALTERNATIVE WASTE FORMS

J. M. Rusin - Project Manager

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

One vitreous and seven glass-ceramic waste forms were subjected to static leach tests. The glass-ceramic materials included basalt, celsian, and fresnoite, each containing 20 wt% simulated high-level waste calcine. The highest leach resistance was obtained for the basalt-based glass ceramic followed by basalt-based glass. All the glass ceramics are superior to 76-68 waste glass in the containment of all species except strontium.

Matrix metals and coatings have been characterized by the MCC-1 static leaching procedure. Aluminum-coated marbles exhibit negligible dissolution of glass constituents. The metal matrix experiments have been completed using a 1:10 surface area to solution volume, SA/V, ratio and a 1:1 SA/V ratio. Significant durability gains are noticed for lead, to a lesser extent for aluminum/silicon, while the lead/tin material shows an apparent leaching enhancement. Changing the SA/V ratio from 1:10 to 1:1 increases leachability.

Efforts to measure carbon leach rates in an oxygen-free system have been discontinued, and those in a radiation field have been resumed.

Water permeability testing to date has indicated the NiS-bonded graphite is water-tight and appears to be the probable best candidate. This material was also intact after hydrothermal testing at 250°C.

Twenty matrix samples containing simulated waste-glass marbles and supercalcine pellets have been produced for testing. Matrix materials consisted of metals, graphite, glass, cement, and castable refractories with waste-particle loadings of from 30-60 vol%.

Matrix waste-form samples have been successfully fabricated from titanium, aluminosilicate glass, and lead glass containing either SPC-4E supercalcine pellets or 76-68 glass beads. Glass matrices can be hot-pressed to full density at viscosities at least as high as $10^{11.5}$ poise. Glass-waste marbles should be kept over 10^4 poise to avoid expensive interaction with the matrix. Green, unsintered supercalcine pellets were densified during hot-pressing of a glass matrix, thereby eliminating the pellet sintering operation.

A review of the literature suggests that corrosion-resistant, castable ceramic materials that do not require sintering for solidification may be grouped into three

general classifications: 1) calcium silicate (Portland) cements, 2) calcium aluminate cements, and 3) chemical setting cements. The applications of the first and second groups to nuclear waste treatment have been extensively studied. In those studies, however, the waste was incorporated in the cement as a slurry or a calcined powder and not as a consolidated aggregate, which is the present application.

Commercial castable refractories were evaluated for use as a ceramic matrix for waste forms containing glass beads and supercalcine pellets. Three of the eleven products examined are being subjected to 14-day, 95°C deionized water leach tests. Preparations are being made to fabricate and test hot-pressed, ceramic-matrix samples containing supercalcine pellets.

All major equipment required for hot-cell fabrication of crystalline waste forms has been procured. Concentrations of additives required to formulate the SPC-4 composition from the high-level liquid waste solution in Tank 112, 324 Building hot cells have been calculated. Crystalline phases present in a nonradioactive hot-pressed SPC-4 pellet were identified by x-ray diffraction.

Most of the checkout is now complete, including major modifications to some of the purchased equipment for hot-cell fabrication of crystalline waste forms. Some limitations have been identified; however, they will not severely affect the work. The procedures are in final form, but a pre-startup review will be necessary before operations can begin. Progress has slowed, pending resolution of the D-cell suspension of operations.

Two lots of pellets were produced by disc pelletization using calcined simulated Savannah River Plant (SRP) sludge and two different frit additives. The sintered pel-

lets from both lots are strong and have a matte surface. The cesium, cerium, strontium and neodymium concentrations of the pellets are very near the values specified by the Savannah River Laboratory (SRL).

About 80 kg of marbles, "spiked" with cesium, strontium, neodymium and cerium, were produced for coating tests. A glass coating of SRL Frit 211 was applied to 10 kg of these marbles. The rest of the marbles were used for flame-spray coating tests. The glass coating was about 0.5 mm thick and had closed porosity. Initial leach test results indicate rapid attack on the rough-textured coating, but no release of spiking elements.

Low-temperature (LT) carbon vapor deposition coatings have been applied to samples of supercalcine (SPC-4E) pellets. One sample was coated with 20 to 25 μm of LT-PyC (pyrolytic coating), whereas the other sample was first coated with 25 to 30 μm of LT-PyC followed by a 6- μm coating of chromium carbide, Cr_7C_3 .

LT-PyC coating of SRP simulated waste pellets (MB-2) was improved by heat treatment at 500°C for 2 hr in a fluidized bed followed by a precoat of Cr_7C_3 . However, the LT-PyC coating quality is still less than desired.

Several ceramic and metallic coatings have been applied to TDS-211 simulated waste glass marbles using thermal spray equipment. The particles were agitated either by vibration or mechanical tumbling during the coating step. The coated particles are undergoing a partial MCC-1 leach for scoping purposes.

A document covering the metal encapsulation process development work at PNL in the last 2 years has been prepared and is in final clearance.

WASTE FORM DEVELOPMENT AND CHARACTERIZATION

Glass Ceramic Leaching - R. O. Lokken

One vitreous and seven glass-ceramic waste forms were leach-tested. The leaching conditions employed in the tests were similar to those outlined in the Materials Characterization Center's static leach test procedure. The major deviation was the use of polypropylene containers instead of Teflon.[®] The samples were monolithic solids with a nominal surface area of 400 mm² by cutting with

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200-mesh diamond-impregnated blades. Three leachant solutions (deionized water, silicate water, and brine) were used with a solution volume to sample surface area ratio of 10 m⁻¹. The materials were allowed to leach at 90°C for 3, 7, 14, or 28 days.

Figure 2.1 compares normalized elemental losses of silicon, molybdenum, cesium, and strontium for four of the waste forms from this study with those for 76-68 reference waste glass following leaching for 28 days at 90°C in deionized water. As seen in the figure, the releases from basalt glass ceramic with PW-8a-2 are quite low, with the largest release ≈ 1.5 g/m². Recrystallization decreased leachability, as seen by comparing

FIGURE 2.1. Normalized Elemental Losses for Glass Ceramics and 76-68 Waste Glass

the basalt glass ceramic with basalt glass containing PW-8a-2. For these species shown, the improvement is about fourfold. The cesium release from celsian and fresnoite glass ceramics is roughly the same, $\sim 20 \text{ g/m}^2$, while molybdenum releases are quite different— 21.5 g/m^2 compared to 3.5 g/m^2 for celsian and fresnoite, respectively. The figure shows that under these conditions the glass ceramics are superior to 76-68 waste glass in the containment of all species except strontium, which approaches zero release from 76-68.

The results of the leach tests permit the following conclusions:

- Basalt glass ceramics containing simulated high-level waste calcines show normalized elemental losses lowest of the glass ceramics investigated.
- Waste stream compositional variations have an insignificant effect on the overall durability of any of the glass ceramic waste forms.
- Recrystallization of basalt-based products improve leach resistance by factors of ~ 2 to ~ 10 over their vitreous counterparts.
- The leachability of basalt glass ceramics in silicate water is nearly the same as in deionized water.
- The leachability of celsian and fresnoite glass ceramics in silicate water is lower than in deionized water, except for the release of molybdenum from fresnoite, which increases slightly.
- All eight waste forms tested demonstrate normalized elemental losses lower than a reference high-level waste glass (76-68).

Carbon Leach Testing - W. J. Gray

Efforts to perform leach tests in an oxygen-free system have still not been suc-

cessful; therefore it was decided to abandon them. Since earlier results showed that the leach (oxidation) reaction of carbon was with oxygen rather than water, it follows that the reaction with water is much slower. Thus the leach (oxidation) rate of carbon in oxygen-free water is known to be several orders of magnitude lower than for any other material that has been measured, despite the fact that we have been unable to actually measure a rate for carbon.

Efforts to measure the reaction of carbon with water in the presence of a ^{60}Co radiation field have been resumed, but no results are yet available.

Coated Particle Leaching - C. Q. Buckwalter

Glass marbles of Savannah River TDS-211 composition spiked with selected rare earth metal oxides that were coated with aluminum (described here under Thermal Spray Coating Development) were subjected to the MCC-1 static leach tests in deionized water. The results of this experiment show that this coating is an effective barrier to water/glass interaction. Figure 2.2 shows the results of selected glass constituents detected in the leachate of spiked and aluminum-coated marbles. All glass constituent leaching is retarded by aluminum coating to near solution analyses detection limits.

Metal Matrix Leaching - C. Q. Buckwalter

To compare the effect of metals on the leaching of 76-68 glass marbles, MCC-1 static leach tests were conducted using metal containers in place of the reference Teflon container. Materials used in these containers were Pb, Pb - 10%Sn, Al - 12%Sn, Ti, and Ti - 6%Al - 4%V. A constant

FIGURE 2.2. Leach Resistance of Uncoated and Aluminum-Coated TDS-211 Simulated Waste Glass Marbles

surface area to solution volume, SA/V, ratio of 1:10 was first employed to evaluate the relative effect of the metal materials. A 1:1 SA/V was also used to determine whether varying the SA/V ratio significantly changed the leaching results. All experiments were run at 90°C in deionized water for 14 days.

Table 2.1 reports the leachate analysis in normalized units for Si, B, Mo, Na and pH for the 1:10 SA/V ratio. The materials are listed in the order of improved leach resistance. A good indication of glass leach resistance is the amount of glass formers, in this case silicon and boron, which leach. The lead container shows about two orders of magnitude improvement in leach resistance as compared to Teflon. The aluminum alloy improves leaching by one order of magnitude. Both Pb/Sn and the titanium alloy have a negligible effect. The titanium matrix shows an apparent increase in glass leaching.

Changing the SA/V ratio from 1:10 to 1:1 increases leaching by one to three orders of

magnitude. The leach resistance of 76-68 glass in lead containers at a SA/V of 1:1 is still better than that of glass in Teflon at a 1:10 ratio. The Pb/Sn alloy exhibits greatly increased leaching as a consequence of the SA/V ratio change.

Ceramic Matrix Literature Review - H. T. Blair

The current investigation of castable ceramic matrix materials for encapsulating pelletized nuclear waste forms has identified three general types of cements that may have potential. One group includes the hydraulic-bonded calcium silicate or Portland cements. These cements are further subdivided into five types, plus various Portland cements and pozzolan combinations. Another castable cement group is the calcium aluminates that are also hydraulically bonded. These cements are often used in refractory applications, but are also superior to Portland cements in resistance to attack by sulfates, seawater,

TABLE 2.1. Ranking of Matrix Materials and Their Effect on the Chemical Durability of PNL 76-68 Glass^(a)

Container Material	Element Leached, normalized g/m ²				
	B	Mo	Na	Si	pH
Pb	0.7	<0.08	1.1	0.1	7.53
Al - 12%Si	4.6	1.1	5.7	1.1	6.94
Pb - 10%Sn	24.5	9.0	25.7	9.5	8.81
Teflon	23.0	23.1	21.4	25.6	9.52
Titanium alloy	22.3	24.1	21.8	16.0	9.48
Titanium	32.1	35.5	35.4	24.2	9.49

(a) MCC-1 static tests, SA/V = 1:10, 90°C deionized water, 14 days.

carbonic acid, and weak mineral acid solutions. The third group is chemical-setting cements based on alkali silicates that form silicon polymers to bind the materials together. These cements are extensively used in the chemical processing industries. They are resistant to most acids and alkalis from a pH of 0 to 9 and are highly resistant to sulfates. However, they are more difficult to process and may leave highly alkaline liquid residues when set.

The Portland and the calcium aluminate cements were studied at SRP (Stone 1977), Oak Ridge National Laboratory (Moore et al. 1979), Pennsylvania State University (Roy and Gouda 1974) and Kernforschungszentrum Karlsruhe (Rudolph and Koster 1979) for fixation of nuclear waste sludges or calcines. These studies included the addition of fly ash, pozzolan, bentonitic and illitic clays, and barium silicate hydrate to the waste and cement mixture to improve the leach resistance. Various heat and pressure treatments were also evaluated, and the thermal and radiolytic behaviors were studied. The conclusions of these studies are that concrete is a suitable material for

fixation of nuclear waste. Several of these studies have also found that the high-alumina cements are superior to the Portland cements and that the Portland-pozzolan cements are slightly better than the other Portland types. Many of the additives mentioned above did reduce the leaching of specific waste isotopes such as cesium and strontium.

None of the studies reviewed so far has evaluated the use of a pelletized waste form as an aggregate in a cement matrix. Encapsulation of a waste pellet in concrete was evaluated at Pennsylvania State University, and the results were promising (Roy and Gouda 1974). No reports of the use of chemical-setting cements for the fixation of nuclear wastes have been reviewed yet, but we know that some work has been done in this area.

Commercially produced cements of all three types were selected and ordered to represent the complete spectrum of compositions available. Initially samples for leach testing are being cast and cured according to the suppliers' recommendations. Additives and heat and pressure treating may be evaluated later.

Ceramic Matrix Fabrication - D. W. BriteCastable Refractories

A series of commercial castable refractories was evaluated for use as a ceramic matrix for waste forms containing glass beads and supercalcine pellets. Preliminary screening tests using only the matrix materials were conducted on eleven products from three different companies. All the samples tested were very porous after curing according to the manufacturer's recommendations. Open porosities of the samples that were not badly distorted, cracked, or excessively chalky were in the 30 to 40% range.

Four castables were selected for further testing with glass beads and supercalcine pellets. The powders were mixed with water to form a thick slurry and poured into 1-in. ID Teflon vials, the beads or pellets were added, and the vials were vibrated until the beads or pellets were completely submerged in the slurry. The lids were placed on the vials without engaging the threads, and the castings were allowed to cure over a week-end at room temperature.

Two of the samples were oven-dried at 93°C for 4 hr. The other samples were fired at 850°C for 1 hr for those containing supercalcine pellets, and those containing glass beads were fired at 500°C for 1 hr. The samples are being evaluated for waste retention properties using 14-day, 95°C deionized water MCC-1 leach tests.

Hot Pressed Ceramics

Preparations are being made to hot-press ceramic matrix samples containing supercalcine pellets. Materials to be evaluated include Al_2O_3 , TiO_2 , and ZrO_2 . Specimens similar in size to the castable refractory

samples will be vacuum hot-pressed at 1200°C in graphite dies.

Titanium/Glass Matrix Development -

W. E. Gurwell

Small, mini-matrix waste forms (2.2 cm dia) were successfully hot-pressed for various waste core-matrix combinations. They are SPC-4E supercalcine pellets in matrices of Ti-6Al-4V alloy, lead glass (Corning 7570®), and aluminosilicate glass (Corning 1720®) as well as 76-68 glass beads in matrices of lead glass and aluminosilicate glass. Typical hot-pressing temperatures were 400°C for lead glass, 800°C for aluminosilicate glass and 1100°C for Ti-6Al-4V. Metallography shows thin reaction layers (nil to about 50 μm) between the waste cores and matrix materials.

Hot-pressing experiments to date indicate that the fabrication behavior of both glass matrices and glass marbles can be related to their viscosity-temperature characteristics. For example, glass matrices pressed at 10 MPa can be fully densified in about 20 min at a temperature where the glass viscosity is $10^{10.5}$ poise; furthermore, at $10^{11.5}$ poise 60 min are required, and at $10^{9.5}$ poise <5 min. Glass marbles need to be kept over 10^4 poise to avoid infiltrating coarse, -36 mesh, titanium matrix powder or reacting excessively with the fine, -100 mesh, glass matrix powder.

Normally, supercalcine pellets are densified by sintering at 1200°C before encapsulation in a matrix. However, it has been shown that pellets can be densified during the matrix hot-pressing. Green SPC-4E pellets were dispersed in aluminosilicate glass

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powder and hot-pressed at 10 MPa and 1000°C. The pellets were densified to about 3.3 g/cc, and the glass matrix was fully dense. The pellet density is typical of pellets sintered at 1200°C, but volatilization losses should be much lower at the 1000°C hot-pressing temperature.

Graphite Matrix Materials - L. R. Bunnell and W. J. Gray

Two graphitic materials are currently being examined as candidate matrices. One of these is made from natural graphite flake bonded with NiS by NUKEM in West Germany. The other is similar to the matrix used by General Atomic (GA) to make HTGR fuel, and is graphite flour bonded by either petroleum pitch (thermoplastic) or an artificial resin (thermosetting). Samples of NiS-bonded graphite, with and without supercalcine, have been provided free by NUKEM, and GA has produced samples of supercalcine-containing matrix under contract. In addition, water permeability tests were done on a few selected graphites that were impregnated with various resins with good radiation resistance.

Water permeability of several candidates was determined using an experimental apparatus in which dry helium sweeps over the dry face of a graphite sample that is water-wetted and gas-pressurized on its other face. Any water picked up by the gas is detected by use of a downstream P_2O_5 cell. By its design, this apparatus operates in the range of water flow of 5×10^{-10} ml/sec to 4×10^{-6} ml/sec. A sample that has permeability measurable by this apparatus is probably unsuitable as a matrix material. Results to date are summarized in Table 2.2.

Thus far, only the NiS-bonded graphite appears to be completely impermeable. When

polycrystalline graphites are impregnated with resin, penetration is limited to that fraction of the pore system with communication to the outer surface. Thus, when some of the outer surface is removed, the material becomes permeable again. The materials produced by General Atomic are permeable. However, it may be possible for them to produce impermeable materials, for example, by increasing the binder fraction.

The NiS-bonded graphite made by NUKEM and containing SPC-2P supercalcine was submitted for leach testing under hydrothermal conditions (150, 200, 250°C) for 336 hr in Parr bombs. ICP analyses are not yet complete, but the samples appeared to be in good condition. Some signs of hydration products were seen on pellet ends, but the sides were in remarkably good condition, clearly showing the scratches made by the die they were pressed in. The graphite is well-aligned on these surfaces, in a skin which presents little NiS to the water.

Matrix Waste Forms Evaluation - J. W. Wald

Matrix samples, incorporating simulated 76-68 glass and SPC-4E supercalcine, have been fabricated for leach testing as part of a scoping evaluation of matrix waste-form composites. The matrix materials included metals, graphite, glass, and ceramics and were formed into right circular cylindrical specimens, ~25 mm dia by 40 mm length. Each candidate matrix was produced in pairs, one containing 76-68 glass, the other containing SPC-4E supercalcine, with waste particle loadings ranging from 30 to 60 vol%. The variation in waste-particle loading was not by design, but merely an experimental limitation due to the relatively small diameter of the matrix cylinders compared to the waste-particle diameter. In a full size

TABLE 2.2. Water-Permeability Test Results

Sample Description	Pressure, psig	Time To First Water Detection, hr	Comments
NiS-Bonded Graphite (NUKEM)	180	17 hr, no penetration	Specimen appeared completely impermeable.
ATJ graphite- vacuum-impregnated with polyfurfuryl alcohol	180	6 hr, no penetration. Immediate penetration after 0.120 in. was machined off each face.	Resin apparently does not penetrate all internal porosity.
Karbate, [®] graphite impregnated with phenolic resin	180	8	Sampling eliminated original outer surfaces, apparently opened new flow paths.
Graphite flour, pitch binder, uncarbonized, containing 3-mm glass beads (General Atomic)	180	<1	This material and the next, probably do not contain enough binder to make them impermeable.
Graphite flour, resin binder, uncarbonized, containing 3-mm glass beads (General Atomic)	180	<1	
Flowrate, ml/sec			
Graphite flour, bonded with Polyfurfuryl alcohol	100	<5 x 10 ⁻¹⁰ (undetectable)	
	140	7.4 x 10 ⁻⁸	
	160	2.8 x 10 ⁻⁷	
	180	4.3 x 10 ⁻⁷	

[®]Registered trademark of Union Carbide Corporation.

scale-up; it is expected that the waste-particle loading will approach 64%. Specific matrices under investigation include vacuum-cast lead, Pb - 10%Sn, and Al - 12%Si; hot-pressed Ti - 6%Al - 4%V; Corning 7570 and 1720 glass; resin- and pitch-based graphite; graphite bound with inorganic binders; Type II Portland cement; Al₂O₃-based castable ceramic; and an MgO-based castable ceramic. Currently under development are sintered ceramics based in titania, alumina, or zirconia and additional chemically stable ceramic castables.

The chief consideration in this scoping evaluation is the chemical stability of the

matrix waste-form composite. This is being assessed by a static leach test in deionized water at a temperature of 90°C for a period of 14 days using a surface area to solution volume ratio of 1 to 10. Solution analyses are conducted by standard ICP techniques.

Preliminary analyses have indicated that castable ceramics and graphite matrix samples have a high water permeability. Since all leach results are not yet compiled, it is not possible to consider high permeability necessarily disadvantageous, since it may be that matrix buffering could conceivably reduce the leaching process. This type of buffering has been observed recently in the

metal-based matrices, where even though metal-glass-solution contact was made, the leach rate was reduced over a similar test of glass in solution alone. This effect is under investigation. From a physical standpoint, the hot pressed matrix materials appear to offer a good barrier with specimens produced with no waste particles showing on the outside surfaces. Detailed matrix material waste material compatibility investigations are being accomplished to better define the fabrication details.

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

Additional equipment purchased for hot-cell fabrication of crystalline waste forms was received and transferred to the 324 Building this quarter. This equipment included an electronic analytical balance for weighing to 0.0001 g, a cut-off saw for sectioning sintered or hot-pressed pellets, and platinum/platinum-rhodium thermocouples for sintering and hot-pressing temperature control.

Concentrations of additives to the high-level liquid waste solution in Tank 112, 324 Building hot cells, required to formulate the SPC-4 composition, were provided by Professor G. J. McCarthy of North Dakota State University. The additives and their required concentrations in Tank 112 solution prior to spray calcination are:

Calcium	16.06 mM/l
Strontium	6.33 mM/l
Aluminum	19.36 mM/l
Silicon	62.90 mM/l

A SPC-4P supercalcline pellet, hot-pressed in air in an alumina die for 2 hr at 1200°C and 3100 psi, was examined for crystalline phases using x-ray diffraction. The material appears to have well-formed crystallinity of

the following major supercalcline phases: apatite, fluorite, monazite, scheelite, and spinel. However, pollucite is absent.

Absence of pollucite may be related to the pollucite behavior observed for cold-pressed and sintered SPC-4P powder samples fired at 1200°C for 2, 6, and 24 hr. The intensity of the pollucite XRD peak decreased with firing time. Cesium volatility measurements showed that cesium loss did not fully account for the 92% reduction in pollucite after 24 hr at 1200°C. It was suggested that the pollucite disappears due to reaction with other SPC-4P components. The absence of the pollucite in the hot-pressed sample after only 2 hr could be due to a more rapid rate of reaction of the pollucite and other SPC-4P components under the enhanced interparticle contact pressure and increased surface area existing during hot-pressing.

HOT-CELL DEMONSTRATION - L. L. Petkus and C. A. Knox

Most of the preparations for the supercalcline run in D-Cell have been completed. The vessels in the facility have been flushed. A new venturi nozzle has been fabricated to replace one that was plugged. The press and both furnaces have been extensively modified for remote operation. All process operations have been simulated for cold-pressing and sintering and hot-pressing. A drill press has been tested for removing hot-pressed pellets from the alumina die using a diamond core drill. The drill press allowed for pellet removal without damage. Some of the equipment is recognized to be potentially short-lived items. Remote repair or replacement has been provided for in all cases.

The Run Book is in final form and ready for approval. The final pressing parameters

have been decided upon, and the Hot Run Plan will be completed and routed for comment. After all elements of the demonstration are ready, a prestartup review will be conducted.

PROCESS AND EQUIPMENT DEVELOPMENT

SRL Pellet Development - H. T. Blair

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

Two different lots of pellets that meet these criteria were produced at PNL during the last reporting period. Approximately 20 kg of one lot, which was identified as MB-1, were made by adding 25 wt% Frit 131 and 5 wt% $\text{Ba}(\text{PO}_3)_2$ to the calcined sludge,

pelletizing, and sintering at 1000°C. The other lot, identified as MB-2, consists of ~10 kg of pellets made from a mixture of 30 wt% lead glass frit and 70 wt% calcined sludge. These pellets were sintered at 1060°C. Samples from these pellet lots were fully characterized, and the important physical and chemical properties are reported in Table 2.3. The pellets in both lots have good physical integrity. Their surfaces are free of pits and have a matte finish. The level of the trace elements cerium, cesium, strontium, and neodymium in pellets are very close to the values specified by SRL. The oxide contents of the specified elements are presented in Table 2.4 as a ratio to the Fe_2O_3 content, as directed by SRL, to avoid the shifts in the values of weight percent caused by the additives used to produce the desired ceramic phases in the pellets.

Low-Temperature Pyrolytic Carbon -

B. L. Blanco and M. F. Browning (BCL)

During this quarter two samples were prepared of low-temperature (LT) PyC-coated SPC-4E supercalcine particles (0.7 to 1.4 mm). One sample had a single coating of

TABLE 2.3. Physical Properties and Trace Elements in MB-1 and MB-2 Sample Pellets

Property	MB-1	MB-2
Total porosity, vol%	20.25-24.71	19.22-20.80
Surface connected porosity, cc of Hg	0.0016-.0131	0.0012-.0076
Open porosity, vol%	<1	<1
Immersion density, g/cc	2.69 ± 0.04	3.22 ± 0.01
Crush strength, lbft	1150	710
Thermal expansion 100-400°C, °C ⁻¹	12 x 10 ⁻⁶	10 x 10 ⁻⁶
Thermal expansion 400-700°C, °C ⁻¹	13 x 10 ⁻⁶	11 x 10 ⁻⁶
Carbon content, ppm	≤10	120-160
Sulfur content, %	0.22-0.28	0.14-0.21
Chlorine content, ppm	925->1000	114-204
Fluorine content, ppm	57-59	131-204

TABLE 2.4. Comparison of Specified Oxide Content and Analytical Results for MB-1 and MB-2

Oxide	Specified Ratio to Fe_2O_3	MB-1 Ratio	MB-2 Ratio
Fe_2O_3	1	1	1
Al_2O_3	0.782	0.604	0.650
MnO_2	0.275	0.304	0.300
CaO	0.074	0.072	0.079
NiO	0.124	0.113	0.118
SiO_2	0.024	0.619	0.544
Na_2O	0.140	0.361	0.273
Na_2SO_4	0.026	0.041	0.028
Ce_2O_3	0.021	0.022	0.023
Nd_2O_3	0.021	0.025	0.024
SrO	0.011	0.014	0.012
Cs_2O	0.011	0.010	0.008

LT PyC with thickness ranging from 20 to 25 μm . The second sample contained an inner coating of LT PyC 25 to 30 μm thick and an outer coating of chromium carbide, Cr_7C_3 6 μm thick.

Both samples were prepared in a 25-mm fluidized bed using a diluent. The LT-PyC coatings were applied at $\sim 500^\circ\text{C}$ using 2.85 mol% C_2H_2 , 1 to 7×10^{-3} mol% $\text{Ni}(\text{CO})_4$, and the balance H_2 in a diluent of molybdenum. A diluent of zirconia was used to apply the chromium carbide at 450°C using chromium dicumene as the reactant.

The nonuniform quality of SPC-4E (0.7-to-1.4 mm) material made the preparation of a uniformly-coated material impossible. It was determined that the most satisfactory method of conditioning the substrate to receive a uniform LT-PyC coating was to apply a 1- μm chromium carbide precoat to infiltrate and coat the substrate particles. The chromium carbide appears to strengthen the SPC-4E and minimize spalling of the particle surface. The use of a thin film of chromium carbide did not reduce the quality of the LT-PyC coating as had the nickel or iron coatings applied last quarter for the same

purpose. Therefore, samples 1 and 2 above were precoated with 1 μm of chromium carbide.

Diluents of several combinations of density and particle size were examined for achieving uniform circulation of MB-2 sintered pellets (<13 mm dia SRP waste composition) in a 60-mm fluidized-bed reactor. A diluent bulk density of between 2.5 and 4.0 g/cm^3 is desirable for the temperature range and flowrates typical of the LT-PyC coating process. A diluent of iron with a bulk density of 3 to 3.5 g/cm^3 and a particle size of 100 to 250 μm was identified and will be used to apply LT-PyC coatings to MB-1 substrate.

LT-PyC coverage of the MB-1 pellets was improved, but not sufficiently to produce a satisfactory coated particle, by subjecting the MB-1 substrate to a treatment in the fluidized bed for 2 hr at 500°C followed by a precoat with chromium carbide.

Thermal Spray Coating Development - K. H. Oma and L. E. Peterson

Several coating materials were applied to simulated TDS-211 waste glass marbles as part

of a screening study to identify the more leach-resistant and corrosion-resistant coatings. The glass marbles are of a SRP simulated waste composition and contain neodymium, cerium, strontium, and cesium trace elements. The thermal spray systems and coatings used are as outlined in Table 2.5.

Particles were agitated during the coating step to ensure a uniform coating. A vibrated agitator was used with the metallizing wire gun, and a larger drum type tumbler was used with the other spray processes. The drum agitator is equipped with a variable speed reversible drive motor and a barrel which has screened ports to facilitate gas and heat removal from the particle bed.

Glass-Coated Marbles - S. C. Slate,
D. P. Williams, and M. L. Longaker

The purpose of this activity is to develop a technique for applying a glass coating to a 1.0-cm waste glass marble while it is being formed. The technique that has been developed consists of applying the coating glass in the form of a fine powder to the marble as it forms. Heat from the marble and external heaters melt the glass powder, causing it to fuse to form a glass coating with closed porosity.

About 10 kg of marbles were coated with SRL Frit 211, which is a low-melting borosilicate glass. This frit is white and has a maximum particle size of 0.074 mm. The

TABLE 2.5. Thermal Spray Systems and Coatings Used To Coat Glass Marbles

System	Coating Material
Plasma spray system	TiO ₂
	Al ₂ O ₃
	Al ₂ O ₃ - 13.0% TiO ₂
	Ni - 9.0% Cr, 7.0% Al, 5.5% Mo, 5.0% Fe
	Cu
	Ni - 5.5% Al, 5.0% Mo
	TiH ₂
	Al
	Polyester
	Ni Alloy/TiO ₂ (Duplex)
Metallizing arc gun	Al
Flame spray system	TiO ₂
Metallizing wire gun	Al - 6% Si
	Zn
	Cu
	Sn - 7.5% Sb, 3.5% Cu, 0.25% Pb
	Pb
	Sn Alloy/Zn (Duplex)

frit was applied to the forming marbles, which were then exposed to high-intensity, infra-red heaters. Some fusing of the frit occurred, although not as much as predicted. It was discovered that the adsorbency of the white frit was very low for the spectrum of energy from the heaters. The addition of iron oxide to the frit improved its adsorbency and the amount of fusion in the coating.

Leach tests have been started on several of the glass-coated marbles. Initial results show that attack on the rough-textured coating is high. This is due to the coating composition, which has not been optimized for leach resistance, and to the high surface area due to roughness. No release of cesium, cerium, neodymium, or strontium from the glass marbles has been detected.

Process Development - R. G. Nelson, J. F. Nesbitt, and S. C. Slate

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

The demonstrations described in the report have shown that glass marbles 5 to 10 mm in diameter can be encapsulated on an

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

REFERENCES

- Moore, J. G., E. Newman, and G. C. Rogers. 1979. Radioactive Waste Fixation in FUETAP (Formed Under Elevated Temperature and Pressure) Concretes - Experimental Program and Initial Results. ORNL/TM-6573, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- Roy, D. M. and G. R. Gouda. 1974. Hot-Pressed Cement in Radioactive Waste Management. Materials Research Laboratory, University Park, Pennsylvania.
- Rudolph, G. and R. Koster. 1979. Material Studies on Solidification of Medium-Level Waste Solutions with Cement: Leachability of Cesium and Strontium. PNL-TR-387. Translated from German, Stoffliche Untersuchungen zur Verfestigung mittelaktiver Abfällösungen mit Zement: Auslangbarkeit von Cäsium und Strontium. KFK-2842, Kernforschungszentrum, Karlsruhe, GmbH, Karlsruhe, Federal Republic of Germany.
- Stone, J. A. 1977. Evaluation of Concrete as a Matrix for Solidification of Savannah River Plant Waste. DP-1448, Savannah River Laboratory, Aiken, South Carolina.

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

Four MCC test methods were submitted to the MRB for its approval. These methods are MCC-1 Static Leach Test; MCC-2 Static, High-Temperature Leach Test; MCC-6 Method for Testing Alpha-Decay Effects in Radioactive Waste Forms; and MCC-11 Tensile-Strength Test. Once these test methods and others scheduled for submission to the MRB are approved, they will be included in the first edition of the Nuclear Waste Materials Handbook, which will be issued in September 1981.

The MCC invited experts from national laboratories, the National Bureau of Standards, industry, and a university to PNL to discuss and further define the MCC-10 Impact Test. Conclusions based on this meeting will be considered in preparing the final draft of the MCC-10 Impact Test, which is expected to yield data that can predict the relative impact resistance of waste forms in a full-scale accident.

Studies to compare glass and SYNROC waste-form specimens using MCC tests are under way for Savannah River Laboratory. Similar studies are also under way to compare transuranic (TRU) waste forms for the Transuranic Waste Systems Office.

Publications this quarter included Workshop on the Irradiation Effects in Nuclear Waste Forms Summary Report, PNL-3588, and Workshop on Corrosion of Engineered Barriers Summary Report, PNL-3720. A State-of-the-Art Review of Materials Properties of Nuclear Waste Forms, PNL-3802, was prepared and will be published next quarter.

STANDARDIZED TEST PROCEDURES - R. D. Nelson, J. E. Mendel, M. D. Merz, and D. M. Strachan

Work is continuing on the preparation of standardized test methods to be submitted to the MRB for their approval and for inclusion in the Nuclear Waste Materials Handbook. Four of the planned test methods have already been submitted: 1) MCC-1 Static Leach Test, 2) MCC-2 Static High-Temperature Leach Test, 3) MCC-6 Method for Testing Alpha-Decay Effects in Radioactive Waste Forms, and 4) MCC-11 Tensile-Strength Test. These and other drafted test methods are listed below, with a summary of their purpose:

MCC-1	Static Leach Test - To evaluate chemical durability of waste forms by measuring elemental mass loss from monolithic specimens exposed to aqueous solution at <100°C.
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- MCC-2 Static, High-Temperature Leach Test - To evaluate chemical durability of waste forms by measuring elemental mass loss from monolithic specimens exposed to aqueous solutions between 100 and 190°C.
- MCC-3 Maximum Solubility Limits Test - To evaluate chemical durability of waste forms by measuring elemental mass loss from powered specimens during exposure to aqueous solutions between 90 and 190°C.
- MCC-4 Low-Flow-Rate Leach Test - To evaluate chemical durability of waste forms by assessing the leach rate of monolithic specimens as a function of flow rate and temperature in aqueous solutions <100°C.
- MCC-5 Soxhlet Test - To evaluate chemical durability of waste forms by measuring elemental mass losses from monolithic specimens at the boiling point of water under ambient conditions and in redistilled water.
- MCC-6 Method for Testing Alpha-Decay Effects in Radioactive Waste Forms - To prepare waste-form specimens in which the effect of alpha-emitting radionuclides is accelerated so that changes in waste-form properties induced by alpha decay can be measured in experimentally practicable times.
- MCC-7 Method for Testing Thermal Phase Stability in Radioactive waste Forms - To prepare waste-form specimens for measurement of the effects of thermally activated phase transformations on waste-form properties.
- MCC-8 High-temperature Vaporization Test - To evaluate waste-form stabilities at 100°C by measuring elemental mass loss due to vaporization of fission products and other condensable elements.
- MCC-9 Thermal Gas Generation Test - To establish conditions by which waste forms can be tested for potential pressurization of a canister up to 800°C due to loss of noncondensable gases from the waste forms.
- MCC-10 Brittle-Materials Impact Test - To obtain the fragmentation characteristics of brittle waste forms as a function of impact energy absorbed by the specimen by specifying standard conditions for impact loading and subsequent analysis of the post-test fragments.
- MCC-11 Tensile-Strength Test - To measure the static tensile strength of brittle waste forms.
- MCC-101 Unstressed Static-Immersion Corrosion Test - To evaluate the uniform and localized corrosion response of candidate engineered-barrier materials under static exposure to solutions simulating the ground waters characteristic of geologic repositories.
- MCC-102 Unstressed Flowing-Immersion Test - To evaluate the uniform and localized corrosion response of candidate engineered-barrier materials under exposure to flowing simulated ground waters.
- MCC-103 Stress-Corrosion-Cracking Test - To measure stress-corrosion-cracking susceptibility in smooth, statically loaded specimens.
- MCC-104 Stress-Corrosion Crack Growth Threshold Test - To determine the threshold stress intensity for crack growth of candidate engineered-barrier materials using precracked-tension specimens.

- MCC-105 Radiation Corrosion Test - To measure the effects of radiation on uniform and nonuniform corrosion rates, including stress-corrosion cracking of candidate engineered-barrier materials.
- MCC-106 Corrosion Test with Near-Field Materials - To determine possible additional crevice and pitting effects introduced by near-field materials (backfill, rocks, etc.).
- MCC-107 Mechanical Depassivation Test - To determine corrosion resistance when protective film is disrupted in a "scratch test."

CORROSION OF ENGINEERED BARRIERS - M. D. Merz

The MCC is defining standardized corrosion test methods that will be used to characterize potential canister and overpack materials for the waste package. Seven test methods have been identified to account for the effects of temperature, site-specific water chemistry, possible stresses, radiation, and near-field materials in contact with barriers. The test methods selected can be used for screening of candidate materials, but MCC intends to define the corrosion evaluation used in conjunction with the tests such that test data can be used to predict the service life of barrier materials. Accelerated testing will be an essential element of these test methods to allow extrapolation to service times much greater than test durations.

The MCC will define seven corrosion tests to provide corrosion rate data that can be extrapolated to 1000-year service with, as yet undetermined, statistical confidence. Various methods for accelerating corrosion will be identified by each test where appropriate. Principal emphasis will be on accel-

eration by temperature, stress, and water chemistry, as discussed in the Corrosion Workshop Report issued this quarter.

MCC WORKSHOPS - M. D. Merz

A report summarizing the results of the MCC Workshop on Corrosion of Engineered Barriers was published. The report identifies test procedures that address failure modes of uniform corrosion, pitting and crevice corrosion, stress corrosion, and hydrogen effects that can cause delayed failures. Some conclusions are that the principal areas requiring further consideration beyond current engineering practices involve the analyses of pitting, crevice corrosion, and stress corrosion, especially with respect to quantitative predictions of the lifetime of barriers. Also, special techniques involving accelerated corrosion testing for uniform attack will require development.

The MCC conducted a meeting on March 25 and 26 to discuss and further define the MCC-10 Impact Test. This meeting included experts on impact testing from several national laboratories, the National Bureau of Standards, industry, and a university.

TESTING - D. M. Strachan, J. E. Mendel, and J. W. Johnston

Testing is under way using the MCC test methods. Glass and SYNROC waste-form samples were received from Savannah River Laboratory (SRL) and are being prepared for the MCC waste-form tests. Initial testing will emphasize MCC-1 Static Leach Test; MCC-4 Low-Flow-Rate Leach Test; MCC-2 Static, High-Temperature Leach Test; and possibly MCC-3 Maximum Solubility Limits

Test. Results of this testing will assist in selecting waste forms.

A 6-month test matrix for the TRU specimens using the MCC-1 Static Leach Test is under way. Also, an analytical method involving the extraction of americium and plutonium from the leachates of TRU waste forms was developed. In other TRU waste efforts, tests to determine the sorption of plutonium on the Teflon® walls yielded inconclusive results because the plutonium concentrations were too low. Higher plutonium concentrations are currently being studied.

Data from the MCC-1 Static-Leach-Test round robin are being analyzed and a summary report is being prepared. Data to be included in the first report come from Radian, Exxon Idaho, Lawrence Livermore Laboratory, University of Florida, Oak Ridge National Laboratory, and the Materials Characterization Center. A subsequent report will include the complete data from all the participants. Test materials have also been sent to five foreign countries (Australia, Sweden, West Germany, France, and Italy) because of their interest in participating in the round-robin study.

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

Efforts are being directed toward obtaining the most suitable and effective equipment for use in developing and conducting MCC tests. The shielded x-ray diffractometer (SXR) has been permanently placed next to the hot cells. All power supplies and additional control equipment were received, and the complete SXR is being assembled.

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The scanning electron microscope (SEM) for nuclear waste materials will soon be installed. The associated x-ray fluorescence unit will be delivered later. Low-level radioactive materials will be permitted in the instrument shortly after installation.

Conceptual planning and tentative selection of an inductively coupled plasma spectrometer (ICP) were completed and detailed purchase specifications prepared. A free-standing shielded glovebox approach was selected, with only the plasma section of the spectrometer enclosed in the glovebox. Test specimens will be prepared in the adjacent hot cell, with dissolved specimens and test solutions to be transferred to the glovebox in a small transfer cask.

Basic hot-cell metallography equipment has been selected. In addition, interfacing between the transfer cask and the hot cell was conceptually designed.

The MCC-10 Impact Test is based on the concept of using a drop tower, which has now been installed. In addition, the test-specimen holding fixture was delivered that will be used to collect the fines from the impact test.

INFORMATION DISSEMINATION – R. D. Nelson, J. E. Mendel, O. F. Hill, and J. L. Hooper

The Nuclear Waste Materials Handbook is being prepared for issue in September. The format of this handbook, which will contain MCC test methods, data, and supplementary information, will permit easy updating by additions, revisions, and deletions. The Nuclear Waste Materials Handbook will be the authoritative reference for all waste package materials going into geologic repositories. It will emphasize data related to chemical, physical, mechanical, and radiation stability, interactions with other

materials, chemical and microstructural analyses, and other properties that relate to long-term safety.

In the interim before publication of the Nuclear Waste Materials Handbook, the MCC has prepared A State-of-the-Art Review of Materials Properties of Nuclear Waste Forms, which summarizes the existing materials

properties data for the nuclear waste forms being developed for immobilization of high-level radioactive waste. This report, which will be published next quarter, includes physical properties, mechanical properties, chemical durability, vaporization, radiation effects, and thermal-phase stability.

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4. TRU WASTE IMMOBILIZATION

W. A. Ross - Project Manager

The objectives of this project are to develop new waste-form concepts, to conduct a comparative assessment of alternative immobilization systems for selected transuranic wastes, and to recommend the most promising technology for development and application.

SUMMARY

This quarter's activities have focused on the comparative study of and development of high-durability waste forms. A preliminary study on monazite formation with TRU wastes and development of a second-generation basalt glass ceramic were completed. Leach testing of the comparative study samples was started along with detailed microstructure and physical property measurements. The cost estimate for the in-can glass melting system was completed, and estimates for transportation and repository costs were obtained.

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

Rare earth (RE) monazite (REPO_4) has been proposed as a plutonium host phase for several ceramic waste forms. The present study was undertaken to evaluate whether or not TRU-containing monazite could be prepared. Four oxides were selected as tailoring additives to the "blended TRU waste residue" (Platt and Powell 1980) currently being studied at PNL. The principal additives for all samples were 5 wt% mixed RE oxides and 0.1 wt% ThO_2 . The RE oxides are necessary for formation of monazite and ThO_2 was se-

lected to simulate PuO_2 in this phase of the study. The other three oxides (Al_2O_3 , P_2O_5 , and TiO_2) are already present in the original waste composition. However, the original composition was modified by further additions of these oxides as shown in Table 4.1. P_2O_5 was selected as a variable in the composition because it is a primary component of monazite. Al_2O_3 is a glass network former, as is P_2O_5 ; and TiO_2 is a glass network intermediate, as are the RE oxides. Because Al_2O_3 and TiO_2 are thus potential competitors of P_2O_5 and the RE oxides in crystal formation, they were also varied in the composition to determine their effects on monazite formation and to investigate the possibility of forming another RE crystal phase instead of monazite.

The 14 different compositions listed in Table 4.1 were prepared by melting about 4 g of well-mixed powders in covered alumina crucibles at 1300°C (for all P_2O_5 enriched compositions) or 1500°C for 1 hr. This was immediately followed by a crystal-nucleating heat treatment consisting of a 6°C/hr slow cool between 900 and 500°C . These samples were then heat-treated at either 650, 800, 950, or 1100°C for 15 days to promote crystal growth.

TABLE 4.1. Monazite Present After 15-Day Anneals at 650, 800, 950, and 1100°C

Additives to Blended TRU Composition	Wt% Monazite ($\pm 0.5\%$)			
	650°C	800°C	950°C	1100°C
None	2.0 ^(a)	3.0	3.5	5.0
15 wt% Al ₂ O ₃	4.0	5.0	7.0	8.0
15 wt% P ₂ O ₅	4.5	8.0	7.5	5.5
15 wt% TiO ₂	3.5	2.5	4.0	7.0
10 wt% Al ₂ O ₃	6.0	5.5	6.0	NT ^(b)
10 wt% P ₂ O ₅	6.0	5.0	6.0	NT
10 wt% TiO ₂	6.0	6.0	7.0	NT
5 wt% Al ₂ O ₃	3.5	NT	NT	NT
5 wt% P ₂ O ₅	NT	5.0	NT	NT
5 wt% TiO ₂	NT	NT	4.5	NT
10 wt% Al ₂ O ₃	4.0	4.0	5.5	5.5
10 wt% P ₂ O ₅				
10 wt% Al ₂ O ₃	2.0	4.0	7.0	8.5
10 wt% TiO ₂				
10 wt% P ₂ O ₅	5.0 ^(a)	6.5	8.0	5.5
10 wt% TiO ₂				
5 wt% Al ₂ O ₃	4.0	4.5	6.5	5.5
5 wt% P ₂ O ₅				
5 wt% TiO ₂				

(a) Some x-ray diffraction evidence for a RE-Ca-B-Si-O phase but <2 wt% maximum.

(b) NT = not tested.

Monazite was the only RE crystalline phase observed in these specimens except for some inconclusive evidence of a RE borosilicate at 650°C in two compositions. Table 4.1 shows the amount of monazite detected by x-ray diffraction for each annealed composition. It seems that adding 5 wt% RE oxides to the original composition is sufficient to form significant monazite. Monazite yield tends to increase with anneal temperature; the maximum monazite yield observed for compositions not enriched with P₂O₅ is at 1100°C, but is lower, near 950°C or 800°C, for P₂O₅-enriched compositions. This could be a result of the lower viscosity in the P₂O₅-enriched compositions.

Increasing the amount of P₂O₅ in the TRU composition does increase monazite yield as expected. The excess phosphate, however, caused higher crystalline yields of other phases as well. The suitability of these other phases must also be considered in designing a final tailored composition. The results show that monazite readily forms for various compositions. Generally, the yield is between 50 and 80 wt% of maximum, indicating that a "tailored" heat treatment may produce a higher yield of monazite than do large (>10 wt%) compositional additives. The distribution of ThO₂ or TRU elements between the glass and the monazite remains to be determined.

BASALT GLASS CERAMIC DEVELOPMENT -

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

In an effort to develop and optimize basalt-based TRU waste forms, five materials were produced and subjected to 13 heat-treatment schemes to determine total and specific crystallinity. The materials tested include:

- 100% TRU blended waste (TBW-R-G)
- Pomona basalt with 20 wt% TBW-R (BG-20)
- Pomona basalt with 35 wt% TBW-R (BG-35)
- Pomona basalt with 50 wt% TBW-R (BG-50)
- Synthetic basalt glass with 63 wt% TBW-R (SBG-63).

Each waste form was melted at 1300°C, then subjected to nucleation temperatures from 700 to 800°C for 1/2 to 6 hr and then to growth temperatures of 950 to 1050°C for 1 to 8 hr. The total crystallinity of all materials ranged from 18.5% to 52.5%.

Four crystalline phases were observed in the samples, with the formation and relative amount dependent on composition and heat treatment. The two major phases include a solid solution between a calcium-magnesium-iron-aluminum silicate and sodium-calcium-magnesium-aluminum silicate, and a continuous solid solution of Fe_3O_4 to TiFe_2O_4 . The other two phases include Fe_2O_3 (hematite) with zinc, chromium, aluminum, titanium, and magnesium as phase impurities, and a sodium-calcium-aluminum silicate (plagioclase). The latter phase was detected in samples that had been heat-treated to 1050°C, and only in the samples containing pomona basalt.

The phase compositions and amounts varied little with large changes in heat treatments. Single-stage slow cooling also produced similar phases. This indicates that basalt glass ceramics may be practically produced on a large scale because the product would not be sensitive to small changes in process parameters.

Based on the x-ray diffraction analysis, four glass ceramic materials were prepared for MCC-1 type leach testing. The materials and heat treatment conditions are listed in Table 4.2.

The decrease of leach rates for sodium and the alkaline earths after heat treatment is evidence that these materials are largely absorbed from the residual glass into the crystals during heat treatment. Table 4.3 shows the normalized mass losses after 7 days of the MCC-1 static leach test at 90°C in deionized water. Results for only one parent glass and its corresponding glass ceramic are shown because results for the other materials were almost identical. Shown for comparison are 7-day results for 76-68 glass (Ross 1978) and for 3203M glass, a high-temperature borosilicate waste glass. With the BG-35 as with the other basalt products, the release of silicon, aluminum, and calcium is reduced by factors of 15 to 20 after heat treatment; sodium release is reduced by a factor of 9. Iron release increases after heat treatment, possibly because of the lower pH in the leachate.

COMPARATIVE TESTING - J. H. Westsik, Jr., and R. P. May

The TRU program, in cooperation with the Materials Characterization Center, is conducting leach tests on six TRU waste forms. The TRU program is conducting 40°C tests for 28 and 182 days, while the MCC is conducting 90°C tests for 1, 7, 14, 28, 56, 91, and 182 days. The leachants are the standard silicate, brine, and deionized waters specified in the MCC-1 static leach test procedure. During the quarter, the 40°C and 90°C, 182-day tests were started on the cast hydraulic cement, cold-pressed hydraulic cement, borosilicate glass, aluminosilicate glass, sintered silicate ceramic, and basalt

TABLE 4.2. Composition and Heat Treatment of Basalt Glass Ceramics

Constituent	Wt%		
	BG-35 Basalt Glass with 35 wt% TRU Waste	BG-50 Basalt Glass with 50 wt% TRU Waste	SBG-63 Synthetic Basalt Glass with 63 wt% TRU Waste
SiO ₂	47.7	46.1	47.0
P ₂ O ₅	2.3	2.7	3.3
Al ₂ O ₃	10.9	10.1	9.4
Na ₂ O	4.9	5.2	5.5
MgO	5.7	5.4	5.3
CaO	9.1	8.8	9.1
SrO	0.08	0.09	0.09
BaO	0.16	0.18	0.20
TiO ₂	4.1	4.2	4.2
Cr ₂ O ₃	0.07	0.08	0.09
MnO ₂	0.14	0.13	0.14
Fe ₂ O ₃	14.6	15.4	15.4
CuO	0.11	0.07	0.06
ZnO	0.21	0.23	0.30
CeO ₂	--	1.3	--
Two-stage heat treatments used to produce	No. 1 700°C, 1/2 hr 950°C, 4 hr	700°C, 1/2 hr 950°C, 4 hr	700°C, 1/2 hr 950°C, 4 hr
Glass ceramics	No. 2 700°C, 2 hr 1050°C, 8 hr		

TABLE 4.3. Seven-Day Static Leach Results, Normalized g/m²
(conditions: deionized water, 90°C, SA/V = 10 m⁻¹)

Element	76-68 Low-Temp. Borosilicate Ground	BG-35 Parent Basalt Glass	BGC-35-2 Basalt Glass Ceramic	3203M High-Temp. Borosilicate Glass
Si	14.8	4.9	0.31	0.5
Al	NP(a)	4.3	0.23	0.4
Fe	0.05	0.01	0.02	0.02
Na	18.5	4.4	0.47	0.7
Ca	1.55	3.9	0.29	0.6

(a) NP = not present in glass.

glass-ceramic. The 28-day tests on the two cements and the borosilicate glass were also started.

Measurements of density, porosity, surface area, microstructure and crystallinity were also begun.

ANALYSIS OF ACTINIDES IN TRU WASTE FORM

LEACHATES - C. O. Harvey and F. P. Roberts

Testing of the di(2-ethylhexyl) phosphoric acid extraction method for the measurement of plutonium indicates that it will be suitable.

Several areas of concern have been investigated. The standard deviation of the results with the extraction method on each of the three solutions used in the leach testing was found to be not significantly different from that expected from counting statistics.

Acid treatment tests for particulate or polymeric plutonium in borosilicate glass were conducted. The effect of this treatment was insignificant, indicating the absence of nonextractable plutonium.

The valence state of the plutonium present in the leachate can affect the extraction efficiency. Extraction of the +3 and +4 is complete if contacting is vigorous. Plutonium in the +6 state is not efficiently extracted. Overall, the method appears satisfactory for our application and will be used for our subsequent analysis of plutonium in leachates.

The determination of americium by gamma counting was further investigated by counting the leachates from a 7-day leach test on glass. While the measurement is possible this way, the low count rate and poor counting efficiency would require long (12 hr or more) counting times and produce large uncertainties. An extraction technique using the same extractant-scintillator as for

plutonium is being investigated. The method looks promising but is not yet fully developed.

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

A detailed description of the in-can glass melting (ICGM) process has been worked out as the basis or reference process for the TRU immobilization processes. Specific unit process descriptions for the ICGM process completed to date include:

- Low-specific activity (LSA) ash load-in system
- High-specific activity (HSA) ash load-in system
- Process sludge drying system
- Solids blending/feeding system
- In-can melting system
- Canister processing.

Many of the above systems will also be used as descriptions of the other processes. These detailed descriptions form the bases of our process evaluation task.

A preliminary cost estimate of the in-can melting process was completed by Kaiser Engineers and is summarized as follows:

ICM Cost Estimate, 1981 \$M

Facility and construction costs	\$31.1
Operating costs/yr (30-yr life)	5.3
Maintenance costs/yr (30-yr life)	0.4
Decommissioning (after 30-yr life)	1.8

Evaluation of these costs indicates that 30-yr operating costs would be the major portion of the overall costs. The major operating cost is that for the stainless steel canisters, 28 in. dia by 5 ft tall. It appears that for ICGM to be competitive, other designs need to be considered to reduce container costs.

Other costs to be determined as an integral part of this comparative study include

transportation and repository disposal costs. The transportation costs were determined assuming truck transport with the TRUPACT as the shipping container. The truck TRUPACT container will hold six 6-pack arrangements of 55-gal drums or two 4-pack arrangements of the 28-in.-dia-by-5-ft-tall canisters. The charges for each round-trip truck shipment between Rocky Flats and the Waste Isolation Pilot Plant were determined in another study to be ~\$1500. Using these data, a transportation cost/year was calculated for each process and is shown in Table 4.4.

The preliminary repository costs assume a reference repository as described in the Commercial Waste Management GEIS. That document enumerates the costs per 55-gal drum in 1978 dollars for four types of repositories. These costs/drum for each geologic medium are: salt \$900; granite \$1400; shale \$1300; and basalt \$1800. The repository costs need to be updated and also determined for the large canisters, and adjusted for quantity.

These preliminary estimates indicate that processing will probably be the predominant cost and that transportation costs will not be very significant.

TABLE 4.4. Transportation Cost Estimates, 1980 \$

Process	Containers/yr	Truck Shipments/yr	Truck Charges/yr
In-can glass melting ^(a)	308	39	\$ 58,500
Joule-heated glass melting	795	32	48,000
Glass marble	1590	45	67,500
Basalt glass ceramic ^(a)	440	55	82,500
Cast cement	2450	69	103,500
Pressed cement	3505	98	147,000
Cold-pressed sintered ceramics	2880	80	120,000

(a) Canisters 28 in. dia. by 5 ft tall; all others 55-gal drums.

REFERENCES

Department of Energy. 1979. Technology for Commercial Radioactive Waste Management. DOE/ET-0028, Vol. 5, p. 10.A.81.

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

Ross, W. A. et al. 1978. Annual Report on the Characterization of High-Level Waste Glasses. PNL-2625, Pacific Northwest Laboratory, Richland, Washington.

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5. TRU WASTE DECONTAMINATION

R. P. Allen - Project Manager

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

SUMMARY

Three TRU-contaminated glove boxes with 258 ft² of contaminated surface area were decontaminated to non-TRU levels. Improved procedures were developed for the removal of HEPA filters and stored material from inside the glove boxes, and for high-pressure water cleaning of the interior surfaces prior to disassembly. A new transition piece was installed to connect the high-production vibratory finisher to the supporting glove box line. A multi-energy gamma assay system has been assembled under subcontract with the Los Alamos Scientific Laboratory (LASL). The data acquisition system for automated collection and monitoring of criticality safety data was installed. A ³He neutron slab detector system was assembled for the manual acquisition of criticality safety data.

PROCESS DEMONSTRATION

Substantial progress was made in the process demonstration work during this reporting period. Routine integrated operation of the disassembly, sectioning, and decontamination systems continued with the processing of three TRU-contaminated glove boxes. Im-

proved procedures were developed for the initial glove box preparation and precleaning process: high-efficiency particulate air (HEPA) filter removal, removal of equipment stored inside the glove boxes, and precleaning of the glove boxes with a high-pressure water spray.

Three TRU-contaminated glove boxes with 258 ft² of contaminated surface area were disassembled; sectioned using nibblers, plasma arc torch, hydraulic shear, and circular and reciprocating saws; and decontaminated to non-TRU levels using vibratory finishing. The decontaminated material and components included the Plexiglas® glove box panels, the plastic glove ports, the Hypalon® gloves, and the stainless steel frame. The only major component of the glove boxes not decontaminated was the HEPA filter. The glove boxes occupied a volume of ~130 ft³.

The metallic portions of the glove boxes were sectioned into strips ~6 in. wide using a nibbler and the plasma arc torch. The nibbler was used wherever possible because it is a fast, effective cutting tool that does not entrain contamination during cutting. The plasma arc torch was used only as

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required to make cuts in irregularly shaped portions of the metal. The 6-in.-wide strips were then sectioned into pieces 6 in. by 8 in. using the heavy-duty, double-cut hydraulic shear. The combination of the nibbler and shear greatly facilitated the sectioning task and significantly reduced the time required for this operation.

Previous experience has shown that the HEPA filter is a major contributor of loose contamination in a glove box during disassembly and sectioning. Therefore, removal of the HEPA filter should be an initial step in the processing of a glove box. A successful procedure for the removal of HEPA filters from glove boxes with minimal contamination spread was developed and demonstrated during this reporting period.

The procedure for HEPA filter removal involved taping a plastic bag around the opening of the HEPA filter compartment. The HEPA filter was then carefully removed into this bag and the bag was twisted to seal in the filter. The bag and filter were then removed. This procedure proved to be fast and effective and virtually eliminated spread of contamination from the HEPA filter.

Another major contributor of loose contamination in a glove box during disassembly and sectioning is the equipment inside the glove box. During decommissioning, it is standard procedure to put extra equipment inside glove boxes before removal to save on storage space for the waste. While storage of equipment inside glove boxes may reduce the storage volume of the waste, it makes it virtually impossible to adequately preclean the inside of glove boxes and fix loose contamination. Therefore, like HEPA filters, all stored equipment must be removed from glove boxes early in their preparation.

The stored equipment is removed after the glove box has been placed in the sectioning/

pretreatment facility. Personnel, wearing suitable protective clothing and equipment, must enter the sectioning/pretreatment facility to remove the stored equipment from the glove box. This can be done with minimal spread of contamination following the traditional procedure of removing the equipment into a bag-out bag and sealing the bag. Previous attempts to remove the equipment directly into the sectioning/pretreatment facility through open glove box ports had resulted in high airborne contamination levels inside the sectioning/pretreatment facility.

The final procedural improvement involved the precleaning of the glove box interior with high-pressure water sprays after removal of all loose equipment. A high-pressure spray wand is inserted through a glove or bag-out bag that is attached to the glove box, and the penetration is sealed by taping. During the cleaning operation, the water is removed from inside the glove box by a wet/dry vacuum cleaner. Previous attempts at spray-washing through open glove box ports had resulted in high airborne levels within the sectioning/pretreatment facility.

Contamination spread during HEPA filter removal, equipment removal, and spray-washing was further controlled by the installation of an auxiliary HEPA-filtered exhaust system in the sectioning/pretreatment facility capable of maintaining negative pressure in the glove boxes during these procedures. The system (Figure 5.1) consists of a filter housing, HEPA filter, and flexible duct. The system was permanently installed in the sectioning/pretreatment facility and connected to the existing HEPA filtered exhaust system, which services the entire building. This approach provides a quick and effective method of maintaining glove boxes at a negative pressure with respect to the sectioning/

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FIGURE 5.1. HEPA-Filtered Exhaust System in Sectioning/Pretreatment Facility Used To Maintain Negative Pressure in Glove Boxes During Pretreatment Operations

pretreatment facility during pretreatment operations. The system is connected to a glove box prior to initiation of any work inside the glove box and remains attached until the loose contamination has been properly immobilized with fixatives.

VIBRATORY FINISHING DECONTAMINATION SYSTEM

The redesigned transition piece that connects the high-production annular vibratory finisher to the supporting glove box line and sectioning/pretreatment facility has been installed. The transition piece (Figure 5.2) is supported by the glove box line and is completely isolated from contact with the vibratory finisher. Only a flanged adaptor and flexible bellows are attached to the containment lid of the vibratory finisher process tub. The flexible bellows is protected by an internal metal shield that is part of the transition piece. This new design appears to have overcome the problems encountered with the original design, which

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FIGURE 5.2. Redesigned Transition Piece Connects Annular Vibratory Finisher to Supporting Glove Box Line and Sectioning/Pretreatment Facility

had the transition piece bolted directly to the vibrating containment lid of the vibratory finisher process tub (Chikalla and Powell 1980).

CRITICALITY SAFETY/CONTAMINATION MEASUREMENT STUDIES

A multi-energy gamma assay system (MEGAS) has been assembled under the LASL subcontract. This system will screen low-density ($\leq 0.1 \text{ g/cm}^3$) combustible TRU wastes at the 10 nCi/g level. The MEGAS uses a columnated NaI detector 5 in. dia by 0.08 in. thick to scan a translating and rotating container of waste. A complete pulse height spectrum, corrected for room background, is collected for the waste container, and photon yields are computed and compared to a calibration curve to give the net activity of plutonium and americium in the waste. The MEGAS can also be interfaced with the automated data acquisition system (see below) to provide automated operation of the system and a

permanent printed record. The size and shape of the waste container are critical to the accurate determination of TRU content in the waste. Table 5.1 summarizes the results of using a ^{241}Am source to measure the transmission of x-rays and gamma rays through standard 11-in.- and 15-in.-dia round vinyl bags. Both bags were filled with cheese-cloth and packed to a density of 0.1 g/cm^3 to simulate low-density combustible waste. The 17-keV x-rays are severely attenuated by the 15-in.-dia bag. Therefore, we shall limit the packaging of waste for the MEGAS to the standard 11-in.-dia vinyl bags.

A data acquisition system for automated collection and monitoring of criticality safety data (Figure 5.3) was installed. This system will collect and analyze data from ^3He neutron slab detectors located near components of the decontamination system where plutonium holdup is possible. The components that will be monitored initially are the sump in the sectioning/pretreatment facility, and the evaporator. Each ^3He neutron slab detector will be specifically calibrated, based on Monte Carlo neutronic calculations, to measure the plutonium holdup of the monitored components. The data acquisition system will continuously monitor each ^3He neutron slab detector and permanently

TABLE 5.1. Effect of Bag Diameter on Transmission of X-Rays and Gamma Rays Through Low-Density Waste Packages

Bag Diameter, in.	X-Ray/Gamma-Ray Energy, keV	% Transmission
11	17	38
	60	80
15	17	15
	60	72

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FIGURE 5.3. Data Acquisition System for Automated Collection and Monitoring of Criticality Safety Data

record the criticality safety status for each monitored component. This data acquisition system can also collect and analyze data from the high-resolution, hyperpure germanium detector to provide isotope identification and quantitative analysis of samples.

A ^3He neutron slab detector and associated electronics system were mounted on a cart for manual acquisition of criticality safety data for components not connected to the automated criticality safety monitoring system. This uniquely designed cart, shown in Figure 5.4, was fabricated in two sections. One section contains the ^3He neutron slab detector and the other the associated electronics system. This design permits the detector to be placed close to the monitored component, while the operator remains removed from the component with the electronics system to record the data, thus minimizing operator radiation exposure.

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FIGURE 5.4. Cart-Mounted ^3He Neutron Slab Detector System. This uniquely designed cart allows the ^3He detector to be placed close to the monitored component while the operator and electronics remain at a distance.

REFERENCE

Chikalla, T. D. and J. A. Powell, compilers.
1980. Nuclear Waste Management Quarterly
Progress Report October Through December
1980. PNL-3000-8, Pacific Northwest Labo-
ratory, Richland, Washington.

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

Although ion implantation of radioactive krypton in a growing sputter-deposited film already appears to be the most attractive process for storing ^{85}Kr , its safety has been further enhanced by the development of a sputtering chamber which also acts as the disposal container. The design of this chamber and testing of the filament and anode arrangement indicate that this system will function very well. A comparison of various sputtering techniques indicate that an amorphous deposit sputtered in a supported plasma is favored on the basis of electrical efficiency, number of storage units, and number of sputtering chambers required.

The parameters for high-pressure loading of low-density glass has been defined for a material called "phasil," which sinters below 700°C . This glass is loaded at about 700°C in 4 hr. Although higher loadings are achieved at higher pressures, the increase is not linear with pressure due to a lower closed-pore volume. Also krypton release occurs at a lower temperature with the very high-pressure loaded samples. Thus loadings at more moderate pressures (~ 70 MPa) may be more desirable.

ION-IMPLANTATION OF KRYPTON DURING SPUTTER

DEPOSITION - E. D. McClanahan, G. L. Tingey, R. W. Moss, and H. L. Butts

From the standpoint of safety, the most promising technique for storing radioactive krypton appears to be the low-pressure, ambient-temperature ion implantation of krypton in a growing sputter-deposited metallic film (Tingey 1981). This approach is particularly attractive because the inventory of gaseous krypton is always very low, no high pressures or high temperatures are required, and a very stable krypton-containing solid is generated. To further increase the safety of this system, we have developed a sputtering chamber that acts as the final containment of the solid waste-containing deposit. This chamber, shown schematically in Figure 6.1, is designed so that it can be installed and removed remotely within minutes. As currently envisioned, the chamber would have a deposition substrate area of about 3000 cm^2 upon which would be deposited a 1-cm-thick deposit of nickel-yttrium alloy containing 8 atom% krypton. The nearly 20-kg deposit would contain about 2 kg of krypton ($\sim 39\text{ kCi}$ of ^{85}Kr).

The disposable sputtering chamber would have both the filament and the anode near

FIGURE 6.1. Disposable Sputtering Chamber for Encapsulating Radioactive Krypton

the top so that all connections could be made on the top surface. This filament arrangement has been tested in our laboratory equipment and yields a stable, easily supported plasma. Thus we anticipate no problems in the full-scale system.

We have compared a variety of sputtering techniques and metallic matrices. Included in the comparison are the glow discharge system used in the United Kingdom, one crystalline metal matrix and several amorphous matrices examined in our laboratory, as well as the disposable chamber discussed above. The data for the comparison are given in Table 6.1. On the basis of the electrical efficiency, number of sputtering chambers required, and storage units, the amorphous metals sputtered using a supported plasma are favored. Further optimization is

possible. For instance, thicker deposits and larger chambers appear to be possible as the technology is further developed.

HIGH-PRESSURE DISSOLUTION OF KRYPTON IN LOW-DENSITY GLASSES - J. M. Lytle and G. L. Tingey

Another technique examined (Tingey et al. 1980) for storage of radioactive krypton is the dissolution or trapping of krypton in low-density glass that is sintered in the presence of krypton, closing the small pores and encapsulating the krypton. The previous studies have largely been conducted using a 96% SiO_2 glass (Thirsty Vycor®) with the optimum loading temperature of 850 to 900°C.

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TABLE 6.1. Comparison of Sputtering Systems

Laboratory Matrix Technique	Harwell (a)	Pacific Northwest Laboratory				
	Cu	Ni	Fe/Y	Ni/Y	Ti	Ni/Y
	Glow discharge pulsed	Supported plasma pulsed	Supported plasma continuous	Supported plasma continuous	Supported plasma continuous	Supported plasma continuous disposable chamber
Fraction Kr, atom%	5	5	9	8	5.7	8
Size						
Diameter, cm	25	14	14	14	14	26
Length, cm	100	56	56	56	56	40
Sputtering yield, $\text{gA}^{-1}\text{hr}^{-1}$	-	3.2	5.3	5.7	1.0	5.7
Trapping rate, (STP)/hr ⁻¹	1.0	1.5	4.2	3.8	0.62	3.5
Efficiency l/kWh	1.04×10^{-2}	2×10^{-2}	5.6×10^{-2}	5.1×10^{-2}	0.8×10^{-2}	5.1×10^{-2}
Units required ^(b)	32	22	8	9	53	10
Time per deposit, hr	2400	250	123	121	450	156
Thickness of deposit cm	2	1	1	1	1	1
Storage units/yr	97	620	450	505	840	435

(a) Whitmell et al. 1981.

(b) Number of sputtering chambers required to handle the output of a 2000-tonne/yr reprocessing plant (232.5 m³ at STP).

In an attempt to reduce the high temperature requirement, we have now investigated a porous glass material fabricated for us by Catholic University called "phasil," which sinters at a temperature 100 to 150°C lower than the silica-based material.

At any given time in the loading process the porosity consists of both open and closed pores. During the sintering, the open porosity closes and the overall pore volume decreases. The net effect is that closed porosity increases initially and then decreases, as shown in Figure 6.2. The data shown were determined at atmospheric pressure with phasil glass. The fraction of

closed porosity has also been observed to vary with loading pressure, as shown in Figure 6.3. With Thirsty Vycor, the pressure that yields the maximum pore volume is 40 to 50 MPa (5800-7300 psia). At the lower pressures, the closed porosity increases with pressure because the krypton tends to expand the pores that contain it. As the pressure increases past 50 MPa, however, the expansion forces are so great that the pores cannot close, resulting in a larger open-to-closed porosity ratio. As a result, the open porosity increases with loading pressure. Furthermore, earlier results have shown that krypton release occurs at a lower

FIGURE 6.2. Closed Porosity Versus Time for Phasil Glass Sintered at Indicated Temperature at Atmospheric Conditions

FIGURE 6.3. Closed Porosity Versus Pressure After Loading Thirsty Vycor with Krypton at the Indicated Temperature

temperature when the loading pressures are higher (Tingey et al. 1981).

Since closed porosity is generated by the sintering process, temperatures must be adequate for reasonable sintering rates. If the temperature is too high, however, the total pore volume is reduced, resulting in reduced krypton content. Using the criteria of closed pore volume, the ideal temperature for krypton loading is about 700°C, as illustrated by Figure 6.2. At 800°C, the material sinters too rapidly and at 600°C the time for sintering is too long (about 2 days). Optimum temperatures for loading krypton in phasil and Thirsty Vycor are also shown from krypton loading data (Figure 6.4) to be about 700 and 850°C, respectively.

It appears that commercial storage of radioactive ^{85}Kr could best be accomplished at moderate temperatures and pressures, reducing both the probability of accidental release of ^{85}Kr and the cost of equipment. From the data presented in this report, the loading pressure of 40 to 50 MPa (5800-7300 psia) is optimum. Higher pressures reduce the krypton-retaining stability of

FIGURE 6.4. Loading Temperature Versus Trapped Krypton in Phasil and Thirsty Vycor Porous Glass

the product. The temperature is selected so that the closed porosity is a maximum in ~4 hr. Thus 700°C for phasil and 850°C for Thirsty Vycor correspond to the temperatures where maximum loading of krypton occurs (Figure 6.4).

REFERENCES

Tingey, G. L. 1981. "Krypton Solidification." In Nuclear Waste Management Quarterly Progress Report October Through December 1980. PNL-3000-8, Pacific Northwest Laboratory, Richland, Washington.

Tingey, G. L., J. M. Lytle, W. J. Gray, and K. R. Wheeler. December 1980. Solid State Storage of Radioactive Krypton in a Silica Matrix. PNL-3617, Pacific Northwest Laboratory, Richland, Washington.

Tingey, G. L., E. D. McClanahan, M. A. Bayne, and W. J. Gray. 1981. "Solid State Containment of Noble Gases in Sputter Deposited Metals and Low Density Glasses." In Management of Gaseous Wastes from Nuclear Facilities - Proceedings of a Symposium, Vienna, Austria, February 18-22, 1980, International Atomic Energy Agency, Vienna, p. 279.

Whitmell, D. S., R. S. Nelson, and M. J. S. Smith. 1981. "Containment of Krypton in a Metallic Matrix by Combined Ion Implantation and Sputtering." In Management of Gaseous Wastes from Nuclear Facilities - Proceedings of a Symposium, Vienna, Austria, February 18-22, 1980, International Atomic Energy Agency, Vienna, p. 263.

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7. THERMAL OUTGASSING

L. L. Burger - Project Manager

The objectives of the Thermal Outgassing Program are to:

1. *develop a method for the safe and effective removal of volatile fission products from irradiated fuels*
2. *evaluate the use of thermal outgassing using various sweep gases or vacuum outgassing for the removal of ^{14}C , ^3H , ^{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

Substantive hot-cell equipment is operational for testing of vacuum and sweep-gas thermal outgassing concepts for the removal of volatile fission products from irradiated fuels. Sweep-gas studies at the 325-B hot-cells were completed to determine the rate of tritium, xenon, and ^{85}Kr released from the fuel at 1500°C. No major differences were found in the gas release data for 1 to 2 pieces of fuel (1 g) and fuel crushed to a 5 to 40 mesh size. Xenon, tritium, and krypton results were obtained simultaneously, eliminating the need for a second 6-hr test. Vacuum outgassing equipment has been installed in the G-Cell of the 327 Building and has been successfully tested at 1600°C. A Shippingport UO_2 fuel rod (10 1/4 in.) was sectioned and is being characterized prior to vacuum outgassing. The literature survey document on thermal treatment is being prepared.

LABORATORY STUDIES - L. A. Bray,
D. L. Baldwin (HEDL), and C. A. Hinman (HEDL)

Thermal outgassing studies at the 325-B hot cells were completed during the last

quarter to determine the rate of tritium, xenon, and ^{85}Kr removal from Shippingport UO_2 fuel as a function of the sweep-gas composition, using 6% H_2 + He or He alone. Samples consisted of 1 or 2 pieces (1 g) of fuel, heated from 35 to 1500°C during the first 2 hr of the 6-hr heating cycle. Tests this quarter included grinding the fuel to a 5 to 40 mesh size and repeating the above work to determine differences in gas-release rates caused by a change in particle size. No major differences were found in the gas content of the crushed fuel before heating or as compared to the previous gas release data at 1500°C. The flow-scheme to simultaneously obtain xenon, krypton, and tritium gas results was successfully demonstrated. In addition, equipment was modified to push the fuel into the preheated furnace versus heating the fuel from 35 to 1500°C over a 2-hr period. Scheduled tests to determine fission gas release rates with the modified equipment were halted when leak-checks of the furnace system indicated that the mul-lite furnace tube (2 in. ID by 36 in. long) had failed due to thermal cycling after twelve 6-hr tests. Replacement furnace tubes have been received, machine-tapered, leak-checked, and reinstalled in the furnace system.

Additional hot-cell studies are in progress to determine the total iodine and undissolved solids in the Shippingport fuel after dissolution with nitric acid and before and after heat treatment. These studies are required to determine PuO_2 solubility and iodine retention under thermal sweep-gas conditions.

Vacuum outgassing studies have been started in 327 Building hot-cells. The vacuum furnace, in-line mass spectrometer, video camera, and optical pyrometer have been installed in G-Cell, as shown in Figure 7.1. The vacuum outgassing equipment

(Figure 7.2) has been successfully tested at 1600°C and is prepared to receive the first zirconium-clad sample of UO_2 . Additional testing and repair of the in-line mass spectrometer will complete the installation. A 10 1/4-in. Shippingport UO_2 fuel rod was sectioned and is being characterized prior to heating. Fission gas is being collected from the cladding void space and being analyzed. Photomicrographs are being obtained from the polished sections of the fuel. Three 1-in. samples are being stored in an inert atmosphere storage container prior to the vacuum outgassing test.

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FIGURE 7.1. Plan View of In-Cell Experimental Vacuum Outgassing System

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FIGURE 7.2. In-Cell Gas Handling and Pressure Monitoring System

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8. IODINE-129 FIXATION

L. L. Burger - Project Manager

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

SUMMARY

In the static leach tests of cements containing barium iodate, mercuric iodate, calcium iodate, and iodine-loaded silver mordenite, iodine leaches from these materials at the same rate (within a factor of 4), 2×10^{-3} cm in 50 days. After 14 days, no iodine was detected in the leachate from the static leach test of silver iodide in cement. The second-generation iodine-containing sodalite had a leach rate of 10^{-6} cm/day. In an IAEA-type test, iodine leached from calcium iodate in cement samples at 3 to 5% per year.

We used a differential scanning calorimeter (DSC) to study the absorption reaction of elemental iodine with various silver-containing sorbents. For each sorbent an exothermic reaction was observed. Silver iodide was detected in the silver zeolites.

Direct sintering and hot-pressing of sodium aluminate, Ludox® AS-40, and sodium iodide or hydrogen iodide were used to produce iodine sodalites. Direct sintering, without pressure, does not appear to be a viable process for sodalite production, nor does hydrogen iodide appear to be a suitable iodine form for this formulation.

®Registered trademark of E. I. du Pont de Nemours, 1007 Market St., Wilmington, Delaware.

WASTE FORM CHARACTERIZATION - R. D. Scheele

One objective of the Iodine Fixation Program is to determine a disposal form for ^{129}I ($t_{1/2} = 1.7 \times 10^7$ years) produced in the nuclear fuel cycle. The first phase involved screening iodine compounds based on their solubility, thermodynamic stability, thermal stability, and cost availability (Platt 1978a). The second phase involved screening the factors suspected of influencing the leaching of iodine from iodine-containing cements (Platt and Powell 1978a,b; Platt and Powell 1979a,b,c,d). In the present phase, we are evaluating those iodine-containing cements that have the greatest promise and/or are likely end products of a particular iodine-trapping process.

Two leach test procedures are being used, the static leach test procedure that is recommended by the Materials Characterization Center (PNL) and the modified IAEA test used in our previous studies.

The candidate disposal forms studied in the static test are barium iodate in cement, mercuric iodate in cement, iodine-loaded silver mordenite in cement (AgZI in cement), silver iodide in cement, calcium iodate in cement, and two iodine-containing sodalites prepared at Rockwell Hanford Operations.

The cement samples contain 0.08 mmol I/g dry Portland III cement; the sodalite contains

1.6 mmol I/g iodine sodalite. The first two cement samples are being tested in distilled water, seawater, and Columbia River water leachates; the remainder are being tested in distilled water leachate.

The candidate disposal forms being tested using the IAEA type test are barium iodate in cement, AgZI in cement, AgI in cement, and calcium iodate in cement. The iodine content is the same as above, and distilled water is the leachate. Analytical results are available only for the calcium iodate in cement sample.

The leach results for the static tests for barium and mercuric iodates in cement and AgZI in cement were presented and discussed in the most recent quarterly report (Chikalla and Powell 1981). Figures 8.1 and 8.2 present the remaining static leach test results. The normalized fraction leached was the same (within a factor of 4) for the barium iodate, mercuric iodate, AgZI, and calcium iodate samples, $\sim 2 \times 10^{-3}$ cm after 50 days. The normalized fraction leached was calculated by multiplying the fraction leached by the ratio of the sample's geometric volume to geometric surface area, which for these samples was 0.5 cm.

Preliminary results for silver iodide in cement indicate that the normalized fraction leached after 14 days was $< 10^{-5}$ cm (less than the detection limit).

Figure 8.2 presents the leaching results for the IAEA test for calcium iodate in cement. Comparison with the static test shows that under semidynamic test conditions the amount of iodine leached is greater. Assuming the leach rates observed at 50 and 60 are typical, the iodine would be removed from the cement at a rate of about 3 to 5% per year. It is difficult to compare results from the two types of tests. The static test indicates that most

of the leaching occurs in the first 1 to 2 weeks and little change in the next 40 to 50 days. The results for barium and calcium iodates are in the direction predicted by solubilities but not as large. Mercuric iodate does not follow this pattern (lower solubility). The relatively high value for AgZI probably reflects the fact that much of the trapped iodine in silver zeolites is not firmly bound.

Figure 8.3 is typical of dynamic leach data. A rate can be estimated at 50 days, in this case ~ 3 to 4×10^{-2} /yr. For AgI in cement the dynamic rates should be several orders of magnitude lower.

For disposal where leaching to ground water exists, there is probably little practical difference between the alkaline earth iodates; e.g., 50% may be removed in 20 to 60 years, and is probably unacceptable in this environment. On the other hand, they should all be satisfactory for disposal to the ocean floor since all that is required is a loss rate low enough to be accommodated by the ocean mixing.

IODINE REMOVAL STUDIES – R. D. Scheele and L. L. Burger

Over the past year effort has been devoted to identifying the trapping mechanism in metal zeolites and the species present. Previous studies have examined iodine removal from loaded zeolites by extraction and by thermal analysis. A knowledge of the mechanisms is important in predicting the effects of other gases, the ultimate decontamination factors achievable for iodine or organic iodide removal, the stability of organic, the "fixed" iodine, and the potential for silver recycle.

During the last few months several experiments have been carried out on the uptake of

FIGURE 8.1. Static Leaching of Calcium Iodate in Cement, 0.4 mmol $\text{CaIO}_3(2)/\text{g}$ Portland III Cement (distilled water leachate)

FIGURE 8.2. Static Leaching of Iodine in Iodine Sodalite, 1.5 mmol I/g Iodine Sodalite (distilled water leachate)

FIGURE 8.3. Dynamic Leaching of Calcium Iodate in Cement, 0.4 mmol $\text{CaIO}_3(2)/\text{g}$ Portland III Cement (distilled water leachate)

iodine using differential scanning calorimetry on the reactions between I_2 and Ag metal, Ag_2O , AgNO_3 , AgZ (silver mordenite), AgX (silver zeolite X), NaZ (sodium mordenite), and AC6120® (silver nitrate-impregnated silica). In each case an exothermic reaction and/or absorption occurred except for AgNO_3 ; here the reaction was endothermic. The presence of silver iodide was indicated except with AgNO_3 and AC6120.

Figures 8.4 to 8.10 present the DSC studies of (a) the reaction and (b) the subsequent reaction products, i.e., reheating after cooling from step (a). Table 8.1 lists the transition points for the pertinent compounds.

Hermetically sealed aluminum pans capable of holding 3 atmos pressure were used. We did not dry the zeolites or AC6120 prior to use, and they contain an estimated 9 to 12 wt% water. Water is involved in some of

the reactions. The reaction mixture was heated to 200°C, cooled, and reheated to 600°C to characterize the reaction products.

All reactions were exothermic except for that of the silver nitrate. Silver and silver oxide apparently reacted prior to initiation of the DSC record, 50°C. The reactions between silver, silver oxide, AgX, and AgZ, produced silver iodide as one reaction product; the characteristic endotherms of silver iodide at 147 and 558°C are both present in Figures 8.4b, 8.5b, 8.7b, and 8.8b. The reaction between iodine and AC6120 may have produced silver iodide; a small peak at 147°C was present.

The reaction between iodine and sodium mordenite was also exothermic, indicating that the physical absorption of iodine is also thermodynamically favorable. Iodine may also react exothermically with zeolitic water, though calculations indicate the reactions of elemental iodine with water are endothermic.

®Registered trademark of Süd Chemie, Munich, Germany.

FIGURE 8.4(a). DSC Study of the Reaction of I₂ with Ag

FIGURE 8.4(b). DSC Characterization of I₂ and Ag Reaction Products

FIGURE 8.5(a). DSC Study of Reaction of I₂ with Ag₂O

FIGURE 8.5(b). DSC Characterization of I₂ and Ag₂O Reaction Products

FIGURE 8.6(a). DSC Study of the Reaction of I_2 with AgNO_3

FIGURE 8.6(b). DSC Characterization of the Reaction of I_2 with AgNO_3

FIGURE 8.7(a). DSC Study of the Reaction of I_2 with AgZ

FIGURE 8.7(b). DSC Characterization of the Reaction Products of I_2 and AgX

FIGURE 8.8(a). DSC Study of the Reaction Between I_2 and AgX

FIGURE 8.8(b). DSC Characterization of the Reaction Products of I_2 and AgX

FIGURE 8.9(a). DSC Study of the Reaction Between I_2 and AC6120

FIGURE 8.9(b). DSC Characterization of the Reaction Products of I_2 and AC6120

FIGURE 8.10(a). DSC Study of the Reaction Between I₂ and NaZFIGURE 8.10(b). DSC Characterization of the Reaction Products of I₂ and NaZ

TABLE 8.1. Transition Data

Compound	Crystal Change, °C	Melting Point, °C	Boiling Point, °C
Ag	-	961	2210
AgI	147	558	1506
AgIO ₃	-	-	Decomposes 415
AgNO ₃	160	210	Decomposes 400
Ag ₂ O	-	-	Decomposes 420
I ₂	-	114	184

In summary, elemental iodine reacted exothermically with AgZ, AgX, or AC6120. Silver iodide was produced for AgZ and AgX, and possibly in AC6120. The reactions of these silver-containing sorbents did not closely resemble any reaction between a simple silver compound and iodine. Even the reaction with AC6120, which is silver nitrate-impregnated silica, does not correspond exactly to the reaction with silver nitrate. These studies indicate that the iodine sorption reaction is very complex.

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

The preparation of sodalite from an aluminosilicate gel starting mixture was studied. Gels were prepared from a mixture of sodium aluminate, Ludox AS-40 (A SiO₂ sol in NH₃) and NaI or HI. Both direct sintering and hot-pressing were used to form sodalite. Direct sintering of the gel feeds resulted in large iodine losses. Products prepared from HI feed materials exhibited greater iodine losses and weaker sodalite x-ray diffraction patterns than products prepared with NaI, although a portion of the iodine loss resulted from insufficient sodium in the starting mixture. The hot-pressed products prepared from NaI gel feeds had negligible iodine losses, high density, and strong sodalite diffraction patterns. Hot-pressed HI gels lost ~30% of the original iodine content and had other, unidentified phases in the diffraction patterns.

Based on the present work, direct sintering does not appear to be a viable process for producing sodalite. Feed using HI should also be studied for the kaolin clay sodalite formation process.

The evaluation of the effect of kaolin clay variations on the formation of sodalite

has been initiated. Feed materials have been prepared from three different kaolin clays, and hot-pressing of the pellets is in progress. Sodalite aluminosilicate gel feeds containing HI and the proper quantity of sodium are also being prepared for sintering and hot-pressing.

REFERENCES

Platt, A. M., compiler. 1978. Nuclear Waste Management Quarterly Progress Report October Through December 1977. PNL-2377-4, Pacific Northwest Laboratory, Richland, Washington.

Platt, A. M. and J. A. Powell, compilers. 1978a. Nuclear Waste Management Quarterly Progress Report January Through March 1978. PNL-2378-1, Pacific Northwest Laboratory, Richland, Washington.

Platt, A. M. and J. A. Powell, compilers. 1978b. Nuclear Waste Management Quarterly Progress Report April Through June 1978. PNL-2378-2, Pacific Northwest Laboratory, Richland, Washington.

Platt, A. M. and J. A. Powell, compilers. 1979a. Nuclear Waste Management Quarterly Progress Report July Through September 1978. PNL-2378-3, Pacific Northwest Laboratory, Richland, Washington.

Platt, A. M. and J. A. Powell, compilers. 1979b. Nuclear Waste Management Quarterly Progress Report January Through March 1979. PNL-3000-1, Pacific Northwest Laboratory, Richland, Washington.

Platt, A. M. and J. A. Powell, compilers. 1979c. Nuclear Waste Management Quarterly Progress Report April Through June 1979. PNL-3000-2, Pacific Northwest Laboratory, Richland, Washington.

Platt, A. M. and J. A. Powell, compilers. 1979d. Nuclear Waste Management Quarterly Progress Report July Through September 1979. PNL-3000-3, Pacific Northwest Laboratory, Richland, Washington.

Chikalla, T. D. and J. A. Powell, compilers. 1981. Nuclear Waste Management Quarterly Progress Report October Through December 1980. PNL-3000-8, Pacific Northwest Laboratory, Richland, Washington.

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9. NWVP OFF-GAS ANALYSIS

M. S. Hanson - Project Manager

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

SUMMARY

The filter assembly was removed from the spray calciner in B-Cell of 324 Building. The filters, which were used to separate entrained calcine from the off-gas, were axially gamma-scanned to determine areas of high activity. Two filter candles were removed from the assembly and sectioned into small pieces. The sample pieces were mounted in resin blocks and partially polished in preparation for microprobe analysis. Flushing tests have been initiated on sample pieces to determine the amount of activity removable and to determine fixed activity by enrichment during washing.

TECHNICAL PROGRESS

The sintered metal filter assembly was successfully removed from the spray calciner in B-Cell. Visual examination of the filter candles found the calcine coating on the filters to be very uniform, with no obvious anomalies present. Disruption of the filter cake with the tip of a manipulator showed the cake to be ~1 to 2 mm thick. Visual examination showed no significant differences leading to a choice of filters for sampling. Samples of the filter cake were taken for analysis.

Gamma-energy analysis equipment was brought in, standardized, and set up to use a 4-in. wall plug penetration to scan the filters. The filters were positioned by viewing through the wall penetration with a mirror. The gamma-energy analyses were then taken through a collimator tube with a 1/4-in. aperture. The gamma analysis showed significant differences in gamma activities of different filters. The 511- and 662-KeV energy gamma rays, which correspond to isotopes of ruthenium and cesium, were analyzed. Activity differences from 0.7 to 1.35 times the mean were found for both elements. The filter candle showing the highest activity was then chosen for axial analysis for the same isotopes. Activity differences from 0.75 to 1.37 times the mean were found, with the highest activity found near the bottom of the filter candle.

Based on the gamma-energy analysis, two filter candles were chosen for sampling: the most active and the least active. Two filter candles were removed from the filter assembly, and each was sectioned into ten 1/2-in. by 1/2-in. samples. Five samples from each filter candle were sent to the Hanford Engineering Development Laboratory Post-Irradiation Testing Laboratory for mounting and preparation for microprobe

analysis. The remaining five samples from each filter candle were then transferred to C-Cell, 324 Building for gamma analysis.

The ten filter-candle samples received by the Post-Irradiation Laboratory were mounted in resin blocks. The first phase of the surface preparation polishing and pore filling for microprobe analysis is complete, and fine polishing is under way. The mounted samples are being photographed for identification and indexing as required for microprobe analysis.

On the second set of filter samples (transferred to C-Cell, 324 Building) the surface area (neglecting the filter pores) was calculated to allow normalization of the elution data to a common base. The availability of the filter-pore surface area per

unit volume ratio will allow further refinement of data normalization.

Three flushing solutions--deionized water, 0.5M HNO_3 , and 5M HNO_3 --were tested on the samples in 24-hr soaking periods. The initial test was with deionized water for 24 hr. After gamma-scanning the eluted filter sample and the water separately, the elution tests were repeated using 0.5M HNO_3 and finally with 5M HNO_3 . Successive elutions removed cesium as expected. Nonvolatile (calcine) material on the filter was only partially removable, indicating penetration into filter pores. Ruthenium-to-non-volatile and ruthenium-to-cesium isotope ratios were not constant, however, indicating ruthenium enrichment.

10. 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

The monitoring system at the Burial Waste Test Facility (BWTF) has been replaced with new equipment. A new system designed to automate the weighing lysimeter data is being tested. Data collected during the 2-1/2 years of BWTF operation are being organized for evaluation.

The quench curve for the liquid scintillation cocktail used in the sample oxidizer has been refined. This curve provides information necessary to compare results of the field tracer study obtained with the new oxidizer method and the leach method.

A cooperative project has been started with Washington State University to study the role of nonisothermal vapor transport in evaporation and to help evaluate techniques for characterizing soil water. Preliminary results shown here illustrate the response of tensiometers modified for sandy soils.

FIELD MEASUREMENTS - R. R. Kirkham and
K. O. Schwarzmiller

The Burial Waste Test Facility (BWTF) monitoring system has been replaced with new equipment. The micrometeorological instrumentation has been expanded to include more measurements of wind speed, air temperature and soil surface temperature. A new system

is being tested that will automate the reading of the weighing lysimeter data. Early results look promising; however, certain electronic instabilities need to be overcome. This automated system is needed to better characterize daily evaporation rates.

Several computer programs have been written that will help organize and evaluate the large amount of data which has been gathered over the past 2-1/2 years at the BWTF. This large data set presents a significant data management problem. The old data tapes are being edited and verified against the paper tapes available. Data available on the paper tapes that were not recorded are being typed into the computer by hand. Data taken manually, such as neutron probe data and weighing lysimeter data, are also being entered into the computer system so they can be analyzed.

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

Refinements were made in the quench correction efficiency curve developed last quarter for the sample oxidizer. It was found that the curve is independent of the tritium concentration and therefore can be applied to the full range of sample concentrations existing in the field. Confidence limits were calculated for the efficiency

curve. The 1% limits of the regression line are shown in Figure 10.1. At the BWTF soil samples' average external standard ratio (ESR) of 0.600, the limits equal a 3% range in efficiency, well within the expected range considering deviations due to other experimental factors.

The soil samples from the September 1980 sampling were oxidized for comparison with the leaching method. Even after 4 months, tritium was detected in samples that the 2-month-old leach solutions had indicated contained less than detectable levels. This is evidence that the oxidizer technique provides greater sensitivity than the leaching method. At the shallower caisson depths, the oxidized soils showed higher concentrations than the leach solutions. The sample values determined by the different preparation methods are listed in Table 10.1. From these findings, it was decided that another sampling of the caisson soils would be beneficial.

A cooperative project was initiated with Washington State University. The objective is to investigate the role of nonisothermal vapor transport in evaporation, as well as to assist in the field and laboratory measurements of soil water. A literature review has been completed and measurements of soil thermal properties have begun. In addition, some experimental work has been done on the response of tensiometers in sandy soils.

A tensiometer is a simple instrument that measures soil water matric potential, which is an indicator of soil moisture content. It has a very limited range but high accuracy within this range. It is, however, difficult to use in sandy soils because of the coarse texture. A possible solution to this problem is to place a layer of fine-textured soil around the tensiometer to act as a contact medium between the instrument and the sandy soil. This should allow the tensiometer to track the changes in soil tension more accurately. Figure 10.2 shows

FIGURE 10.1. Oxidizer Quench Curve with 1% Confidence Limits

TABLE 10.1. Comparison of Leach Solution with Oxidized Soil

Caisson	Depth, m	Activity, pCi/g		
		Leach Sept. 17	Leach Nov. 12	Soil Jan. 23
Ambient	0.15	57	<DL (a)	188
	0.46	154	<DL	287
	0.76	277	282	439
	1.07	477	408	563
	1.37	1305	1346	1796
	1.68	2082	2094	2238
	1.98	3566	3938	3036
	2.59	9150	9464	9207
	3.81	9896	9898	7929
	5.03	4884	4730	4463
	6.25	354	346	326
	7.16	1298	1208	1078
Irrigated	0.46	74	<DL	234
	0.76	119	<DL	199
	1.07	80	<DL	119
	1.37	61	<DL	67
	1.68	48	<DL	55
	1.98	50	<DL	75
	2.59	134	<DL	156
	3.81	1331	1214	1221
	5.03	2680	2697	2621
	6.25	764	787	628
	7.16	4362	4391	4363

(a) Less than detection limit.

the response of two tensiometers to changes in soil tension. One tensiometer has a layer of silty clay loam surrounding it (dotted line) and one does not (solid line). The encased tensiometer followed the changes

in tension better than did the unmodified instrument. These results are being analyzed using recently published tensiometer theory in an effort to quantify the effect of the silt encasement.

FIGURE 10.2. Tensiometer Response

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11. WELL-LOGGING INSTRUMENTATION DEVELOPMENT

R. L. Brodzinski - Project Manager

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

SUMMARY

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

Final experiments on application of neutron activation to the analysis of ^{90}Sr are being planned.

Laboratory experiments on the application of x-ray fluorescence technology to the in situ analysis of actinides have continued.

Technology developed in this program has been transferred to UNC Nuclear Industries, Rockwell Hanford Operations, and Argonne National Laboratory through written and oral communications with personnel from those organizations.

An open literature publication entitled "In Situ Subterranean Determination of Actinides by High Resolution Gamma-ray Spectrometry," by R. L. Brodzinski, has been prepared for the proceedings of the International Symposium on Methods of Low-level Counting and Spectrometry.

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

Development of software for field data reduction of the ^{90}Sr bremsstrahlung spectra

is nearly completed. An undisturbed site for establishing a calibration facility, which will provide the necessary parameters for the spectral deconvolution program, has been selected, and a site characterization program has been planned. A portable shelter for protecting the electronic equipment during data acquisition has been obtained, and arrangements have been made for drilling the calibration wells.

Effort has begun on measuring fast neutron reaction cross sections on ^{90}Sr , and a publication is being prepared that includes these data and the thermal neutron capture cross section measured earlier.

Discussions have been held with personnel from UNC Nuclear Industries regarding potential application of the ^{90}Sr bremsstrahlung analysis technique developed in this program to the analysis of ^{90}Sr in reactor retention basin waters.

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

Tungsten collimators designed for improved spatial resolution and reduced "cross talk" have been ordered for use with the actinide photon detection logging equipment.

A final written report has been delivered to Rockwell Hanford Operations describing the actinide photon detection technology developed in this program as well as the results of some field tests performed in Rockwell controlled facilities in cooperation with work sponsored by the long-term Transuranic Defense Waste Program. A seminar was also presented to personnel from the Environmental Analysis and Monitoring Department of Rockwell describing application of the actinide photon detection technology to transuranic monitoring and measurement requirements on the Hanford reservation. These exchanges of information constitute transfer of technology developed in this program to Rockwell Hanford Operations personnel. A general technology transfer to Argonne National Laboratory has also been effected

through discussions and a laboratory visit by personnel from that organization.

Laboratory experiments on the application of x-ray fluorescence technology to the in situ analysis of actinides have been continued. Current efforts have employed a ^{57}Co isotopic activation source and samples containing uranium in order to optimize source-sample-detector geometries for maximum sensitivity and selectivity. Depending on the results of these experiments, additional tests will be performed on other actinides and/or with other activation sources.

An open literature publication entitled "In Situ Subterranean Determination of Actinides by High Resolution Gamma-ray Spectrometry," by R. L. Brodzinski, has been prepared for the proceedings of the International Symposium on Methods of Low-level Counting and Spectrometry to be held in Berlin, April 6-10, 1981.

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12. VERIFICATION INSTRUMENT DEVELOPMENT

R. L. Brodzinski - Project Manager

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

SUMMARY

Site visits have been completed at four low-level disposal operations, and preliminary design requirements for verification instrumentation based on discussions with these site operators are given.

Arrangements have been made to visit with scientists involved in the disposal of low-level radioactive waste in the Federal Republic of Germany.

Generic data storage and reduction requirements have been determined, and appropriate electronic equipment is being procured.

A passive TRU assay system is being optimized for evaluation as a package assay system.

WASTE RECEIPT INSTRUMENTATION DEVELOPMENT - R. L. Brodzinski and E. A. Lepel

Visits have been completed at the commercial disposal sites in Beatty, Nevada, and Richland, Washington, operated by U.S. Ecology, Inc., and at the defense disposal operations at the Nevada Test Site and the Hanford site. Discussions with the operations manager at each of these facilities have been held, and a great deal of prac-

tical, as well as idealistic, information has been obtained for inclusion in the design of a waste verification instrumentation system.

These sites all receive the majority of their wastes in 200-l steel drums or large plywood boxes ~1.2 x 1.2 x 2.1 m, although numerous additional container shapes, sizes, and construction materials are also received when it is more convenient for the generator. The orderliness and efficiency of the operations at these sites range from very good to very bad. Several inescapable conclusions regarding the design of a waste receipt assay system have been reached following these site visits:

1. A single generic assay instrument suitable for use at all sites under the current method of operations is impossible.
2. To make generic package assay a possibility, it will be necessary to specify perhaps two, no more than three, acceptable waste packages. These would most likely be the 200-l steel drum and the large plywood box. All waste generators would then be required to package their waste in one of these containers or provide the necessary assay capability for any nonstandard packages they may choose to use.

3. The volume of wastes received at some sites approaches an average of one package every few minutes. This allows only marginally adequate time to assay each package. It will probably be expedient to assay only select packages, for example, only one out of a batch of similar waste from a single generator.
4. Similarly, it may be most useful to separate the assay capability into different generic waste types, e.g., TRU, fission products, ^{99}Tc , ^{129}I , etc., or appropriate combinations of these, since some waste types can be ignored when the generator is known. For example, it would rarely be necessary to analyze medical wastes for transuranics.
5. Perhaps the assay function can be performed more efficiently at some location other than the disposal site, such as by brokers or third-party inspection. A large percentage of commercial waste is collected and shipped by brokers who could conceivably also assay the packages. The State of Nevada has instituted a third-party inspection requirement for commercial waste disposed of in that state, and perhaps assay could be performed as a part of that function. Other alternatives also exist, and further consideration of who will perform the assay is necessary.
6. It will probably be necessary to specify only one or two matrix materials for filling the void space in the waste package in order to reduce possible assay error caused by matrix effects. However, this requirement should be imposed for reasons much more important than facilitation of package assay. Solid matrix

materials should be incorporated to introduce another barrier to radionuclide mobilization and to eliminate problems caused by trench subsidence.

7. Finally, package assay will be of small benefit unless other aspects of waste disposal operations are substantially improved. Trench design, space utilization, package design, waste form, matrix material, generation volume reduction, waste volume reduction, waste segregation, and many other aspects of waste disposal will need to be optimized in order to make waste package assay a useful information system.

Arrangements have been made to visit with the principals involved in West German low-level waste disposal operations while on business in that country. The monitoring, assay, and disposal methods used in Germany will be discussed with scientists at Karlsruhe and Frankfurt. Additional site visits and discussions with operations personnel in the United States are also planned in order to finalize design requirements and constraints for the verification instrumentation.

Generic data storage and reduction requirements have been determined, and appropriate electronic equipment is being procured.

Alteration and testing of the amplifier discriminator assemblies used in a passive TRU assay system are continuing. Discriminator curves are being determined for each $^{10}\text{BF}_3$ tube and its associated preamplifier/amplifier assembly. Optimization of this instrument to verification of waste package contents will be completed for comparison to other TRU analysis procedures.

13. MOBILITY OF ORGANIC COMPLEXES OF RADIONUCLIDES IN SOILS

J. L. Swanson - Project Manager

The objective of this project is to develop and employ standard procedures for evaluating how and to what extent organic complexants affect the mobility of low-level waste radionuclides in soils.

SUMMARY

Procedures are being developed to meet the stated objective. Distribution coefficient data have been obtained with Hanford soil and EDTA complexant for radionuclides of europium, cesium, strontium, nickel, and cobalt. Little or no effect of EDTA was observed with cesium or strontium. Marked effects of EDTA were observed with europium, nickel, and cobalt. Kinetic effects appear to be quite important with nickel and cobalt.

PROCEDURE DEVELOPMENT

Procedures are being developed for evaluating how and to what extent organic complexants affect the mobility of low-level waste radionuclides in soils. Efforts are being emphasized to provide a logical experimental approach that will efficiently give the needed data. The standard experimental tool is taken to be a batch contact test, in which portions of solution and soil are shaken together, and the distribution of the nuclide of interest between the liquid and solid phases is measured.

In a batch contact test, known amounts of soil, solution, radionuclide, and complexant are mixed and the concentration of radionuclide in solution is determined after various times (the pH is also measured). Results

are generally expressed as a distribution coefficient, which is the ratio of the quantity of radionuclide per gram of soil to the quantity of radionuclide per milliliter of solution. The term "apparent K_d " is used for this distribution coefficient.

Within this standard experimental tool, factors can be varied to evaluate the effects of complexants on the retardation of radionuclide mobilities by soils. The factors defining a given system (radionuclide, soil, ground water, complexant) must be varied to provide a broad data bank, and, within a system, other factors must be investigated as well to ensure that the data obtained are appropriate to be used in predictions of radionuclide migration. This is because there are several ways by which soils can retard the mobility of radionuclides as well as several ways by which organic complexants can affect the retardation. Unless the operative mechanisms are understood, predictions of radionuclide migration could be grossly in error.

Among the mechanisms by which soils can retard the mobility of radionuclides are 1) ion-exchange processes, 2) precipitation processes, 3) physical adsorption processes, and 4) formation of mineral phases that include the radionuclide within the structure.

Organic complexants can decrease the retardation (increase the mobility) by, for

example, forming soluble complexes that shift radionuclide ion exchange, physical sorption, or solubility equilibria; by dissolving soil-originated materials that were sorbing the radionuclide; or by the complexant itself sorbing onto the soil and "blinding" sorption sites. Organic complexants can also have the opposite effect, that is, increase the retardation (decrease the mobility) by forming insoluble complexes with the radionuclide.

The proposed procedure for evaluating these effects on radionuclide mobility involves a stepwise approach. At the current stage of development, the steps (all employing the batch contact test) are:

1. Determine the effect of a high concentration of complexant on the radionuclide distribution coefficient. Current evidence indicates that this test should be in the sorption direction, with the nuclide and complexant being mixed together before being contacted with soil. If the effect is not significant, no further study is necessary.
2. Determine the effect of varying the concentration of complexant.
3. Test the effect of approaching equilibrium from the opposite direction, by contacting the radionuclide solution with soil before the complexant is added.
4. Investigate the effects of complexant to radionuclide ratio (at ratios significantly higher than the stoichiometry of the expected complex), solution-to-soil ratio, and multistage contacting of solution with soil (or of soil with solution).

If the same distribution coefficient value (at a given complexant concentration) is obtained in all these cases, then the system should be simple enough to allow accurate prediction, using the simple K_d concept, of the effect of the complexant on the

radionuclide mobility. If different distribution coefficient values are obtained, then more tests must be run to provide the information needed to allow accurate prediction. The specific tests to be run would be determined by the results obtained in the tests outlined above.

Some other factors of importance to radionuclide mobility tend to be self-defining within a soil/ground-water system. Included here are the acidity (pH), the oxidation potential (Eh), and the concentration of some dissolved components. The oxidation potential is one factor that deserves special mention because considerable effort may be necessary to achieve conditions in the laboratory comparable to those in the environment. Natural ground waters often have low oxidation potentials because of the absence of air and the presence of decaying organic matter. Since the oxidation potential can affect not only the oxidation state of multivalent radionuclides but also the presence or absence of radionuclide-sorbing hydrous oxides of multivalent soil elements, in some systems the radionuclide behavior in simple laboratory experiments may not be at all comparable to its behavior in the environment.

DISTRIBUTION COEFFICIENT DATA COLLECTION

Distribution coefficients are being measured with radionuclides and complexants of interest to low-level waste disposal. This work is currently contributing in two areas: development of the experimental approaches required to explain the observed results, and the value of the data themselves. The current status of the study of these systems is summarized below. These results were all obtained with Hanford soil and with air-saturated solutions. The concentrations of radionuclides were determined after filtration through 2-nm filters.

Eu-Na₂EDTA. Data were presented in the preceding quarterly report to show that the apparent K_d at a given EDTA concentration was essentially independent of europium concentration and of direction of approach to equilibrium. Those data indicated the system to be simple and straightforward. However, the data obtained since that time have illustrated the effects of some complicating factors.

Additional data have shown that the europium distribution coefficient increased with decreases in the solution-to-soil ratio. With $4.5 \times 10^{-6}M$ EDTA and a pH of about 8, the apparent K_d was about 500 at a solution-to-soil ratio of 150 ml/g (compared to about 1300 at a ratio of 30 ml/g). With a tenfold higher EDTA concentration and a solution-to-soil ratio of 3 ml/g, the apparent K_d was about 300 (compared to about 100 at a ratio of 30 ml/g). These differences may be due to variations in free EDTA concentration caused by increased complexing by ions dissolved from the soil. In separate experiments at a ratio of 30 ml/g, the concentration of calcium found in solution after 1 week was $9 \times 10^{-5}M$ in a water leachate and $18 \times 10^{-5}M$ in a $9 \times 10^{-5}M$ EDTA leachate (the calcium concentration increased by an amount equal to the total EDTA concentration). Because of the stability of the Ca-EDTA complex, the concentration of free EDTA must be much lower than the concentration of EDTA added.

Europium distribution coefficients were measured at a solution-to-soil ratio of 30 ml/g and an EDTA concentration of $4.5 \times 10^{-6}M$ with different sieve-size fractions of soil (the soil used previously had passed through a 500- μm sieve; additional sizing showed 48% to be smaller than 75 μm in diameter, 35% to be in the 75 to 150 μm range, and 18% to be in the 150 to 500 μm range.) The

apparent K_d values were comparable for the 150 to 500 and 75 to 150 μm portion (1100 and 1000 respectively), but the value with the <75- μm portions was markedly higher. Such a difference is not necessarily surprising since, although K_d is defined and measured on a soil weight basis, several of the possible retardation mechanisms could be expected to depend more on the soil-surface area than on the soil weight.

The soil size also appeared to affect the rate at which the europium was removed from solution to a steady-state concentration. With both the 75 to 150 and 150 to 500- μm portions, the apparent K_d values changed little between 1- and 2-week equilibration times; however, with the <75- μm portion the change was appreciable and continued even longer (values of 2200, 3300, and 5000 were measured after 7, 14, and 23 days). In the experiment with the 75 to 150- μm soil, data obtained after 1 day and 3 days indicated that the attainment of a steady-state europium concentration was first-order in europium concentration, with a half-time of 0.8 days.

Cs-Na₂EDTA. As expected, little effect of complexant was observed in the Cs-EDTA system. The apparent K_d was measured to be 7×10^3 in the absence of complexant and 6×10^3 in the presence of $9 \times 10^{-5}M$ EDTA.

Sr-Na₂EDTA. The apparent K_d for strontium was measured to be 160 both in the absence of complexant and in the presence of $9 \times 10^{-5}M$.

Ni-Na₂EDTA. In this system, a pronounced effect of the direction of approach to equilibrium is being observed. When precomplexed nickel is contacted with soil, a steady-state condition appears to be established within a week, with the apparent K_d diminishing markedly at EDTA concentrations $\geq 10^{-6}M$.

However, when the nickel solution is contacted with soil for a period of time before the complexant is added, the nickel reenters the solution only slowly. Presumably the same steady-state condition will eventually be established, but this has not yet been demonstrated.

In one experiment where an uncomplexed nickel solution was contacted with soil for 20 days before the EDTA was added, 2.3% of the total nickel was found in solution before the EDTA was added and 2.6, 2.9, and 4.7% was found in solution after 1, 3, and 8 days in the presence of the EDTA. In another experiment, in which the nickel was complexed with EDTA before it was contacted with soil, the nickel found in solution amounted to 43% after 7 days and 45% after 14 days. In both of these experiments, the solution-to-soil ratio was 100, the soil was the 75 to 150 μ m size fraction, and the EDTA concentration was $1 \times 10^{-5} \text{M}$.

This presumably kinetic difference between the directions of approach to equilibrium will require additional investigation.

Ni-DTPA. When nickel was precomplexed with DTPA ($1 \times 10^{-5} \text{M}$) and contacted with soil, the apparent K_d was markedly lower than with an equivalent concentration of EDTA (this is as expected from the fact that the DTPA complex is more stable than the EDTA complex). With $1 \times 10^{-5} \text{M}$ complexant and a soil-to-solution ratio of 100, the apparent K_d after 2 weeks was 4 with DTPA complexant and 120 with EDTA complexant.

Co- Na_2 EDTA. Preliminary results indicate that the direction of approach to equilibrium is kinetically important in this system also. In experiments employing $1 \times 10^{-5} \text{M}$ EDTA and 100 ml solution/g soil, 100% of the cobalt remained in solution after 6 days when the cobalt was complexed before it contacted the soil, but only 50% had reentered the solution 7 days after the EDTA was added to a cobalt solution that had contacted the soil for 4 days.

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14. LOW-LEVEL WASTE GENERATION REDUCTION HANDBOOK

M. J. Schliebe - Project Manager

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

SUMMARY

A problem description has been drafted discussing the philosophy of low-level waste generation reduction. The problem description will give guidance during the compilation of the handbook.

Background information identifying low-level waste streams and the respective generation points has been gathered. The information is necessary to determine which industries would be interviewed concerning low-level waste generation reduction (LLWGR) plans.

A literature search for relevant low-level waste generation reduction information has been completed. It is quite apparent that the area of waste generation reduction has yet to become an exploited field. A minimum amount of information was uncovered by the literature search.

There has been little revolutionary work conducted in the LLWGR area in the nuclear industry. Common sense items prevail, with a number of process-related improvements being undertaken, generally in the private sector. Trips to low-level waste (LLW) generator sites were completed. Telephone contacts were also used to help identify LLWGR technology.

A draft of the cost bases to be used for the cost benefit analysis has been completed.

The cost bases will provide a consistent baseline for cost analysis throughout the document.

BACKGROUND INFORMATION

To determine the areas of major emphasis, waste generating industries and main waste streams were identified. Spent Fuel and Waste Inventories and Projections (ORO-778), along with a number of its support documents, was used to specify waste generation areas of concern. The four main low-level waste generation sources addressed in the handbook are:

- 1) commercial nuclear fuel cycle related to the production of electricity
- 2) defense-related activities
- 3) institutions such as hospitals, universities and research foundations
- 4) industrial uses of radioisotopes.

The handbook will not include low-level wastes generated from uranium mining and milling operations.

A literature search was conducted to identify the current technology being developed in the area of minimizing low-level waste. Technological and process-related LLWGR development is quite scarce. Work is being done in the nuclear power reactor area that will help minimize the potential for

generating low-level waste (e.g., redesign of resin load-in/load-out equipment, tighter process control to minimize rework potential, refitting with better, more durable equipment). Other industry is involved not only in minimizing the generation of low-level waste by educational and administrative means but also in the implementation of better packaging of wastes (e.g., being careful physically to get the most waste feasible in a container; consolidating waste forms to more efficiently utilize the waste container volume).

IDENTIFICATION OF CURRENT TECHNOLOGY

Trips were made to low-level waste generation sites to gain familiarity with current LLWGR efforts. A reference trip was made to visit at least one waste generator in each of the four major low-level waste generation categories.

Following plant visits, further contacts are being made via telephone to ensure that no major LLWGR techniques have been omitted. Vendors have provided a number of LLWGR practices/techniques, particularly those dealing with clean-room/contamination control techniques. Development in these areas has given low-level waste generators better control over the amounts of waste generated.

Consulting firms have also indicated work in LLWGR areas, mainly by providing policy and procedure preparation work for LLW generators. The policies and procedures dealing with LLWGR-related practices are nearly impossible to obtain from consulting firms and very difficult to obtain from the clients involved. The contacts made with industry thus far, however, have aided in the enumeration of LLWGR techniques.

COST/BENEFIT ANALYSIS - G. M. Holter

The draft appendix giving cost estimating bases has been completed. The cost/benefit analyses developed in this study must be based on consistent information to ensure the compatibility of results and the validity of comparisons between alternatives. The cost information supporting these analyses is based on unit cost data presented in this appendix.

Basic cost data are given for labor, waste packaging, transport, waste disposal, special equipment, and services and supplies. The data presented are all late 1980 or early 1981 costs.

The unit cost data presented can also be used to develop cost estimates for alternatives other than those considered in this study.

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15. 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.

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

Efforts on this program began at a high level this quarter as a result of the resolution in January on FY 1981 tasks to be pursued. Progress on the seven tasks during the second quarter is presented below.

Task 1 is the revision and issuance of topical reports from FY 1980. Three reports are involved. The first report, regarding the applicability of conflict mediation to waste management facility siting, received clearance in March. It is entitled Nuclear Waste Management and Environmental Mediation: An Exploratory Analysis, PNL-3678 (BHARC-411/80/038). Final corrections were made and the document was copied. The report will be distributed in April. The second report, regarding social science research needs in waste management, was rewritten in February and is undergoing a final revision in March. It is entitled Implementation Research for Radioactive Waste Management, PNL-3814. A draft copy for clearance will be finished in early April. A decision on the third report, preservation of information at repository sites, was made early in March. The scope of this report changed over the period of performance, with concurrence by the PNL

project manager in February of this quarter. Thus clearance will be requested for the report under the new scope, and clearance and publication should occur during the third quarter.

Task 2, technical services for the public participation aspects of the National Plan for Radioactive Waste Management, was carried out at a low level during the second quarter. No rewriting was needed regarding the Plan, but several meetings were held at HARC regarding specific suggestions that could be made to DOE regarding public participation programs for specific waste management programs.

Task 3, completion of reports regarding public perceptions of waste management facilities and other hazardous facilities, was largely completed during the second quarter. Four reports were completed and sent to PNL for clearance and should be cleared and published during the third quarter.

Task 4, the comparative analysis of existing national surveys on waste management, was begun late in the second quarter. HARC has begun to contact research firms for survey data. Most of the work on this task will occur in the third and fourth quarters.

Work on Task 5, the analysis of the public hearings process, was begun in the second

quarter. A work plan was agreed upon, a literature search was conducted, a meeting was held with staff at HARC who have participated in such meetings to gain and exchange first hand information, and a draft of the report was begun.

Task 6, an analysis of regional issues in the siting of waste repositories, also began during the second quarter. A work plan was drawn up and agreed upon, and four chapters of the report have been drafted.

Task 7, the decision incentives task, also began last quarter. A work plan was agreed upon in January, a literature search was conducted in February and March, and a first draft of the report was begun in late March.

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

PNL Dose Overview Committee comments have been incorporated into the report, Standardized Input for Hanford Environmental Impact Statements, PNL-3509. The final report should be published in April. Publication of HADOC - A Computer Code for Calculation of External and Inhalation Doses from Acute Radionuclide Releases, PNL-3503, has slipped, but also should be published in April.

Current EISs containing descriptions of the Hanford area are being reviewed in connection with the development of a standard description of the so-called "Affected Environment." These include the double-shell tank EIS (DOE EIS/0063) and the draft for the EIS relating to resumption of operations of the PUREX/UO₃ facilities at Hanford. A literature search, now under way, will supplement and update the area descriptions

contained in those EISs. Work is in progress on preparing portions of a standardized, current description of the Hanford Area.

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

The Salt Lake City Uranium Mill Tailings Remedial Action (UMTRA) EIS was selected as the first EIS for this task. PNL will also be involved in another UMTRA EIS (either Shiprock or Durango) and a Formerly Utilized Sites Remedial Action Program (FUSRAP) EIS (Middlesex, New Jersey, Sampling Plant and Associated Properties).

On February 11, 1981, the EIS Support Team and R. Scott, DOE-HQ, met to provide a better understanding of the objectives of the EIS support effort and to ensure consistent interpretations of NEPA, the CEQ Regulations, and the DOE NEPA Guidelines.

A. H. Schilling, lead contact on the Salt Lake City UMTRA EIS, met with Mel Merritt, Martin Tierney, and Shelton Bingham of Sandia Laboratories on March 6 to review their progress to date, learn of the project's general status and determine contributions that PNL might make to their efforts. The Notice of Intent (NOI) for the Salt Lake City UMTRA EIS was reviewed by task team members. Scoping meetings for that EIS have been set for May 5 and 6. A task member will attend both meetings.

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

A draft report entitled Understanding Nuclear Waste Management, PNL-3570, was revised by R. L. Murray this quarter based

(a) For background information see PNL-3000-8, an earlier report in this series.

on comments received from a variety of reviewers. The final draft will be submitted to PNL in April for DOE clearance.

Work was begun on a plan to guide the preparation of information on nuclear waste management and related subjects written in lay language. Contacts were made with DOE contractors to determine the availability of pamphlets, brochures, etc., published by or approved by DOE. A letter report will be prepared early next quarter summarizing the results of the analysis.

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

A workshop on "Waste Management Health Physics" was held last quarter at DOE-HQ. Planning was completed this quarter for a second workshop to be held at DOE-HQ April 20 through April 23. The course outline was improved based on the experience of the first workshop and was submitted to DOE-RL for clearance; final agreements with the lecturers were reached; and the handbook to be used was revised to reflect the new course outline. In addition to DOE staff it is expected that some NRC personnel will attend the workshop.

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

A draft report entitled Radionuclide Transport Studies for Assisting in Confirming the Integrity of Potential Nuclear Waste Repositories, PNL-3698, was revised based upon comments received from Sandia's Subseabed Program Office, the Waste/Rock Interactions

Technology project office, other PNL technical staff, and Office of Nuclear Waste Isolation. The report was sent to RL for clearance.

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

A final draft report entitled Selection of Containment Systems for Commercial High-Level Waste Management, PNL-3803, was submitted to PNL by TASC. This completed their subcontract agreement with PNL. The final draft incorporates PNL comments on an earlier draft received in February. It will be submitted to RL for clearance in April.

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

A paper by A. M. Platt and J. V. Robinson entitled "Commercial Nuclear Reactors and Waste: The Status as of December 1980" (PNL-SA-9231) was presented at the ANS Waste Management '81 Meeting in Tucson, Arizona, on February 23, 1981.

The paper states that between March 1 and December 15, 1980, the declared^(d) size of the commercial light water reactor (LWR) nuclear power industry in the U.S. decreased another 9 GWe. Conclusions reached include that, for the presently declared size of the industry:

- The 165 declared reactors will peak at a capacity of 153 GWe in 2001 and will consume about 820,000 MTU as enrichment feed.
- The theoretical rate of enrichment requirements will peak at about 19M SWUs/yr in the year 2014.

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

(b) For background information see PNL-3000-8, an earlier report in this series.

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

(d) Power plants that either have operated, are operating, are being built, or have been announced.

- As few as two repositories each with capacity equivalent to about 77,000 MTU would hold the waste.
- Predisposal storage in reactor basins and at AFRs (away-from-reactor basins) would peak at 65,000 MTU in the year 2016 if the two repositories were commissioned in the years 1997 and 2023, respectively.

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16. WASTE MANAGEMENT SAFETY STUDIES

P. J. Pelto - Project Manager

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

Work continued on the methods development and assessment tasks during the reporting period. The system description of a reference away-from-reactor spent fuel storage basin was completed. The independent spent fuel storage basin used in the Environmental Impact Statement on Management of Commercially Generated Radioactive Waste, DOE/EIS-0046F, was selected as the basis for the reference AFR. A safety assessment of

this reference AFR is being performed to demonstrate and refine the methods development task. A preliminary hazards analysis was begun to identify areas requiring more detailed safety analyses. An investigation is under way on the use of simple indices to permit comparative analysis of occupational exposure, routine releases, and accidental releases. Work continued on the state-of-the-art methods survey report.

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

F. H. Dove - Project Manager

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

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

SUMMARY

For the past several months, two approaches to the numerical solution of the inverse problem for hydraulic conductivity have been pursued, and two approaches to the stochastic analysis of ground-water flow have been examined. A computer code for the analysis of basic flow principles in a complex fractured material is essentially finished. Results to date, though preliminary, suggest that some important characteristics of flow through fracture systems may have been overlooked in the past.

Geostatistical modeling of ground-water pore velocity within a region of the Hanford Reservation was completed. A two-dimensional analytic solution was calculated to check the stochastic transport code currently under development. The dispersive effects analysis done in past months has indicated that the flow velocity autocovariance function is the fundamental statistical basis of the methodology. For geohydrologic response functions, several test optimizations were conducted assuming a square configuration

for the repository area. The results were subsequently plotted to show the relationship of the optimal trajectory to a reduction in quantity/arrival-time maximum values.

The Salt Dome Reference Site Initial Assessment (PNL-2955, Rev. 2) was submitted to clearance, and the Basalt Reference Site Initial Assessment (RSIA) draft report was prepared and submitted, completing two Department of Energy milestones. Results of the basalt analyses were presented to the Basalt Waste Isolation Program staff in Richland.

The Geologic Simulation Model (GSM) was used in the Monte Carlo mode to generate a 200-simulation analysis for inclusion in the Basalt Reference Site Initial Assessment draft report. The simulations helped delineate areas of model data still needing attention and also gave useful results. The analysis is considered preliminary because the input data are not finalized.

The DITTY1 code was used to calculate population doses from five scenarios applied to a high-level-waste repository as a comparison with EPA (Environmental Protection Agency) criteria.

The results of the well-water scenario match the EPA criteria of 10 health effects better than do the other four scenarios studied. It was concluded, however, that differences in opinion with EPA criteria would revolve around their definition of "accessible environment" rather than the code used to calculate health effects.

PROJECT MANAGEMENT - F. H. Dove and
M. G. Foley

An internal review of AEGIS program progress for the first quarter of FY 1981 was conducted on January 23. Proceedings included review of each task by the respective task leader followed by a management forum for obtaining a programmatic consensus related to task finances, manpower, milestones, and scheduling. Significant accomplishments discussed were application of geostatistics to a Hanford data set by J. L. Devary and simplification of computer routines for contaminant transport with uncertainty by C. A. Oster. The review provided each attendee with the opportunity to obtain:

- a balanced perspective on the overall AEGIS program
- an improved familiarity with each AEGIS task
- a first-hand diagnosis of programmatic health.

The AEGIS Technology Program Plan (TPP) for FY 1981 was submitted to the Nuclear Waste Technology Program Office (NWTPO) for approval.

The AEGIS Field Task Proposal/Agreement for FY 1983 (budget year) was completed and transmitted to the Nuclear Waste Technology Program Office for review by DOE/RL. Beginning in FY 1982, another functional element, methodology integration, will be incorporated

into the AEGIS structure. This structure, shown in Figure 17.1, establishes a separate branch for receiving and integrating other AEGIS performance assessment methodology not currently a part of the AEGIS program. Demonstrations of AEGIS methodology require the translation of the release scenario into a profile of contaminant concentration versus time (near-field, short-term consideration) before introduction into the hydrologic flow field. This has typically involved, on an ad hoc basis, personnel from scenario analysis, consequence analysis, and waste-form leach and sorption studies. In FY 1982, the technical interchange between AEGIS and WRIT, initiated in FY 1980, will be strengthened and maintained for package and repository release investigations (WRIT), geochemistry (WRIT), geologic simulation (AEGIS), and hydrologic and contaminant transport analysis (AEGIS). INTERA Environmental Consultants, Inc., will provide AEGIS with reports on new methodology (primarily near-field, short-term methodology) and with magnetic tapes and associated documentation of computer codes and will advise AEGIS staff in the use of this methodology in subsequent years.

The Materials Characterization Center (MCC) Program, sponsored by Savannah River Laboratory, is developing an extensive data base for waste management information. The AEGIS Program will eventually need access to such data for comprehensive evaluations of performance. At present, a single VAX computer, shared by both programs, would accommodate MCC's data storage requirements and AEGIS's analytical requirements. In addition, the VAX computer would be tied into a large mainframe computer equal to or greater than the capacity of a CDC 7600. This hybrid arrangement would anticipate the extensive numerical applications of the future after

FIGURE 17.1. Planned AEGIS Organization for FY 1982

code or model development requirements have been accomplished. A justification and implementation study is being prepared for submission to DOE/RL. The proposal includes a cost-sharing arrangement between MCC and AEGIS for the VAX system and peripheral equipment. The procurement schedule suggests receipt of bids near the end of FY 1981 for purchase of the system in FY 1982.

The NWTs Performance Assessment Plan and a draft outline were discussed at a Waste Isolation Performance Assessment Program (WIPAP) working meeting at the Pacific Northwest Laboratory (PNL) on January 14 and 15. Agreement on the detailed outline was obtained, and a writing schedule was established for exchange of initial draft sections of the plan by February 13. Because of unexpected difficulties in completing the Basalt RSIA, the exchange of initial draft sections was postponed until early in the third quarter.

The Systematic Comprehensive Evaluation of Performance and Total Effectiveness of Repositories (SCEPTER) Annual Review at INTERA Environmental Consultants, Inc., was attended in Houston, Texas, on March 3 and 4. AEGIS technical comments on the Quality Assurance Procedure for Code Transfer and suggested changes in procedure format were submitted to INTERA at that time. Organizational implications of the procedure will be discussed with PNL management in April.

Although formal authorization of a change in scope to program funding has not been received, work has continued to provide written contribution to the licensing topical report entitled "Performance Modeling for Site Selection." A working meeting at PNL for ONWI (Office of Nuclear Waste Isolation), Bechtel and AEGIS staff on January 7 helped to clarify concepts and coordinate writing responsibilities. Draft sections of the

licensing topical report were submitted to ONWI on February 5. Review comments and additional guidance are pending.

Seven coordinated presentations were made by AEGIS staff at the Symposium on Uncertainties Associated with the Regulation of the Geologic Disposal of High-Level Radioactive Waste at Gatlinburg, Tennessee, on March 12. These were given by F. H. Dove, M. G. Foley, R. Schalla, J. T. Zellmer, G. M. Petrie, J. L. Devary, and R. W. Nelson. Technical contents focused on various aspects of site-specific experience gained from demonstrations of AEGIS methodology. As of the end of this quarter, the AEGIS methodology has been demonstrated on six site-specific applications for bedded salt, dome salt, granite, and basalt.

At the request of DOE in Germantown, AEGIS consultant M. A. Harwell participated in a presentation of the Salt Dome RSIA (PNL-2955 Rev. 2) and of the ONWI Task Force Report on Salt Domes to C. A. Heath, C. R. Cooley, T. Longo, and C. Newton. Approval was received to participate in such a presentation later for the Nuclear Regulatory Commission (NRC) and the EPA.

METHODOLOGY DEVELOPMENT - R. W. Nelson

Flow Methodology Development - C. T. Kincaid

Recently two approaches to the numerical solution of the inverse problem for hydraulic conductivity have been pursued. These two methods, when used in sequence, give a promising tool for calculating conductivities with minimal requirements on data smoothness. The methods include 1) a path-integral technique which yields a global picture of the conductivity surface and 2) a variational algorithm which gives more refined local results.

Two approaches to the stochastic analysis of ground-water flow are currently being examined. First-generation simulation codes are being developed to test both the Keller smoothing and the Taylor expansion approaches to perturbations on the hydraulic conductivity and boundary conditions. The Keller smoothing approach developed and applied to contaminant transport by Alan Gibbs and C. A. Oster has been extended to fluid flow. This method is being implemented by the finite element technique. This implementation generates large arrays of stochastic quantities that must be subsequently manipulated. Development of codes for performing these manipulations effectively is continuing. The Taylor series approach to fluid flow advocated by Sagar (1974) and later by Dettinger and Wilson (1981) has been transformed into a stochastic simulation code. The code is designed to characterize a steady-state distribution of ground-water potential for a two-dimensional (e.g., horizontal) region.

The computer code for analysis of the basic underlying flow principles in a complex fractured permeable material is essentially finished, including the debugging and testing. The code considers the flow as a superposition of the singularity analytical solutions for single fractures and intersecting fractures in a permeable matrix. Using the analytical results, a very complete and detailed analysis of flow through and between complex fracture systems of specific statistical fracture lengths, apertures, and configurations can be considered.

The primary purpose in the analytical singularity approach solved by the code is to gain greater understanding of the peculiarities of fracture flow and its more realistic description. Results to date,

though preliminary, suggest some important characteristics of flow through fracture systems that may have been overlooked or certainly not emphasized in the past.

Flow through fractured materials, though having earlier first arrival times, when compared to flow through porous media, are found to have longer time intervals between the first and final arrival fronts. First results suggest that the advantage of the longer time between first and final fluid arrival may in many cases more than compensate for the seeming disadvantage of earlier first arrival times in fracture flow. More study will be required to evaluate this effect; the developed code, however, provides significant additional insight into such fracture flow characteristics.

Transport Methodology Development - E. M. Arnold

The geostatistical modeling of groundwater pore velocity within a region of the Hanford Reservation was completed. This involved the geostatistical estimation (kriging) of effective porosity, hydraulic conductivity, and potential (head) gradients and the propagation of kriging errors through pore-velocity calculations to characterize the pore-velocity estimating error.

This work was presented at the NRC symposium on "Uncertainties Associated with the Regulation of the Disposal of High-Level Nuclear Wastes" at Gatlinburg, Tennessee, in March and will be published in the symposium proceedings and also as a PNL document. The geostatistical modeling task is currently involved with supplying realistic (Hanford Reservation) input to the stochastic flow and transport models in the methodology development tasks.

To check the stochastic transport model under development, a two-dimensional analytic solution was calculated by Alan Gibbs. This solution is being encoded to become part of a testing procedure for the results of the "Transport Under Uncertainty" part of the methodology development program.

The dispersive effects analysis done in past months has indicated that the flow-velocity autocovariance function is the fundamental statistical basis of the methodology. Application of a hydrologic system's velocity autocovariance function in conjunction with the stochastic convective flow equation has been shown to result in a transport equation describing the expected solute concentration distribution. Autocovariance functions associated with field-scale velocity variations have been demonstrated to result in transport equations different from the classical convection-dispersion equation based on a dispersion coefficient representation. On the other hand, the convection-dispersion equation is known to provide a valid description of solute transport in laboratory-scale soil column tracer experiments. These results suggest a need to reconcile the descriptions of transport in the transition from macroscopic scale to megascopic field scale. The current column tracer experimental analysis relates macroscopic scale statistical properties to standard measurements of hydrodynamic dispersion based on a dispersion coefficient.

In the past quarter, the geohydrologic response functions were used as a contamination measure in an optimization procedure that yields optimal repository locations as an output. This methodology is founded on a view of the contaminant migration problem as

a distributed parameter control system. Application of this procedure results in the selection of mitigation and control strategies that satisfy the following criteria:

- ground-water flow and transport equations
- boundary constraints
- minimization of contamination outflow and related measures.

The controls, or design parameters, are the repository location coordinates and repository geometry. In particular, Powell's (1969) nonlinear conjugate direction minimization algorithm was adapted for the solution of the case where contaminant addition does not change the flow field, employing an analytic potential function. Several test optimizations were conducted assuming a square configuration for the deposition area. Initial results were highly favorable. Bounding penalty functions were adjusted to provide a more efficient means of limiting acceptable deposition regions. The results of the test problems were subsequently plotted to show the relationship of the optimal trajectory to a reduction in quantity/arrival time maximum values.

In flow methodology development, the need to meet major milestones has delayed somewhat the internal report on Keller smoothing applied to fluid flow, and computer availability could still become a problem in developing stochastic transport and flow models.

The major problem for the column experimental analysis subtask remains the selection of the proper theory supporting experimental results from the column dispersion literature. This may necessitate analysis of various experimental results. An extensive literature search was completed, and the papers are being studied for relevant results. To overcome this selection problem more rapidly, the dispersion study will be

divided into two papers--theory and experimental verification.

SITE APPLICATIONS - M. G. Foley

The Basalt RSIA draft report was prepared and submitted to clearance, completing that DOE milestone. Results of the basalt analyses were presented to the Basalt Waste Isolation Program staff in Richland on March 26. The presentation included a review of the source term model developed for AEGIS by WRIT.

The greater complexity than anticipated for work with the Basalt RSIA and the GSM is necessitating reassessment of programmatic priorities.

Scenario Analysis - M. G. Foley

The Geologic Simulation Model (GSM) was used in the Monte Carlo mode to generate a 200-simulation analysis for inclusion in the Basalt RSIA draft report. The analysis was of a preliminary nature because the input data are not yet finalized. This problem is related to input data difficulties reported previously, but the problem during the quarter became one of not so much obtaining data from consultants as of adjusting those data so that GSM submodels behave in accordance with observed behavior of the real geologic systems. The simulations helped delineate those areas of model data that still need attention and also gave some useful although not quantitatively reliable results.

The results indicated that near-repository faulting events, whether by extension of existing faults or creation of new ones over geologic time, dominate disruptive processes affecting the repository. At present this result is valid only for the first 10,000 years or so after closure because the

Continental Glaciation Submodel does not yet reproduce the effects of past glaciations let alone predict the behavior of future ones, and the Hydrology Submodel has not been modified to reflect calibrations of the regional variable thickness transient (VTT) and the Pasco Basin finite-element three-dimensional ground-water (FE3DGW) hydrologic model. Modifications to input data for the GSM submodels are in progress for future simulations, but the ones already exercised do not have realistic behavior in the areas of glacially-enhanced or blocked recharge, glacially-induced rock fracturing, Missoula flood effects, and overall ground-water flow rates. Effects of glaciation, however, will probably not be important for the next 10,000 years, so the present GSM results are qualitatively reasonable for that period.

The draft report describing these results was submitted and included in the Basalt RSIA draft report. If appropriate, a separate report describing GSM results for the Columbia Plateau will be issued later. However, such a report will not be prepared until production runs with well-behaved submodels have been performed.

Hydrogeologic and Transport Analysis - C. R. Cole

Hydrologic and transport analysis and computer modeling efforts for the Basalt RSIA were completed and documented. The hydrologic efforts for the Basalt RSIA consisted of a regional model of the Columbia River basalts covering about 21,000 square miles in southeastern Washington. The boundaries of the model region were described in an earlier working paper. The recharge to the regional basalt system and the distribution of this recharge were the subject of the working paper on "Aquifer Recharge Calcula-

tions for the Basalt RSIA." Recharge and recharge distribution were carefully estimated to provide the additional constraint necessary to determine the transmissivity in the Grande Ronde basalts and vertical permeability distribution in the basalts during the model calibration phase of the regional modeling effort.

The VTT multilayer two-dimensional code was used to model the regional system. The system was modeled as three layers with the surface layer consisting of the alluvial systems, the rivers, the lakes and the basalt seepage faces. The second layer consisted of the combined Saddle Mountains and Wanapum basalt system of aquifers. The third layer consisted of the Grande Ronde system of aquifers. Each of these layers contained a 55 by 55 finite-difference grid with a 3-mile grid spacing. Layers were connected by an interlayer transfer coefficient.

Potentiometric data on more than 350 Saddle Mountains and Wanapum basalt wells and an interpreted potentiometric surface for the Saddle Mountains-Wanapum system of aquifers were used in calibrating transmissivity and interlayer transfer coefficient values. This was done to match model-predicted and observed or interpreted potentials for the Saddle Mountains-Wanapum system of aquifers.

Estimates indicated ~1,700,000 acre ft/yr of recharge to the basalt systems over the area of the regional model. Pumping withdrawal estimates amounted to ~204,000 acre ft/yr. In the calibrated regional model, the average transmissivity of a Saddle Mountains-Wanapum model node was 85,000 gal/day/ft, and 51,000 gal/day/ft for a Grande Ronde node. Vertical hydraulic conductivity in the basalts was on the order of 0.001 ft/day.

After developing and calibrating the regional model, a more detailed model of essentially the Pasco Basin area was developed. The regional model was used to provide boundary conditions as input to the local model because much of the flow in the local (or Pasco) basin area has its origin in the regional system and enters the local system through the northern and eastern boundary of the local model area.

The FE3DGM code was used in the local modeling effort. Gephart (1979), Myers (1979), and other sources were utilized to prepare structural, transmissivity, and potential interpretations for:

1. the alluvial aquifer systems within the Pasco Basin
2. the Saddle Mountains aquifer systems
3. the Wanapum aquifer systems
4. the Grande Ronde aquifer systems.

In addition to the above data, a joint recharge calculation effort, similar to that for the regional system but more detailed, was undertaken by AEGIS and BWIP for the Pasco Basin area. All these data were utilized in the four-layer, fully three-dimensional model of the Pasco Basin. This model consisted of 606 surface nodes connected to form 555 surface elements. The input data on structures and potentials were used to infer the extent of the saturated zones in each of the four layers within the local model, and only saturated elements in each layer were modeled. The local or Pasco Basin model area consisted of ~1870 square miles.

Recharge estimates within the Pasco Basin for pre-man conditions amounted to ~55,000 acre ft/yr, while estimates for current conditions amount to 287,000 acre ft/yr with pumping withdrawal estimates ~27,000 acre ft/yr.

Various sensitivity studies were carried out during the calibration of the local modeling effort. These efforts, not easily summarized out of context, are detailed in the Basalt RSIA draft report.

After the model was calibrated, it was used to predict travel times to the biosphere discharge point. Data from the hydrologic modeling effort and the scenario analysis task, along with water chemistry data and data on distribution coefficients, were then used to provide input to the transport modeling effort. Only the base case fault intersection event was examined, with all transport model input parameters set at best-estimate values. Transport results were analyzed on three different time frames, 1000 years, 10,000 years, and the long term 2,000,000 years. The results of these analyses are detailed in the Basalt RSIA draft report.

A meeting was held in March at Los Alamos Scientific Laboratory (LASL) to discuss the AEGIS involvement with the nuclide migration field experiments being performed jointly by LASL, Sandia National Laboratories (SNL), and Argonne National Laboratory (ANL). A plan for cooperative effort was identified that would satisfy ONWI's desires to check Waste Isolation Performance Assessment Program (WIPAP) methodology versus field and laboratory measurements via a set of pre-test predictions and also serve to aid the LASL-SNL-ANL program. AEGIS plans to publish a preliminary model of sensitivity results as a letter report to ONWI about July or August. The current experimental design and test plans were explained, and PNL indicated that after the SNL and LASL information on tuff was received AEGIS would design a modeling plan for the sensitivity study in May and June. Full-scale, pre-test calculations probably would not be completed before May 1982.

Dose Analysis J. K. Soldat

The DITTY1 code was again debugged and used to calculate population doses from five scenarios applied to a high-level waste (HLW) repository by B. A. Napier. Two of these were completed last quarter: 1) direct consumption of the entire allowable release by a single person and 2) contamination of wells at the site boundary, with about 200 persons consuming contaminated water and irrigated foods. The latter scenario was, however, rerun with the newly debugged DITTY1 code during January.

The three new scenarios were based on a Hanford-type site with the released quantities of each radionuclide being diluted in the Columbia River, assuming a flow rate of 10^5 cfs. In the first of the three runs, the nuclides were released to the river uniformly over the 10^4 -year period; in the second, they were released uniformly over the first 10^3 years; and in the third, they were released over the last 10^3 years.

The results of the direct ingestion and well water scenarios are not much different than reported last quarter. The direct ingestion case leads to upper-bound, large numbers of health effects, 10^3 to 10^5 per 10,000 years. The results of the well water case match the EPA criteria of 10 health effects better than do the other four scenarios studied. The three Hanford scenarios lead to a very small number of health effects 10^{-2} to 10^{+1} . It appears that the EPA statement that no population was defined for their analysis may be correct, and perhaps they did use a scenario somewhat like the well water case. If so, any differences of opinion with EPA criteria would revolve around their definition of "accessible environment" rather than the code used to calculate health effects. The major problem in dose analysis is still a lack of knowl-

edge of exactly how EPA calculated population radiation doses and health effects for their criteria for radionuclide releases from a HLW repository.

A draft report on the dose code, MAXDOS, was received from the author, B. L. Serini, EPA, for review in January. This code was not the one used by EPA to derive their HLW criteria. It was instead a code for calculating doses from accidents at a HLW repository. Review of MAXDOS was completed by D. L. Streng and forwarded to Mr. Serini in February. Documentation of the DITTY1 code was started but delayed by other work; the completion date of June 1 may, however, still be achievable.

The tapes and summaries of the four codes (ARRG, FOOD, PABLM and DACRIN) were sent to the ANL Code Center in January.

REFERENCES

- Dettinger, M. D. and J. L. Wilson. February 1981. "First Order Analysis of Uncertainty in Numerical Models of Groundwater Flow Part 1. Mathematical Development." Water Resources Research 17(1):149-161.
- Gephart, R. E. et al. 1979. Hydrologic Studies Within the Columbia Plateau Washington. An Integration of Current Knowledge. RHO-BWI-ST-5, Rockwell Hanford Operations, Richland, Washington.
- Myers, C. W. et al. 1979. Geologic Studies of the Columbia Plateau, A Status Report. RHO-BWI-ST-4, Rockwell Hanford Operations, Richland, Washington.
- Petrie, G. M. et al. April 1981. Geologic Simulation Model for a Hypothetical Site in Basalts of the Columbia Plateau. PNL-3542, Pacific Northwest Laboratory, Richland, Washington.
- Powell, M. J. D. 1964. "An Efficient Method for Finding the Minimum of a Function of Several Variables Without Calculating Derivatives." Computer Journal 7:155-162.
- Sagar, B. December 1974. "Galerkin Finite Element Procedure for Analyzing Flow Through Random Media." Water Resources Research 14(6):1035-1044.

18. WASTE/ROCK INTERACTIONS TECHNOLOGY PROGRAM (WRIT)

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

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

- 1. identify and quantitatively characterize mechanisms of waste from radionuclide release and subsequent geochemical interactions with engineered barriers and natural geologic media, e.g., leaching, solubility, and sorption*
- 2. develop and evaluate the effectiveness of models to predict leaching, sorption and release processes in the repository and surrounding media*
- 3. obtain, through verification studies and documentation, the most acceptable test methodologies for sorption, leaching, solubility, limitations and waste package-geomedia interaction studies*
- 4. support repository site characterization licensing.*

PROGRAM MANAGEMENT - R. J. Serne

During the second quarter of FY 1981, several documents were reviewed and meetings attended to facilitate useful interaction among the various groups involved with the nuclear waste isolation issue. Efforts were also made to improve project administration to reduce the technical staff's time spent on administrative tasks.

A proposal from Harvard University on Nonequilibrium Chemical Reactions and Colloidal Transport Phenomena in Radionuclide Migration was reviewed and comments sent to Harvard and ONWI (Office of Nuclear Waste Isolation). Comments on a Climax Stock nuclide migration field experiment and a Climax Stock field block test proposal were also sent to Lawrence Livermore National Laboratory, ONWI and DOE Headquarters. The Test Plan for Nonradioactive and Fully Radioactive Tests of Waste/Rock/Barrier Interactions under Hydrothermal Conditions in Basalt, prepared by the Basalt Waste Isolation Program (BWIP), was reviewed and

comments forwarded to ONWI. Comments on the ONWI site characterization plan also were prepared for N. Hubbard, and W. J. Deutsch worked several days at ONWI on this effort.

In a meeting held with the Materials Characterization Center (MCC) their procedures and needs for the Materials Handbook were discussed. An internal quarterly review of AEGIS (Assessment of the Effectiveness of Geologic Isolation Systems) was also attended to facilitate WRIT and AEGIS coordination.

G. L. McVay gave a presentation to the National Academy of Sciences Panel on Waste Isolation Systems, at ONWI's request, on "Performance Testing of Spent Fuel Waste Forms" in Washington D.C. on March 19-20, 1981. On March 26, R. J. Serne presented a guest seminar to the USGS in Denver on "Current Status and Future Direction in Chemical Aspects of Nuclear Waste Isolation."

Experimental procedures were reviewed; five new procedures were written and are now under review. The measuring and testing equipment used in WRIT was checked by internal quality assurance staff, and minor

changes made on calibration levels. Priorities for capital equipment for Tasks 3, 4 and 7 were established so that purchasing could begin. Capital equipment requests for the subcontractors were also reviewed.

The first quarterly reports were prepared and distributed to ONWI and PNL's Nuclear Waste Technology Program Office (NWTPO). A final draft of the FY 1981 Technical Program Plan was approved by ONWI. D. J. Bradley discussed FY 1981 and FY 1982 budgets, WRIT program status, and current WRIT waste package testing at ONWI. Field task proposals were prepared and submitted to the NWTPO.

LEACHING MECHANISMS - G. L. McVay

Surface Investigations

X-ray photoelectron spectroscopy (XPS or ESCA), Auger electron spectroscopy (AES), and secondary ion mass spectrometry (SIMS), in combination with ion milling, can be used to obtain compositional depth profiles in corroded glasses. However, because of the use of ion milling, all three methods are affected by sputtering artifacts such as differential sputtering, sputter-broadening of interfaces, and surface topology changes. In the case of differential sputtering, different results will be obtained for SIMS versus XPS and AES because SIMS analyzes particles that are sputtered off the sample's surface while AES and XPS analyze material remaining on the surface after sputtering. Thus, comparing the results of XPS or AES sputter profiling with those of SIMS is potentially useful in evaluating the extent to which certain elements in a reacted glass sputter faster or slower than the average matrix.

A direct comparison of SIMS and XPS depth profiles (Figures 18.1a-f) demonstrates that, for most elements, either technique could be applied with reasonable accuracy. The same conclusion was reached in an earlier study for sodium and calcium in a soda-lime-silicate glass (Malm et al. 1978), although the data presented were less than convincing. The fact that SIMS and XPS analyses essentially agree indicates the glass matrix sputters essentially uniformly; i.e., material is sputtered from the sample surface at a rate proportional to its concentration in the solid. In addition, since SIMS and XPS profiles for silicon are analagous and show a variable profile (Figure 18.1b), a real variation in the concentration of silicon as a function of depth in the leached waste glass must occur. The practice of normalizing all SIMS profile data to the profile for silicon (McIntyre, Strathdee and Philips 1980), thereby assuming that the concentration of that element does not vary as a function of depth, should be avoided as significant distortions in the shapes of the depth profiles of all elements will result.

Because of the high sensitivity of the SIMS technique, cesium analysis can be routinely performed as given in Figures 18.2a-c. Figure 18.2a shows that cesium becomes depleted to greater depths as a function of time at 50°C. At 70°C (Figure 18.2b) resorption of cesium at shallow depths is found at 14 and 28 days. At 90°C, resorption is much more extreme. The fraction of cesium lost from the reacted zone of the glass at times >14 days at this temperature is actually less than is found for shorter leach times. Solution analyses concur with the above in that the concentration of cesium in solution has been found to decrease after an initial increase.

1(a)

1(b)

FIGURE 18.1a-f. SIMS and XPS Sputter Profiles for 76-68 Glass Static Leached 5 Days at 70°C in DI Water ($S/V = 0.2 \text{ cm}^{-1}$)

1(c).

1(d)

FIGURE 18.1 (contd)

1(e)

1(f)

FIGURE 18.1 (cont.d)

2(a)

2(b)

FIGURE 18.2a-c. Normalized SIMS Cesium Data for 76-68 Glass Leached for Varying Times at (a) 50°C, (b) 70°C, and (c) 90°C

2(c)

FIGURE 18.2. (contd)

Concentration profiles for iron and zinc by SIMS and XPS do not agree (Figures 18.1e and 1f). Differences could be due to uneven sputtering or to variations in the ion-to-neutral yield with changes in the chemical matrix, the latter of which will affect only SIMS analyses. One method by which the discrepancy may be resolved is shown schematically in Figure 18.3. This device, which was constructed following a recent report (Thompson, Hintermann and Challet 1979), mechanically mills a very fine spherical taper into a sample surface. Auger point scans can then be taken across the taper, resulting in a depth profile without extensive ion milling, thus eliminating sputtering artifacts. Work in this area is proceeding.

Mechanism Studies

pH Effects on Leaching

As leaching is believed to be a pH-dependent phenomenon but investigation has been inadequate, a leach test was performed to compare pH effects in simple glasses, such as fused silica and soda-lime silicate, with those in a more complex borosilicate waste glass. All leach tests were conducted at 90°C, SA/V of 10 m⁻¹ over a pH range of 1.4 to 12. All samples were cut from a larger one and sanded with 600-grit silicon carbide paper to ensure uniform surface preparation. The leachate pHs were adjusted with either NaOH or HCl. Figure 18.4 shows silicon analysis as determined by ICP, plotted as leach rate per day versus pH. The figure shows striking differences in

MECHANICAL MILLING APPARATUS

MECHANICALLY MILLED SPECIMEN

FIGURE 18.3. Diagram of Mechanical Milling Method

FIGURE 18.4. ICP Analysis of Silicon, Leach Rate/Day Versus pH

dissolution rates for borosilicate and silicate glasses. The borosilicate glass exhibits high leach rates at the acid end of the pH scale, while the silicate glasses show negligible dissolution. In the strong base range, the silicate glasses begin to dissolve, while the borosilicate appears to remain stable. All glasses studied appear stable to leaching in the middle pH range of 4 to 8.

Results imply that dissolution kinetics change dramatically as glass-former composition changes from a primarily silicate-based former matrix to a borosilicate matrix and indicate also the leading roles pH and subsequent glass constituent hydrolysis play in the dissolution process. The effect of glass modifiers on leaching remains unclear, as evidenced by the small difference between the fused silica and soda-lime-silica dissolution curve.

UO₂ Dissolution

UO₂ dissolution experiments were designed to identify probable leaching mechanisms for spent fuel that lead to release of radionuclides during contact with an aqueous solution. The oxidation-dissolution mechanisms for single-crystal UO₂ surfaces were investigated based on air oxidation and solution oxidations in severe conditions to identify the effects of temperature, electrochemical potential and oxidants such as H₂O₂ (probably generated by radiolysis of water). A progress report written in FY 1980 has been reviewed, and distribution is expected in April.

Figure 18.5 shows a detailed oxidation-dissolution model of UO₂ in deionized water. The model involves several reaction processes such as surface oxidation, oxidation-dissolution, and transport, hydrolysis and deposition of uranyl hydrates. Both surface oxidation

and oxidation-dissolution processes occur at the same time to oxidize U(IV) to U(VI), which is readily soluble. Both hydrolysis and deposition of uranyl hydrates will occur when the uranyl ions near the UO₂-H₂O interface exceed the solubility limits. Deposition of the uranyl hydrates on the UO₂ surface is an important process affecting the long-term leachability of the spent fuel.

Results indicate the following:

1. Oxidation of UO₂, in air or aqueous solutions, occurs mainly at the surface. For single-crystal UO₂, surface oxidation is limited to several Å deep, and for polycrystalline UO₂ pellets several microns deep, along the grain boundary.
2. The initial dissolution of UO₂ and spent fuel involves the oxidation of U(IV) to U(VI) uranyl ions. The oxidation-dissolution is a rate-controlled process whose rate will increase with temperature. The deposition of uranyl hydrates occurs more rapidly at high temperature to form large hydrate crystals.
3. The presence of H₂O₂, a probable water radiolysis product, enhances the oxidation-dissolution of UO₂ and also increases the deposition rate for hydrate crystals.
4. Dissolution rates for UO₂ in brine solution are low because the surface is passivated by the hydrate film.
5. Electrochemical methods may be used to determine the leaching behavior for UO₂ and spent fuel.

Future work will compare the dissolution rate of UO₂ measured by weight loss and measured by solution analysis by polarography and compared with the measurement of the electron-charge transfer during the dissolution process. After this correlation is established, dissolution of the grain boundary and of the grain surface will be compared by a potentiokinetics method in deionized water and brine solution.

REACTIONS

(1) SURFACE OXIDATION (several Å)

(2) OXIDATION-DISSOLUTION

(3) TRANSPORT

(4) HYDROLYSIS- Film Formation, 25-75°C

(5) HYDROLYSIS- Crystal Growth, 150°C

FIGURE 18.5. Oxidation-Dissolution Mechanisms for Single-Crystal UO_2 Surface in Water

Leaching

Analytical results of the static leach tests at 25 and 75°C on 76-68 doped glass beads showed that in general, leaching is highest in a sodium bicarbonate solution for all of the nuclides except technetium, where

no clear dependence on leachate is evident. The strongest effect is for uranium, where the 341-day release is one to two orders of magnitude higher in bicarbonate than in deionized water or brine. Releases in WIPP "B" brine and water are not substantially different.

ROCK-RADIONUCLIDE RETARDATION STUDIES -

J. F. Relyea

Methodology Development and Application

A large column of Westerly granite was used for the study of the effects of flow rate on effective porosity. Tritium spikes were eluted through a column 25.4 cm long by 3.3 cm diameter, at flow rates from 270 to 4900 m/yr. Figure 18.6 shows the cumulative activity recovered from these runs. The effective porosity was affected little by the flow rate (effective porosity is defined as the volume at which half the added spike is recovered: $CE/CI = 0.50$, where CE/CI = the cumulative effluent activity recovered divided by the total influent activity).

Previously reported experiments with much shorter columns have shown effective porosity decreased as the flow rate was increased. Possibly the decrease is caused by a nonhomogeneous pressure gradient near the column inlet at high flow rates, which would result in a stagnant region near the inlet. This

problem can be simply solved by conducting a few tritium tracer tests to determine the effective porosity of a column at several flow rates near that desired for a dynamic sorption test. A suitable flow rate can then be selected to ensure that Darcy's law is obeyed in the sorption experiment.

An intact (vertical) unconsolidated core from the Wilcox Formation in east Texas is being used for dynamic sorption tests at PNL. The core has been characterized mineralogically, and the dominant mineral phase in the $>2 \mu\text{m}$ particle-size fraction is quartz. Kaolinite is the most abundant mineral, with quartz as the second most abundant in the clay-size fraction ($<2 \mu\text{m}$). A flow rate of 0.29 ml/hr (12.4 m/yr) has been established by applying a driving pressure of 25 psi to the influent solution. The hydraulic conductivity of the core was thus calculated to be 9.0×10^{-6} cm/sec. A tritium spike will be run through the core to determine the effective porosity for comparison with the calculated porosity of 27%. Subsequent elution of neptunium or

FIGURE 18.6. Elution of Tritium Through 25.4-cm Column of Crushed Westerly Granite. CE/CI is the cumulative effluent activity recovered divided by the total influent activity added as a spike.

strontium will yield retardation factors for comparison with predictions of retardation factors from batch K_d data.

Variation of solution-to-solid ratio in batch K_d measurements with granite at LASL was found to affect the measured K_d value for cesium and possibly strontium, but not barium, cerium, or europium. Increasing the amount of solution from 5 ml/g of rock to 30 ml/g resulted in a higher K_d (Cs) by a factor of 2.5 to 3.1. The reason for this behavior is unexplained at this time and is contrary to the results expected if the cesium sorption mechanism were ion exchange. Upcoming experiments may explain the cause of variable effective porosity in disaggregated rock columns. Experiments with an intact core from a typical salt dome region are readily performed, and an unexplained K_d dependence on solution-to-solid ratio has been observed.

Retardation Mechanism Studies

Uranium adsorption on SiO_2 is being studied at LBL using a combination thermodynamic and adsorption model. Figure 18.7

shows the uranium solution species for a given set of conditions predicted using the thermodynamic model. At low pH values (<6) adsorption of UO_2^{++} can be modeled by an ion exchange mechanism. At higher pH values the hydrolyzed UO_2OH^+ and $\text{UO}_2(\text{OH})_2^0$ species dominate and ion exchange is no longer the major adsorption mechanism. It was assumed that adsorption of these two hydrolyzed species could be described by the following equations:

and

where SOH denotes a surface SiO_2 adsorption site. By letting K_1 and K_2 vary, it was found that a best fit could be obtained with $K_2 \approx 10^4$ and that the value for K_1 made little difference. This implies that the neutral species $\text{UO}_2(\text{OH})_2^0$ is very highly adsorbed by the SiO_2 surface. It is not possible, however, with available data to determine whether this is the actual adsorption

FIGURE 18.7. U(VI) Species with an Initial UO_2^{++} Concentration of 10^{-8}M in 10^{-2}M NaCl

mechanism or if some other mechanism (such as hydrolysis of $\text{UO}_2(\text{OH})^+$ at the surface) is actually responsible for the adsorption. Figure 18.8 shows the total uranium solution concentration predicted to be in contact with SiO_2 using the thermodynamic model (for speciation) and adsorption model [ion exchange of UO_2^{++} and surface complexation of $\text{UO}_2(\text{OH})_2^0$]. Ion exchange alone predicts that the concentration should remain near 10^{-8} for an initial concentration of 10^{-8}M (e.g., essentially no adsorption).

Use of the combined models has:

1. aided in eliminating ion exchange as the dominant uranium adsorption mechanism at $\text{pH} > 6$
2. helped identify a possible mechanism for uranium adsorption at $\text{pH} > 6$
3. more accurately fit the experimental data, regardless of the actual adsorption mechanism.

Such geochemical sorption models should predict radionuclide solution concentrations with much more confidence than predictions using a single retardation factor for radioelements having complex chemistries.

At Rockwell Hanford Operations, hydrazine is being used as a reducing agent and Eh buffer to study neptunium behavior in rock-water systems. Neptunium was adsorbed from the Grande Ronde formation ground water by altered basalt and its secondary minerals both with and without hydrazine in the system. However, the neptunium concentration in contact with altered basalt was lower by an order of magnitude with hydrazine than without it. Neptunium concentrations in contact with the secondary minerals were lowered by almost two orders of magnitude after addition of the hydrazine.

The effects of ground-water composition on technetium sorption were also studied at

FIGURE 18.8. Adsorption of U(VI) by SiO_2 from Initial UO_2 Concentration of $1.2 \times 10^{-8}\text{M}$. The upper line is the concentration curve predicted in 1M NaCl. Predictions for U concentrations include both ion exchange and adsorption of hydrolyzed species.

Rockwell using a modified two-level factorial designed experiment (Plackett-Burman). Controlled parameters were: Na^+ , Ca^{++} , Mg^{++} , K^+ , Cl^- , F^- , SO_4^{--} , CO_3^{--} , HCO_3^- , and N_2H_2 (hydrazine) at two levels (a high level and a low level for each). Analysis of the final technetium concentrations in contact with basalt, altered basalt, and secondary minerals showed that hydrazine was the only significant parameter (95% level) associated with technetium adsorption. Without hydrazine, $K_d(\text{Tc})$ values ranged from 0 to 6 ml/g; with hydrazine the K_d values ranged from 150 to >400 ml/g. The greater than values for K_d are caused by the detection limit for technetium in solution. It is not possible from the present data to distinguish between the two possible mechanisms that may be responsible for lowered technetium concentrations (adsorption and precipitation) because the solubility of TcO_2 is not known. Until the mechanism is determined, these " K_d " values should be used with caution; the data, however, do support the thermodynamic predictions that technetium under reducing conditions will be much less mobile/soluble than technetium in oxidizing environments.

The sorption model for uranium has accurately fit experimental data and given clues to possible mechanisms. In granite environments, plutonium appears to readily adsorb/precipitate. Reducing conditions in basalt environments significantly reduce neptunium and technetium mobility.

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

Solubilities of Key Compounds and Elements

Many solubility and hydrolysis constants used in predicting chemical behavior of various radionuclides have been estimated or extrapolated from homologues of other elements.

Rai and Strickert (PNL) have been working during the past quarter to provide experimental values and predictions for the solubility of different solid phases of neptunium in ground waters expected at different repositories. Previous reports have indicated that in dilute CaCl_2 solutions of pH 4 to 7, neptunium exists as Np(V) under oxic conditions (Rai and Strickert 1980). To better understand neptunium solution behavior, experiments were begun to measure the solubility of $\text{NpO}_2\text{OH(s)}$ over a wide pH range. $\text{NpO}_2\text{OH(s)}$ precipitates were prepared, washed, and placed into dilute salt solutions (0.0015M CaCl_2). The suspensions were adjusted to various pH values, and the neptunium concentrations and pH values were then monitored for 155 days. The concentration values of neptunium as a function of pH are plotted in Figure 18.9 for the 155-day period. Oxidation state analysis before precipitation and at times during the experiment confirmed that neptunium was in a higher (V or VI) oxidation state in solution.

Generally the pH values of samples initially at a higher pH tended to decrease with time. The decrease in pH, however, was associated with a corresponding increase in neptunium concentration. The change in pH is most likely caused by alpha radiolysis and the production of nitric acid (Rai, Strickert and Ryan 1981).

Least squares fitting of the data points between pH 7 and 12 gives a straight-line fit with a slope of ~ -0.5 . These results are similar to the $\text{NpO}_2(\text{OH})_2$ solubility results of Moskvina (1971) who also observed a slope of -0.5 of $\log \text{Np}$ (moles/l) at pH values >6.7 . However, no increase has been seen in solubility at pH values >8 due to Np(VI) species (as reported by Moskvina 1971). Possibly more than one neptunium oxidation state is involved, or kinetics may have

FIGURE 18.9. Neptunium Concentration Values as a Function of pH (155 days)

influenced the concentrations over the longer time period of this experiment.

Characterization of Chemical Species of Redox Sensitive Elements

Careful measurement and control of redox potentials are necessary for meaningful solubility determinations of redox-sensitive elements. Previously questions have been raised about the reliability of platinum electrode measurements in unpoised or weakly poised systems. Bondietti and coworkers at Oak Ridge National Laboratory (ORNL) investigated the validity of platinum electrode measurements in their ongoing technetium studies. Fe(II) salts were added to N₂-purged 0.1M KCl solutions adjusted to various pH values. Along with Eh and pH measurements, the Fe(II) concentrations were determined (either colorimetrically or with an ⁵⁵Fe tracer). From the known Fe²⁺/Fe³⁺ couple (0.77 V) and the Fe²⁺ hydrolysis value (pK₁ = 9.5), a log K_{sp} value was calculated for Fe(OH)₃. For log [Fe(II)] values ranging from -3.54 to -7.19, measured Eh values from 0.275 V to 0.272 V, and pH values ranging from 5.6 to 9.2, the mean log K_{sp} value

was -37.8 ± 0.38 . Because an error of ± 60 mV in the Eh reading would only lead to a variation of ± 1 in the log K_{sp} value, the use of platinum electrodes even at Fe(II) concentration of $<10^{-6}$ M would appear valid.

A topical report on the redox behavior of technetium under defined redox conditions is currently under internal review and is expected to be available before mid-April.

Newton and coworkers at Los Alamos Scientific Laboratories (LASL) have been studying the redox control of solutions using Eh buffers which poise the system. An osmium couple, Os (II-III)(bipy)₃, has been studied (bipy stands for 2,2'-bipyridyl). The reported potential is 0.878 V. In a plutonium system the reaction is expected to be:

The compound [Os(bipy)₃](ClO₄)₂·2H₂O was prepared and a spectrophotometric redox titration method was developed for assaying the compound. After recrystallization from

water, the compound was found to have a molecular weight of 889 ± 13 g/equivalent. The formula weight is 894.

To determine the stability of the Os(II) and Os(III) complexes, solutions of each were boiled in 6M NaCl. The spectrum of the Os(II) complex remained essentially unchanged after 18 hr of boiling. The Os(III) complex was refluxed for 1 hr, after which the solution gave a spectrum completely different from the starting material. However, when the material was reduced with Fe^{2+} , the characteristic spectrum of the Os(II) complex was restored. It was also determined that the decomposition rate of $\text{Os}(\text{bipy})_3^{3+}$ is $\sim 2.8\%$ /day at room temperature. Similar derivatives of the Os(II-III) complex will be examined for stability and chemical behavior.

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

Mechanism Studies

Initiated in FY 1981, the mechanisms subtask is intended to emphasize processes that may act to limit radionuclide concentrations in aqueous solutions at the waste-form surface. It is based on previous and concurrent investigations designed to understand release-rate mechanisms from waste forms and is an extension of studies emphasizing the interface between the waste form and backfill, or waste form and rock components. Work on glass-rock interactions and glass-crystal reaction mechanisms is discussed in this report.

Glass-Rock Interactions

Data from the last of a series of mini-canister tests have been examined further to

determine some of the dominant reactions in the system and to provide some guidance for additional mechanism studies. Specifically, additional effort has been devoted to characterizing the solid phase, with emphasis on both surface and materials present within fractures of UO_2 -doped 76-68 glass.

To compare the solution concentration from the glass-rock tests with probable ground waters of granitic and basaltic origin, data from the glass-rock test conducted at 250°C were plotted along with some ground-water compositions (Figure 18.10). Figure 18.10, the activity diagram of the system $\text{Na}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ calculated at 25°C , shows some mineral assemblages that might be expected during alteration or weathering of a feldspathic rock. In a very simplistic sense, the diagram represents alteration in rock systems having a high albite content. However, the data plotted on the figure are concentrations of elements in solution rather than activities, so attempts to deduce actual rock alteration mechanisms from these plots could be misleading. Calculation of activities in these solutions would require an evaluation of activity coefficients and an assessment of solute speciation. Geochemical codes currently available for such calculations may exhibit some uncertainty when applied at 250°C as they do not include some species such as boron or molybdenum which are present in solution from glass leaching. Consequently, for a first approximation, solution concentrations were determined on solutions extracted at experimental pressure and temperature conditions. Some precipitation during sampling could have occurred, making actual concentrations higher than those measured.

Within these limitations, some trends are apparent. The basalt ground-water concentration data lie close to the assemblage:

FIGURE 18.10. Activity Diagram of $\text{Na}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ Calculated at 25°C

albite/analclime/montmorillonite. The association of these phases with basalt ground water may deserve further examination as a possible dissolved silica and pH controlling mechanism; however, calculated activity diagrams assume pure end member phases, while a common assemblage in basalt is an albite component of plagioclase, analclime, and nontronite. Another trend is the increase in silica and alkali content of solutions as a function of time. The trend is toward the albite stability field, which implies that possible albitization of some bentonite back-fill components during the thermal period should be considered in backfill evaluations.

Crystal/Glass Leaching Behavior

An investigation to compare leaching mechanisms in vitreous and crystalline materials

was conducted in support of the waste-form release mechanisms task and as an initial part of the mineral solubility effort. Starting materials used were a natural albite from Amelia County in Virginia (97% $\text{NaAlSi}_3\text{O}_8$), and a glass prepared from this same material. This mineral was selected because considerable information exists in the literature concerning its chemical and thermodynamic properties, and it has been used in related weathering mechanisms studies (Holdren and Berner 1979).

Cleavage fragments of albite and samples of albite glass, with geometric surface areas of about 1 cm^2 , were leached in deionized water at temperatures up to 150°C using a static leach test following the standard test, MCC-2. The surface morphology of these materials was examined by scanning electron microscope (SEM), and the surface chemistry was examined by ESCA sputter

profiling. An example of a typical ESCA sputter profile is shown in Figure 18.11 for a 7 day, 150°C leach test. The albite glass exhibits a surface composition different from the bulk that persists up to 300 μm , while the surface composition of the albite cleavage fragment is essentially identical with the bulk composition. The change in

surface composition of the glass is similar to the development of a "gel layer" in waste glasses, and the lack of compositional change in the crystalline material is in agreement with that observed by Holdren and Berner (1979). Consequently, it appears that a diffusion-limiting barrier does not develop on crystalline albite surfaces as it does on albite glass.

FIGURE 18.11. Sputter Profile for Albite Crystal and Glass for a 7-Day Leach Test at 150°C

Helgeson (1979) has calculated a reaction path sequence for the dissolution of both sodium and potassium feldspars, which shows the sequence of appearance of secondary phases in a static system is in the order: gibbsite $[Al(OH)_3]$ to kaolinite $Al_2Si_2O_5(OH)_4$ to Na montmorillonite $[Na_xAl_2(Al_xSi_{4-x}O_{10})(OH_2)]$. Leaching studies of crystalline albite and albite glass for periods up to 28 days confirm the first part of this reaction path sequence.

Waste-Package Test Design and Analysis

The first intermediate-scale waste-package test incorporating waste, canister, overpack, backfill, rock and ground water was concluded on January 26. This joint PNL/Sandia National Laboratory test utilized an intact rock salt core, bentonite/sand backfill, Ticode-12 overpack, and a ^{238}U doped 76-68 glass waste form in a stainless steel 304 L canister. The test ran for 90 days at 250°C and 2000 psi. A final hot sample was taken, although only 10 ml were collected before the sample lines (heated to 250 C) plugged with salt. After a 24-hr cooldown, the 19-2 autoclave was opened and photographed, and numerous solution samples were taken and distributed for analysis. A 2-day meeting has held with M. Molecke of Sandia to go over the post-test analytical work desired for the package test. Sampling of the solid components (except the glass waste form and canister) of the first test was completed and samples distributed to PNL and Sandia. The samples of the glass and canister will be taken pending the set-up of a new diamond saw.

Although final solution analyses have not been completed, preliminary data are quite similar to the results of the minicanister tests without the backfill and Ticode-12

overpack present. The analysis of the solid constituents of the test are ongoing and should be completed within 6 weeks. At that time, a meeting will be scheduled between PNL and Sandia staff to discuss the results of the test. Visual examination of the test components revealed no significant corrosion to the metallic overpack or the glass waste form and canister. These parts were coated with a film, presumably made of quench products and amorphous silica.

Additional information on the operation and design of complex systems tests was obtained. As a result, we are reevaluating the approach that should be taken to assess waste package performance. A rough draft of our approach was forwarded to ONWI for comments.

We have received the 1-2 and 19-2 autoclaves that will be used for hot-cell tests. Because of the experience gained in waste-package testing to date (and the fact that the autoclaves were designed over a year ago), these autoclaves are being modified in several ways. The changes are mainly in regard to direct sampling at temperature and pressure and to continuous flow capability.

Single-Pass Continuous Flow Tests

A rough draft of a report on the first Livermore test series (waste form/solution interactions only) was finished in late February. It is to be sent to the authors for review in early April. The document, including data, covers rather completely the continuous flow experiment, including detailed conclusions and comparisons to the parallel IAEA test conducted at PNL.

SOURCE-TERM MODELING - W. L. KuhnWaste-Form Modeling

Emphasis is currently on completing the literature review of models applied to leaching of glass. Thus far, diffusion is one of the most common processes cited, although it may not be important to the predicted release of radionuclides from glass over the period of interest (thousands of years). The surface-area-to-volume ratio sometimes appears as a primary variable, but its effect is usually seen to change pH, which then affects leach rate. So far, the review supports our assumptions that corrosion rates need to be characterized in terms of temperature, pH, and radiation field, and that solubility effects need to be better understood.

Experimental Liaison

A list has been developed to determine priorities for designing experiments among the radionuclides whose geochemical behavior in the repository are of primary importance in evaluating the long-term safety of deep geologic repositories. The list shown in Table 18.1 is based on the isotopes that have commonly dominated the radiologic consequences of various repository risk assessments. Primary ranking was based on the frequency with which a particular isotope was found to dominate or significantly contribute to the total dose consequences, the absolute magnitude of the isotope-specific dose, the ratio of the dominant isotope dose to the next most significant isotope, and the range of conditions over which it dominated the result.

TABLE 18.1. Radioelements Important to Long-Term Safety of Geologic Repositories Containing Spent Fuel(a)

<u>Primary Group</u>		<u>Secondary Group(c)</u>	
Iodine	(¹²⁹ I)	Strontium	(⁹⁰ Sr)
Technetium	(⁹⁹ Tc)	Cesium	(¹³⁷ Cs)
Americium		Plutonium(b)	(²⁴⁰ Pu)
	(²³⁷ Np), ²³³ U,	Thorium(b)	
	²⁹⁹ Th, ²²⁵ Ra		(²²⁶ Ra)
Neptunium		Radium	
Uranium(b)			
	(²²⁶ Ra), ²³⁴ U,		
	²¹⁰ Pb, ²¹⁰ Po		
Plutonium(b)			
Carbon(b)	(¹⁴ C)		

(a) Primary isotope or primary daughter isotope in parentheses, secondary daughters following.

(b) Eliminated or greatly reduced significance for reprocessed and/or high-temperature process HLW-form isotope inventory.

(c) Only for extreme conditions of human intrusion.

Emphasis was given to analyses of potential dose consequences by isotope, based on a systems analysis of the release from the repository, transport to the biosphere (including decay chain effects) and resultant human dose from biosphere pathways over a wide range of geologic and hydrologic conditions. Analyses were also considered that used greatly simplified assumptions and calculated relative hazards based on maximum permissible concentrations. A final factor in the ranking was the currently perceived solubility and mobility of specific elements in ground-water systems.

Given the solubility and mobility of neptunium as well as the recent evidence of increased dose significance, the importance of understanding the redox behavior of neptunium in the deep geologic system has increased. The redox behavior of neptunium in reducing geochemical environments may be such that its solubility is smaller and retardation higher than assumed for typical safety assessments, which would then deemphasize its importance. Similar assumptions may be made for the redox behavior of technetium.

Other redox-sensitive elements include plutonium and uranium. As indicated in Table 18.1, their redox behavior is probably less important since the primary group contribution from plutonium is: $^{238}\text{Pu} \rightarrow \rightarrow ^{234}\text{U} \rightarrow \rightarrow ^{226}\text{Ra}$. Plutonium-238 has a half-life of only 88 years, not very significant on the time scale relevant to the repository, although it may be of some importance in the initial distribution of ^{226}Ra for unexpectedly early release from the waste package. The importance of the redox behavior of uranium is somewhat less considering the source of essentially all the long-term hazard from ^{226}Ra , the very long-lived isotope ^{238}U , and the observed behavior of the natural uranium chain in the environment. There is little

reason to believe that the behavior of this chain at the repository will differ from that observed for rich natural uranium deposits, which provide a considerable fraction of the natural terrestrial "background" dose.

The median-lived ^{14}C and long-lived ^{129}I appear on the list because of their dose significance upon ingestion, the large inventory in spent fuel, and the high solubility and lack of retardation in ground-water systems. If significant sorption or reduced solubility in the deep geologic environment cannot be assured for these elements, then some engineered system should probably be provided to limit the release rate of these elements from the waste package, or some means other than geologic isolation should be investigated for ultimate disposition of these isotopes. The latter alternative would be possible if the spent fuel is reprocessed, since these two elements naturally separate from the liquid waste during fuel dissolution and could be available for separate disposal.

This list was based on the state-of-the-art for determining those elements that a long-term assessment should consider; however, it is not a definite list and should be viewed as an avenue for further discussions, leading to refinement.

Source Term Modeling

The source-term model for spent fuel in basalt developed in support of a reference site initial analysis for basalt performed by the AEGIS program was presented for review by staff of the BWIP. The model considered the extreme scenario of rupture of waste packages in a new fault, net oxidizing conditions in the spent fuel due to radiolysis, and significant water flow from the

fault plane into ruptured packages. Nevertheless, the predicted release from the repository was less than 10^{-5} /yr for all cases, due both to the small number of packages that could be ruptured (0.5%) and the solubility constraints on the release of uranium.

GEOCHEMICAL MODELING AND SITE INVESTIGATIONS - W. J. Deutsch

Code Development

This task supports development of the WATEQ and EQ3/EQ6 computer programs for application to site characterization and performance assessment of the geochemical environment of potential nuclear waste repositories. Code development is necessary to adequately represent the existing ground-water/rock chemical system and to simulate the system's response to the thermal period of a repository and the potential interaction of waste material with the host rock.

The WATEQ computer code is operational on the Richland Federal Center Univac system. The efficiency of the link between PNL and the Univac has been enhanced considerably by the generation of software to interface a PNL Tektronix system with the Univac. It is now possible to enter and edit data sets on the Tektronix and send them as a package to be run by the Univac. Software will be written to enable the Tektronix to receive the Univac output for various analytical purposes and to produce graphic displays.

Nontronite, a common fracture-lining clay mineral in the basalts of the Columbia Plateau, is necessarily being added to the WATEQ data base. This addition required a review and evaluation of the available thermochemical data. Estimation methods were then used to calculate the data needed

to add this mineral to the WATEQ suite of minerals. In addition, thermochemical data for lepidocrocite and a variety of zeolite minerals are being reviewed for future addition to WATEQ so as to represent the basalt chemical system more completely.

The computer code EQ3/EQ6 is being developed at Lawrence Livermore National Laboratory by Dr. Tom Wolery for WRIT applications. The EQ3 code performs calculations similar to WATEQ's and they can be used to verify each other if they have similar data bases. EQ6 simulates the reaction path that a rock/water system would follow due to temperature change or the effect of mineral dissolution/precipitation under partial equilibrium conditions. During the first quarter of FY 1981, a computer code (MCRT) was prepared to assist in expanding the EQ3/EQ6 thermodynamic data base. MCRT performs many useful functions, including consistency tests and extrapolation of 25°C data to higher temperatures. Revisions were made in the uranium data set, including the addition of a few net aqueous species. Work was begun to incorporate the dissolution kinetics capability to EQ6, and this will be Wolery's major effort during the next quarter.

Model Applications

In support of work on leaching mechanisms, three sets of data from PNL 76-68 glass leach tests were modeled using EQ3. The solution data came from the static leach tests in deionized water for 26, 56, and 91 days at 90°C. Preliminary results show that the solution is undersaturated with amorphous silica (natural glass) but is at saturation with quartz. As the solution cools to 25°C, it becomes sequentially

saturated with the other forms of silica, i.e., chalcedony, cristobalite and finally amorphous silica. Furthermore, EQ3 results suggest that, with cooling, other minerals may act as concentration-limiting phases for other elements in solution. These minerals are: analcime (for Na, Si, and Al), smithsonite (for Zn), albite (for Na, Si, and Al), laumontite (for Ca, Si, and Al), and ferrous oxide (for Fe; $E^H = -0.3$ V). Not only will these minerals affect the solution concentration of elements present in their structure but newly formed minerals will serve as sorptive substrates for ions in solution and thus may affect the complete solution chemistry.

The purpose of the geochemical modeling study of the basalt ground-water system is to determine the chemical processes (mineral dissolution, precipitation, sorption, etc.) that are occurring in the aquifer chemical environment. Knowledge of these processes will allow us to simulate the environment using a mathematical model, necessary in the safety assessment for a nuclear waste repository system. During the first quarter of FY 1981, 16 waste samples from the upper-confined aquifer system of the Columbia Plateau Basalt in the Pasco Basin were modeled using WATEQ. (Preliminary results used on the 16 samples were discussed in the first quarterly report for FY 1981.) An additional 98 ground-water analyses from throughout the Columbia Plateau in Washington State were modeled this quarter. Initial results of the basalt/ground-water mineral equilibria study will be presented in May at the Symposium on Geochemistry of Radioactive Waste Disposal sponsored by the Geological Association of Canada.

Repository and Site Characterization Support

During this quarter, task personnel helped develop geochemical data requirements to be incorporated into the ONWI Earth Science Data Acquisition Guidelines document. This document will list the earth science data needs to be satisfied by the regional and near-field site characterization studies. Input to the document from this task stressed the need for data that can be used to geochemically model the system at various scales from the far-field to the near-field.

A new study has been initiated in the geochemical modeling task this quarter. It is a study of the migration of natural radionuclides to be performed by J. C. Laul, C. W. Thomas, and R. W. Perkins of PNL. They will use the various naturally occurring radionuclides together with their long-lived spontaneous fission products to place a lower-bound on the time since this material was last transported. If no movement of the natural radionuclides occurs in a given geologic medium for periods of one million years or more, it may be concluded that a site in a similar medium is reasonably suitable for long-term storage.

Task personnel organized a meeting with representatives of the AEGIS program to determine the WRIT's involvement in their Paradox Basin Study. It was decided that WRIT would provide input on geochemical data requirements for submission to the ONWI site characterization effort; the list of data needs was subsequently transmitted to AEGIS. It was decided also that WRIT will develop the geochemical aspects of the AEGIS geologic simulation model if sufficient data are made available for undertaking a geochemical modeling study.

REFERENCES

- Holdren, H. C. and R. A. Berner. 1979. "Mechanisms of Feldspar Weathering I. Experimental Studies," Geochim. et Cosmochim. Acta 43:1161-1171.
- Helgeson, H. C. 1979. "Mass Transfer Among Minerals and Hydrothermal Solutions." In Geochemistry of Hydrothermal Ore Deposits, 2nd ed. Ed. H. L. Barnes. John Wiley and Sons, New York, New York, pp. 568-610.
- Malm, D. L., M. J. Vasile, F. J. Padden, D. B. Dobe and C. G. Pantano, Jr. 1978. J. Vac. Sci. Tech. 15:35.
- McIntyre, N. S., G. G. Strathdee and B. F. Philips. 1980. Surf. Sci. 100:71.
- Moskvin, A. I. 1971. Soviet Radiochemistry, 13:700.
- Rai, Dhanpat and R. G. Strickert. 1980. "Maximum Concentration of Actinides in Geologic Media." Trans. Nucl. Soc. 35:185-186.
- Rai, Dhanpat, R. G. Strickert and J. L. Ryan. 1981. "Alpha Radiation Induced Production of HNO_3 During Dissolution of Pu Compounds." Inorg. Nucl. Chem. Letters 16:551-555.
- Thompson, V., H. E. Hintermann and L. Chollet. 1979. Surf. Tech. 9:421.

19. HIGH-LEVEL WASTE FORM PREPARATION (HLWFP)

D. H. Siemens - Project Manager

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

SUMMARY

Characterization and preparation of the waste log for shipping were completed during this report period. All equipment required for handling the shipping cask and shipping the log to E-MAD has been designed. These designs were submitted to the Nuclear Assurance Corporation (owner of the NLI 1/2 shipping cask) and/or Westinghouse E-MAD for their concurrence. Fabrication of these items is in progress.

CHARACTERIZATION - D. N. Berger

The waste log was placed in an existing furnace where it was heated to 500°C and held at temperature for an 8-hr period. No emission of vapors was observed during heatup. The heatup was performed to ensure no pressurization problem would occur during

shipping or subsequent storage of the log in the Near-Surface Test Facility.

PREPARATION

At the conclusion of the heatup, a lid was installed on the waste log canister and seal-welded. All exterior hardware was removed from the canister and, except for final decontamination, the log is ready for shipping.

CASK HANDLING

The design of all equipment required to handle the NLI shipping cask and for shipping the waste log to E-MAD were completed. These designs were submitted to Nuclear Assurance Corporation and/or Westinghouse E-MAD, as appropriate, for their concurrence. This equipment is currently being fabricated.

20. DEVELOPMENT OF BACKFILL MATERIALS

E. J. Wheelwright - Project Manager

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

SUMMARY

The effects of compaction pressure and material composition upon the compaction density of candidate backfill materials have been examined. As expected, the density of Na-bentonite compacts increases with increasing compaction pressure at constant water content. At constant compaction pressure, maximum densities were obtained at 5 to 8 wt% H₂O.

Four permeability cells have been placed in operation using synthetic Grande Ronde ground water. Pure Na-bentonite has the lowest hydraulic conductivity (6.7×10^{-13} cm/sec) of the materials tested to date.

COMPACTION OF CANDIDATE BACKFILL MATERIALS

Clays, quartz sand, zeolites, minerals, metal powders, and graphite are being mixed in various ratios and pressed in an air-hydraulic press to study the relationship of compaction density to material composition and pressing conditions. The objective is to obtain a backfill material composition that will maintain its physical shape during placement, and will then prevent water intrusion, provide enhanced radionuclide sorptive capacity, provide adequate thermal transport, and buffer the Eh-Ph of the backfill environment.

The results of compaction experiments with undiluted Na-bentonite (Volclay CS-50®) are shown in Figures 20.1 and 20.2. The solid lines in Figure 20.1 show the relationship between applied pressure and final density for Na-bentonite containing differing amounts of absorbed water. A reference point of 0.0 wt% absorbed water was assumed for clay that was heated at 110°C for 16 hr. Vacuum drying at the same temperature for the same time gave comparable dehydration. On this basis, the as-received clay contained 7.5 wt% absorbed water. Clays of higher hydration were obtained by equilibration with water vapor in a sealed system. After the pressed pellets were weighed and measured, each was dehydrated by heating in an oven at 110°C for 16 hr. The dehydration results are shown by the dashed lines in Figure 20.1. The four pellets pressed from previously dehydrated clay powder did not change during the pellet dehydration step.

In Figure 20.2, pressed pellet density is shown as a function of the water content of the unpressed clay for compacts pressed at four different pressures. The importance of using clay with the proper degree of hydration is clearly shown.

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FIGURE 20.1. Density of Na-Bentonite as a Function of Compaction Pressure and Water Content

GROUND-WATER MIGRATION RATES

$$Q = \frac{-KA(h_2 - h_1)}{L}$$

The primary function of a backfill material is to exclude water from contacting the containerized waste. This ability to exclude water is related to the permeability of the backfill. In the laboratory, permeabilities are determined by measuring the parameters in Darcy's Law for flow through porous media.

Darcy developed an empirical relation between the volumetric flow rate and the hydraulic gradient across the process medium:

where Q is the volumetric flow rate, A is the cross-sectional area of the sample, and $h_2 - h_1$ is the difference in hydraulic head across the sample length, and K is a constant called the hydraulic conductivity (Freeze and Cherry 1979). The hydraulic conductivity has the units of length per unit time, and it can be interpreted as the water velocity per unit drop of hydraulic head (Scheidegger 1960). It is a

FIGURE 20.2. Density as a Function of Compaction Pressure and H₂O Content

function of the properties of both the porous medium and the permeating fluid. A parameter $k(L^2)$ known as the specific permeability has been defined to be dependent on only the porous medium. The hydraulic conductivity is related to the specific permeability by the equation

$$K = \frac{k\rho g}{\mu}$$

where ρ and μ are the density and viscosity of the permeating fluid and g is the acceleration due to gravity.

Experiments have been initiated to measure the hydraulic conductivities of pure clay and mixtures of clays with quartz sand, natural and synthetic zeolites, metal powders, graphite, and selected minerals as a function of compaction density, material composition, applied hydraulic gradient, and ground-water composition. Later the effects of temperature and gamma radiation will be examined.

Preliminary results from experiments completed and still in progress are shown in Table 20.1. In these tests, the materials were compacted at 138 MPa. Synthetic Grande

TABLE 20.1. Permeability of Clay/Sand Mixtures

% Na-Bentonite	% Sand (80-120 Mesh)	Initial Density, g/cm ³	Hydraulic Conductivity, cm/sec	Time to Migrate 1 cm, yr
25	75	2.1	$2 \times 10^{-9(a)}$	15
50	50	2.1	3×10^{-12}	11,000
100	0	2.1	7×10^{-13}	45,000

(a) Hydraulic conductivity decreasing with time.

Ronde ground water was used as the permeating fluid. As the ratio of clay to sand is increased, the conductivity decreases by several orders of magnitude to $<10^{-12}$ cm/sec for pure Na-bentonite clay. The hydraulic conductivity of the 25 wt% clay-75 sand mixture shows a decrease by a factor of two over the 189-hr period following the initial breakthrough.

Because of the low permeabilities of these backfill materials, experimental hydraulic gradients must be significantly higher than those expected in a geologic repository in order to obtain data in a reasonable time period. The data in Table 20.2 show that for a 50% clay-50% sand mixture the hydraulic conductivity is reasonably constant over a hydraulic gradient range of 3.5×10^4 to 2.1×10^5 . For these gradients the backfill materials appear to follow Darcy's Law.

Deviations from Darcy's Law are not expected until the hydraulic gradient drops below 100. Extrapolations of experimental data to this region will usually overestimate the flow (Mitchell and Younger 1967). Therefore the laboratory results are conservative.

BACKFILL GEOCHEMICAL STABILITY

One of the more significant problems of backfill development is providing assurance that the backfill materials will maintain their identities and their desirable properties over the required containment time. A test plan for the hydrothermal testing of proposed backfill materials is nearing completion. The testing program described in the plan is designed to set upper limits on the amount of reaction that is acceptable over the required containment time period.

TABLE 20.2. Pressure Effects on Permeability of 50-50 Clay/Sand Mixture

Hydraulic Gradient	Equivalent Pressure Drop, psi	Time at Pressure, hr	Total Time, hr	Hydraulic Conductivity, cm/sec
1.55×10^5	2200	169 ^(a)	169	4.1×10^{-12}
7.03×10^4	1000	72	241	-
3.52×10^4	500	62	309	3.5×10^{-12}
7.03×10^4	1000	72	381	3.1×10^{-12}
2.11×10^5	3000	97	478	3.1×10^{-12}
1.58×10^5	2250	334	812	2.9×10^{-12}

(a) Includes 64 hr before initial water breakthrough.

and under repository conditions rather than attempting to establish the thermodynamic stabilities.

The testing program will consist of both accelerated tests at higher temperatures (up to 400°C) and long-term tests at temperatures representing more reasonable repository conditions. Because of the difficulties inherent in detecting small quantities of solid reaction products, runs of at least several years duration will be required at repository temperatures in order to set reasonable upper limits on the amount of reaction that may be expected during the containment period. These low-temperature tests will be carried out with sets of identical samples that can be opened at regular intervals. This will allow early checks for reactions that may adversely affect backfill performance.

The autoclave tests will be carried out at pressures of 10 and 30 MPa, representing hydrostatic pressure at a depth of 1000 m and lithostatic pressure in basalt, the

densest repository rock under consideration, at a depth of 1000 m. Low-pressure data, to help determine the effects of pressure on backfill material stability, will be provided by tests carried out in Parr bombs under saturated steam pressure. Tests at several pressures are important because many proposed backfill materials are hydrous (i.e., clays, zeolites) and their stability may be strongly affected by variations in water pressure.

REFERENCES

- Freeze, R. A. and J. A. Cherry. 1979. Groundwater. Prentice-Hall, Inc., Englewood Cliffs, New Jersey.
- Mitchell, J. K. and J. S. Younger. 1967. "Abnormalities in Hydraulic Flow Through Fine-Grained Soils." In Permeability and Capillarity of Soils. American Society for Testing Materials, Philadelphia, Pennsylvania.
- Scheidegger, A. E. 1960. The Physics of Flow Through Porous Media. The MacMillan Company, New York.

21. DEVELOPMENT OF STRUCTURAL ENGINEERED BARRIERS

R. E. Westerman - Project Manager

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

SUMMARY

A group of candidate barrier element materials are being evaluated by means of corrosion screening tests, using Hanford ground water at 250°C. The most promising candidates will be subjected to in-depth environmental testing. Current emphasis in the screening tests is placed on cast steels and ductile cast iron in simulated basalt ground water at 250°C.

A dynamic autoclave facility is being constructed for simultaneously exposing specimens to gamma radiation and high-temperature corrosive environments.

A slow-strain-rate test facility has been made operational. Initial tests, of Grade 12 titanium sheet stock strained to failure in simulated basalt ground water at 250°C, suggest embrittlement of the material in one metallurgical orientation, i.e., when the material is stressed in the rolling direction.

SCREENING TESTS

Corrosion screening of a variety of nickel-, iron-, copper-, titanium-, and zirconium-base alloys in simulated Hanford (basaltic) ground water at 250°C was completed. Specimens were exposed in a U-bend configuration, and each specimen contained a

simulated weldment. The final 3-month, high-oxygen-fugacity portion of a 9-month test was completed and weight change data obtained. Both the corrosion deposits plus any depositional scale were removed using the techniques reported by Westerman (1980). As expected, most metals were more susceptible to corrosion with the addition of dissolved oxygen (5 to 7 ppm). The amount of metal weight loss increased about tenfold for most metals. Both Nickel-200 and Zircaloy-2 displayed greater resistance to corrosion in the high-oxygen environment. The ranking of the metals in susceptibility to corrosion remained the same as for the low-oxygen tests. The stainless steels, Inconels, Hastelloy-C® and titanium alloys displayed the lowest corrosion rates; nickel and copper-nickel alloys were intermediate; and the cast irons showed the greatest weight loss. Though cast irons corrode at the highest rate, they still appear to be excellent candidates for structural barrier components in low ion-strength waters. Additional specimens representing thick (5-in.) sections of two cast steels and one ductile cast iron are currently being prepared for additional screening studies in ground waters typical of basalt and tuff formations.

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Emphasis will be placed on determining the time-dependence of the corrosion rate.

RADIATION - CORROSION FACILITY

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

To date, an autoclave test apparatus in a radiation facility has not been available for our program. To remedy this situation, such a facility is currently being constructed. The radiation will be provided by ^{60}Co sources in an existing Hanford Engineering Development Laboratory radiation facility. Provision is being made for electrical resistance heating of the autoclaves; dynamic flow conditions; complete chemical characterization of influent and effluent liquids; and electrochemical monitoring of the specimens and the environment within the reaction vessels.

The three required autoclaves have been received. The sealing system has been found to be acceptable, but will be modified to increase reliability. The preliminary safety assessment has been completed. We expect to have a usable facility by July 1981.

About 50% of the hardware for this facility has been ordered.

SLOW-STRAIN-RATE APPARATUS

A slow-strain-rate test facility is now in use. This facility will ultimately have three pressure vessels and three constant-elongation-rate loading mechanisms. Two of

the three systems are currently in use. An additional (third) autoclave has been ordered. Rupture of metallic specimens under slow-strain-rate conditions in repository-relevant environments, with subsequent fractography and stress-strain analysis, is expected to further define the susceptibility of candidate barrier materials to environmentally induced degradation. This facility became operational in January 1981, achieving the milestone.

Slow-strain-rate tests of Grade 12 titanium have been conducted in flowing simulated Hanford basalt ground water at 250°C. Tests of the LT orientation (specimen stressed in the rolling direction) have been done at 10^{-4} , 10^{-5} , and 10^{-6} in./sec. Preliminary results indicate that ductility as determined by reduction of area and elongation to fracture decreased significantly at lower strain rates. This finding indicates that environmental degradation may exist, and that the operative mechanism requires material deformation and exposure to the environment. Preliminary studies (two tests only) of the material in the TL orientation (specimen stressed perpendicular to the rolling direction) indicated no similar behavior.

OTHER ACTIVITIES

S. G. Pitman attended a "Waste Package Research and Design Interface Meeting" at Sandia Laboratories on February 18 and 19. The purpose of the meeting was to review the new conceptual package designs developed by Westinghouse AESD, Pittsburgh.

REFERENCE

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

22. DISPOSAL CHARGE ANALYSIS

L. L. Clark - Project Manager

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

During this quarter the search for data on repository design, operation and costs was expanded and nearly completed. Extensive data have been compiled for repositories in salt. Less information is available for repositories in granite, basalt and tuff.

The information collected will be used as input to a repository cost model that is concurrently under development. This model will be used to analyze the effect of package types, repository size, thermal loading and other variables on overall disposal costs in each medium. Currently, the basic

core of the model has been outlined and the associated inputs and outputs have been programmed. The model is being constructed in a modular fashion so that new repository designs can be analyzed with little or no reprogramming.

During the next quarter the cost model will be completed and exercised using the available data on each repository medium. The most favorable sets of conditions in terms of costs will be identified for each medium. A preliminary report describing the results is to be issued July 1, 1981.

23. 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.

Work was begun on a data book to summarize the data currently used in the spent fuel storage and fee calculation. Work was continued on writing a methodology description chapter for the fee report, and work was started on documenting the computer models for their eventual transfer to the sponsor.

A meeting was held on March 24, 1981, with Kent Sasser, DOE/SR, and Spence Grotheer and John Clark, du Pont, Savannah River Laboratory, to discuss the program for the remainder of the year in light of the change in the DOE spent fuel policy. It was agreed

that work on the topical report summarizing the fee calculations would continue, but with the focus changed to documenting the assumptions and the methodology. The purpose of this report is to provide documentation of the fee calculation activities for other parts of DOE that may eventually be involved in assessing fees to utilities. Fee-related activities will not be continued in FY 1982. Systems or economic studies may still be needed as part of the next year's program; if so, funding will be at a reduced level.

24. SPENT FUEL AND POOL COMPONENT INTEGRITY PROGRAM

A. B. Johnson, Jr. - Project Manager

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

SUMMARY

The draft of the World Survey of Spent Fuel Storage Experience was typed at PNL and sent to IAEA (Vienna) for distribution to and comment by the 19 countries which contributed.

Final reports are being written summarizing results of Shippingport and Connecticut Yankee fuel examinations.

Studies are continuing to examine important factors which promote intergranular stress-corrosion cracking of alloy 304 stainless steel in low-temperature aqueous environments.

PROGRAM MANAGEMENT - A. B. Johnson, Jr.

Details of discussions regarding high-burnup demonstration fuel and examination results on Connecticut Yankee fuel are summarized in a later section.

INTERNATIONAL

The International Atomic Energy Agency (IAEA), based in Vienna, and the Nuclear Energy Agency (NEA), based in Paris, conducted a world survey of spent fuel storage experience. The draft of the World Survey was typed at PNL and was then transmitted

to IAEA in February for distribution to contributing countries for review and comment.

SPENT FUEL ACQUISITION AND EXAMINATION -

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

Shippingport Fuel Examination

An outline of the formal report that describes the results from the hot-cell examination of Shippingport Fuel Bundles 0551 and 0074 was prepared. A trip was made to the hot-cell facility at Battelle Columbus Laboratories to obtain remaining information needed for the report.

Metallographic examination of the tube sheet (Fuel Bundle 0074) area where it had been in contact with the steel lifting cable showed no evidence of galvanic corrosion or hydriding.

Samples for burnup analysis were taken from the center of one fuel rod from each of the two bundles. The results show burnups of 420 GJ/kgU (4900 MWd/MTU) for the fuel rod from Bundle 0551 and 3100 GJ/kgU (36,000 MWd/MTU) from the fuel rod from Bundle 0074.

Samples for determining the hydrogen content of the cladding were taken adjacent to each of the eight metallographic sections.

The measured values ranged from 50 to 90 ppm and were independent of burnup. Although special attention was given to finding any defects or areas showing cladding degradation, very few specific areas could be identified. What appears to be a shallow crack was noted at the internal surface of one high-burnup fuel rod from Bundle 0074. This rod also exhibited more fuel-to-cladding bonding, and the internal cladding surface was rougher than any of the other fuel rods examined. This apparent crack represents the worst defect found in any of the rods, and it extends through only 5% of the cladding wall thickness.

Work was started on filling out the transfer forms that provide a basis for a decision regarding extended storage of the fuel in a deionized water pool.

Connecticut Yankee Fuel Examination

An outline of the formal report that describes the results from the hot-cell examination of Connecticut Yankee Qualification Fuel Assembly S004 was prepared. A substantial portion of the rough draft of that report has been assembled.

The status of and results from the examination of S004 were presented by A. B. Johnson, Jr., at the Review Committee Meeting on Connecticut Yankee Fuel Examination Projects. The meeting was held at Northeast Utilities Service Company in Berlin, Connecticut, on March 3. Attendees included representatives from the Electric Power Research Institute (EPRI), Northeast Utilities Service Company (NUSCO), British Nuclear Fuels Limited, Babcock & Wilcox, Combustion Engineering, General Atomics, Connecticut Yankee Atomic Power Company, Battelle Columbus Laboratories (BCL), and

Pacific Northwest Laboratory (PNL). After the meeting, PNL sent BCL a letter listing items associated with the hot-cell examination of S004 that need clarification to permit completion of certain entries in the draft of the final report.

The examination results to date indicate that there is no obvious degradation of the stainless steel-clad spent fuel after 5 years of storage in borated water. No cladding breaches with concomitant loss of fission products and/or fuel or ingress of coolant occurred in the pre-characterized fuel rods that were inspected during the post-irradiation examination, based on reactor operating data (NRC docket information), sipping results, rod weight measurements, and eddy-current test results. No evidence of cladding cracks, pitting, or significant general corrosion was observed on the ID and OD surfaces during the metallographic examination of the cladding. No corrosive attack or cracking was observed in or adjacent to the weld areas in the rods examined. A qualitative indication of good ductility was evident in the ring-crush test results from the irradiated cladding from Fuel Rod AHR (the high-burnup rod destructively examined). Irradiation strengthening was observed in the cladding from Fuel Rod AHR (assuming that the unirradiated strength was comparable to that of fuel rod cladding from Fuel Assembly H07). Based on fission gas release and fuel microstructural information, there appear to be at least two categories of fuel rods in Fuel Assembly S004. No impacted pellet chips were found on the cladding ID surfaces of the metallographic sections taken from the two S004 fuel rods that were destructively examined.

Mechanical property testing of cladding from S004 fuel rods has been completed.

Photomicrographs were obtained of the structure of fuel from S004 and two Connecticut Yankee fuel assemblies (H07, G11). These and other results are being studied to establish criteria for selecting fuel rods for surveillance during extended pool storage.

Commonwealth Edison Discussions

A. B. Johnson, Jr., met with Commonwealth Edison staff members on February 5, 1981, in Chicago. The utility, EPRI, and Westinghouse are cooperating on a high-burnup demonstration program. Four assemblies at the Zion Nuclear Power Station are expected to reach burnups near 55,000 MWd/MTU in March 1982. The utility staff indicated that they would reply to a letter expressing PNL/DOE interest in eventually having access to one or more of the high-burnup assemblies for surveillance.

The utility will also consider cooperating in a study to define impacts of defective fuel on spent fuel storage operations at the Dresden Nuclear Power Station.

As a follow-up to these and earlier discussions with Commonwealth Edison about the two proposed PNL studies, efforts were begun to prepare letters to that utility.

Other Items

PNL was contacted by Babcock & Wilcox to see if PNL had an interest in some demonstration fuel. In connection with a DOE-sponsored program, Babcock & Wilcox currently has fuel from Oconee in their hot-cell facility (at least one fuel assembly has a burnup of 40,000 MWd/MTU or more). Once the fuel rods that are to be examined have been extracted, the rest of the fuel assembly is to be shipped back to the reactor spent fuel pool.

POOL COMPONENT EXAMINATIONS -

A. B. Johnson, Jr.

PNL has negotiated to obtain specimens from metallic spent fuel pool components from the Zion reactor (PWR), LaCrosse reactor (BWR) and RBOF storage pool. The Zion reactor specimens (sections from a stainless steel storage rack) have arrived at PNL, and the remaining specimens are expected during the next quarter. The specimens will be examined by visual and metallographic methods to assess whether degradation has occurred during water storage.

MECHANISM STUDIES - S. M. Brummer and J. R. Divine

Constant axial load experiments on specimens from the TMI pipe cracking study are continuing. Two tests are under way on as-welded 304 SS specimens: one with the original ID and OD surfaces intact, the other with these surfaces removed by electropolishing. Both tests are in distilled water plus 13,000 wt ppm H_3BO_3 at 35°C. A third experiment has begun on a furnace-sensitized section of pipe; the environment for this test also is boric acid, but includes 15 ppm chloride. Each specimen has been loaded to a stress about 1.5 times the yield stress.

Tensile and compact tension specimens have been machined from several heats of 304 SS with carbon levels of 0.02 (304L), 0.04, 0.06 and 0.07 wt%. U-bend and crevice corrosion coupons were placed in simulated spent fuel pool environments having 0 to 10 ppm chloride, in deionized water or boric acid solutions 30 to 80°C.

It was observed, prior to placing the coupons in the tanks, that the nominal 0.06% C

U-bends cracked parallel to the stress during the bending process. This was subsequently found to be due to large stringers in that heat. These samples, and no others, showed signs of corrosion at the cracks during the first 48 hr of testing. The coupons were

removed, dried, examined, and replaced in the baths. No additional attack has been observed in subsequent weeks.

Failure of stainless steel heating elements has also occurred in the tanks with 10 ppm chloride. This failure is being investigated further.

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

L. R. Dodd - Project Manager

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

SUMMARY

Efforts during the quarter have been concentrated on completing modifications and subsequent testing of the coupled neutronics and thermal-hydraulics computer code that will be used for modeling several selected accidents hypothesized for arrays of spent fuel. Neutronics and thermal-hydraulics data have been calculated for use in modeling one of the hypothesized accidents.

MODEL DEVELOPMENT

The objectives of this program require the capability to model the time-dependent neutronics and thermal-hydraulics behavior

of a system comprised of an array of spent fuel in a nonpressurized water environment. The two-dimensional, time-dependent neutronics program TWIGL and the thermal-hydraulics analysis code COBRA were selected for use in the analysis. The two codes were modified and combined in previous quarters. Enhancements to the code have been completed during this quarter. The code is currently being tested.

ANALYSIS

Code input preparation has been completed for one of the accidents that will be analyzed. This analysis will be completed during the next two quarters.

26. ASPHALT EMULSION SEALING OF URANIUM MILL TAILINGS

J. N. Hartley - Project Manager

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

SUMMARY

Results of the 1980 laboratory and field studies were presented to the Nuclear Regulatory Commission (NRC), February 3, 1981.

W. M. Shafer and four other members of the Licensing Branch staff and George Burchard from the R&D staff were present. In addition, R. W. Ramsey, Jr., and D. H. Groelsema, DOE Headquarters and P. D. O'Brien, Sandia, attended the meeting.

Laboratory studies continued to include characterization of the tailings present under the 1980 asphalt emulsion seal. Seal formulation studies were continued in order to evaluate other asphalt/asphalt emulsion seals and ways to reduce the asphalt content of the seals. Seal stability tests, including leaching studies and microbial attack studies, have shown no degradation to date. Cyclic freeze-thaw testing was completed, with no failures related to freezing. Slumping during heat-up caused most of the failures. A physical stability analysis of the seal and of the compacted tailings was started to determine seal stability in the event of localized subsidence in the underlying tailings pile. The ultimate bearing capacity of the tailings was also estimated.

Preparations for a joint field test were started. Modifications to the cold-mix paver to increase its production rate were identified, and a screening test was planned. Economic evaluations were started to compare the asphalt emulsion radon barrier system with earthen cover concepts. Development of an improved radon flux measurement system continued. The test will include evaluation of the asphalt emulsion radon barrier system, earthen cover system and multilayer system.

LABORATORY STUDIES

Tailings Characterization - M. R. Elmore and J. M. Sauer

During this quarter, characterization studies were completed on various uranium tailings samples taken from the Grand Junction, Colorado, tailings site. These samples had been collected during the 1980 summer field test in areas where radon-flux measurements were made.

Characterization studies consisted of both physical and chemical evaluations. Particle size distributions (Table 26.1) were determined for the samples by first wet-screening on a 400-mesh screen, drying the residue

and sieving for 15 min. Material remaining on each screen was then weighed, and weight percents were calculated using initial sample weights.

Corresponding samples were leached with distilled water at room temperature with a mechanical vacuum extractor to determine water-soluble materials in the tailings. Thirty-gram samples of tailings were contacted with 50 ml of water at a rate of ~1 ml H₂O per min. Table 26.2 summarizes the total soluble materials in the tailings. This summary is produced from the water leach analyses and from cation analysis by induction-coupled plasma spectrometry (ICP) and anion analysis by ion chromatography (IC). The individual chemical analyses are summarized in Tables 26.3 and 26.4.

The same water leach samples were also analyzed for uranium using the Scintrex® UA-3 uranium analyzer. Results of these analyses are given in Table 26.5.

Also during this quarter plans were established for sampling the 1981 test site at Grand Junction. It was decided to take surface samples and core samples down to 3 m below the surface. Characterization of these samples will include the same test work undertaken for the 1980 samples plus additional physical property evaluations, such as bulk density, moisture content, temperature, etc. Zeta potential may also be determined on some samples.

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TABLE 26.1. Size Distribution Summary of Grand Junction Tailings (1980 Field Test Site)

Sample	Material Type	Wt% Retained							
		Mesh Size							
		8	16	30	50	100	200	400	-400
1A	Sand-Slime	0	0	0.29	10.7	43.4	30.9	4.71	10.0
2C	Sand-Slime	0.12	0.20	0.96	8.82	36.8	29.2	5.67	18.2
3B	Sand-Slime	0.07	0.23	1.23	23.4	46.3	26.4	4.28	8.06
4B	Sand	0	0.07	1.02	14.3	56.7	24.6	1.46	1.83
5A	Sand	0	0.02	1.09	14.9	55.2	24.6	1.77	2.48
6D	Slime	0	0.31	1.01	7.66	33.4	30.9	7.32	19.4
7A	Slime	0	0.24	0.87	6.13	27.7	35.1	8.31	21.7
8C	Sand	0	0.07	0.76	11.2	51.4	29.2	3.60	3.82
9D	Sand	0	0.22	1.56	17.5	51.0	26.1	2.71	1.00
10C	Sand	0	0.02	0.62	16.06	62.1	18.5	1.11	1.52
11B	Sand	0	0.05	0.88	13.1	52.4	27.8	3.25	2.63
12D	Slime	0.26	0.20	0.65	6.19	30.7	32.7	8.35	21.0
13A	Sand	0	0.08	0.94	15.9	46.8	30.8	3.44	2.46
14A	Sand-Slime	0	0.09	0.82	14.0	44.3	31.7	4.35	4.69
15A	Sand-Slime	0.19	0.12	0.69	12.7	40.5	31.6	5.11	9.10
16B	Sand	0	0.33	2.85	20.8	45.2	26.5	2.22	2.05
17C	Sand	0	0.08	0.92	22.3	48.1	24.0	2.63	1.95
18D	Sand-Slime	0	0.07	0.48	11.8	43.7	29.4	4.13	10.4

TABLE 26.2. Water-Soluble Material in Tailings Based on Solution Assays from Vacuum Extraction Tests

Sample	$\mu\text{g/g}$ Tailings			Wt%
	Cation Conc.	Anion Conc.	Total Dissolution	
1A	2246.0	4944.6	7190.6	0.72
2C	2690.9	5806.4	8497.3	0.85
3B	1335.6	2938.0	4273.6	0.43
4B	1209.6	2867.5	4077.1	0.41
5A	1294.0	3105.9	4399.9	0.44
6D	2126.1	4702.3	6828.4	0.68
7A	4514.2	10470.4	14984.6	1.50
8C	1143.0	2747.2	3890.2	0.39
9D	1175.6	2842.2	4017.8	0.40
10C	1002.5	2473.4	3475.9	0.35
11B	1251.7	2888.9	4140.6	0.41
12D	1878.4	3762.9	5641.3	0.56
13A	1040.4	2368.9	3409.3	0.34
14A	1351.8	3074.4	4426.2	0.44
14A	1256.1	2797.1	4053.2	0.41
16B	969.9	1513.3	2483.2	0.25
17C	1148.2	2779.0	3927.2	0.39
18D	1517.7	3229.4	4747.1	0.47

SEAL FORMULATION - R. L. Dunning (Petroleum Sciences, Inc.)

The objective of this task is to evaluate the ability of various aggregate/asphalt/asphalt emulsion mixes to form radon gas seals. The areas of investigation covered during this quarter included: 1) testing macadam-type seal using hot asphalt and cationic rapid-set emulsion (CRS-2); 2) testing aggregate/asphalt emulsion mixes where no moisture was added to aggregate prior to mixing; 3) reducing the asphalt content of the seals; 4) preparing hot asphalt hydraulic mixes; and 5) obtaining historical information on voidless asphalt/aggregate mixes. The emulsions used were a slow-set (ss) emulsion using a Vinsol[®] resin and two cationic

slow-set (css) emulsions, one using an Indulin W-3[®] emulsifier and one using a Tyfo[®] emulsifier.

The hot asphalt macadam seal was prepared by placing -3/4 in. aggregate on a sand base in a 4-in. Marshall mold which had its inside surface precoated with asphalt. Next, asphalt cement (AC-20) was added followed by -5/8 in. + 3/8 in. aggregate, then AC-20 and finally -4 mesh through -200 mesh aggregate. After application of each layer of aggregate, it was tamped into the asphalt, forming the macadam. The macadam using the CRS-2 asphalt emulsion was similarly prepared. The

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TABLE 26.3. Cations in Water Leach Filtrate, µg/g Tailings

Cation	Sample																	
	1-A	2-C	3-B	4-B	5-A	6-D	7-A	8-C	9-D	10-C	11-B	12-D	13-A	14-A	15-A	16-B	17-C	18-D
Al		1.0		4.3		3.5	9.3		8.3	5.3	5.7	3.3	1.5		1.0	20	7.8	0.83
As		28.3				3.0	5.0	1.5			15.0	2.2	1.7	3.3	2.8			4.0
Ba	0.18	0.17	0.15	0.10			0.17	0.10			0.10	0.17			0.17			0.17
Ca	2330	2670	1250	1330	1330	2330	3770	1217	1317	1233	1380	1280	1170	1300	1217	1117	1300	1717
Cd			0.15				0.17		0.10		0.17	0.30		0.17		0.42	0.23	
Cr			0.33				0.70	0.33										
Cu																0.23		
Fe							0.33			0.27						0.23		
K	33	65	48	10	5	43	83	22	5	16.2	42	77	78	18	53	5.0	6.7	63.0
Li	0.17	0.17			0.10	0.17	0.33	0.17	0.15			0.17				0.70		0.15
Mg	150	217	167	73	135	333	567	93	87	33	82	230	57	65	137	48	85	103
Mn	0.90	0.83	2.3	0.33		0.97	0.50	0.50	0.17		0.33	2.2		0.50	0.83	0.50	0.33	0.28
Mo	2.2	2.7	3.2			6.2	14	2.0				3.3	1.5	1.2	2.5			2.33
Na	430	575	283	175	232	83	1520	167	132	35	132	867	67	92	233	62	107	93
Ni						0.33	0.50				0.83	0.33				3.5		
Si	35	23	17	8.0	8.2	18.3	38	14	8.2	7.8	8.3	24.2	9.0	10.5	20	5.8	8.3	33
Sr	6.5	7.2	5.5	4.3	4.5	7.0	10.7	4.5	2.2	3.7	4.2	6.5	4.2	5.3	6.0	4.3	3.2	5.3
Te						1.2	5.5					1.0						
Zn	0.8	0.83	4.2	3.8	7.5	0.83		2.5	8.3	1.7	9.5	0.83	1.0	3.0	1.5	16.7	12.7	0.43

TABLE 26.4. Anions in Water Leach Filtrate, $\mu\text{g/g}$ Tailings

Sample	F^-	Cl^-	PO_4^{3-}	NO_3^-	SO_4^{2-}
1A	1.55	467	8.0	233	5883
2C	2.67	500	9.2	297	6933
3B	1.10	183	7.8	75	3650
4B	0.63	47	2.8	6.5	3766
5A	0.47	103	5.5	15.2	4017
6D	4.33	113	8.7	77	6067
7A	8.83	2467	18.3	2100	9367
8C	0.47	107	12.5	43	3500
9D	0.80	32	3.5	3.7	3750
10C	0.88	9	2.0	2.3	3283
11B	0.98	32	10.5	8.7	3800
12D	5.50	467	35.0	660	3850
13A	1.57	28	9.3	19.3	3100
14A	0.55	25	9.2	14.5	4050
15A	1.07	115	23.3	73	3517
16B	7.00	20	2.3	7.3	2483
17C	0.95	28	1.2	8.2	3667
18D	1.50	18	11.0	42	4233

TABLE 26.5. Uranium Concentration in Water Leach Test Solutions, ppb

Sample	Uranium Conc.
1A	<2.3
2C	2.5
3B	1479
4B	295
5A	172
6D	<2.3
7A	<2.3
8C	<2.3
9D	419
10C	313
11B	1874
12D	<2.3
13A	322
14A	<2.3
15A	<2.3
16B	1479
17C	1684
18D	1158

quantities of aggregate and asphalt/asphalt emulsion used to form a seal ~1 in. thick are shown in Table 26.6.

After the samples had cooled or cured, a helium leak test was performed at 0.21 psi, indicating gas-tight seals. The samples were then sent to PNL for radon diffusion testing.

Nine PNL admix seals were prepared using 25, 30, and 35 wt% asphalt emulsion without water added to the aggregate. The mixes containing 35 and 30 wt% asphalt emulsion passed the helium permeability test, but the 25 wt% sample failed. Results of these tests are shown in Table 26.7. The mixes were prepared with the aggregate gradation shown in Table 26.8. The samples were mixed, placed in a 4-in. Marshall mold on a sand base and then allowed to cure for at least 17 days. After curing, each sample was compacted with 35 blows on each side with a

TABLE 26.6. Typical Macadam Seal Preparation

<u>Hot Asphalt Seal Sample 25-77A</u>	
AC-20 asphalt	0.6 gal/yd ²
-3/4 aggregate	26.8 lb/yd ²
AC-20 asphalt	0.74 gal/yd ²
-5/8 + 3/8 aggregate	27.5 lb/yd ²
AC-20 asphalt	0.6 gal/yd ²
-4 mesh aggregate	16.8 lb/yd ²
<u>CRS Asphalt Emulsion Seal Sample 25-77B</u>	
CRS-2 emulsion	0.88 gal/yd ²
-3/4 aggregate	27 lb/yd ²
CRS-2 emulsion	1.08 gal/yd ²
-5/8 + 3/8 aggregate	37.5 lb/yd ²
CRS-2 emulsion	1.42 gal/yd ²
-4 mesh aggregate	43.1 lb/yd ²

TABLE 26.7. Gradation of Aggregate Used for Mixes

<u>Sieve Size</u>	<u>% Passing</u>
3/4 in.	100
1/2	97
3/8	91
No. 4	76
8	62
16	50
30	29
50	19
100	13
200	10

Marshall compactor. The samples were tested with helium for at least 4 days. The test results show that it is possible to reduce residual asphalt content somewhat and still obtain a gas-tight seal. Also at the 35 and 30 wt% asphalt emulsion levels no water addition to the aggregate is required with those emulsions tested. Further evaluation of these systems is needed before field tests are warranted.

Radon Diffusion Tests - H. D. Freeman

A new radon diffusion test apparatus was designed and constructed to eliminate radon concentration fluctuations encountered in previous tests. The system was tested, and results show that the radon concentration fluctuates by $\pm 3\%$ over a 5 day period.

Six asphalt seals prepared by Petroleum Sciences, Inc., were tested on the system to determine the effective diffusion coefficient for radon through the seal. Results of these tests are shown in Table 26.9. Both macadam and hydraulic hot asphalt mixes show promise as radon diffusion barriers.

Seal Stability

Asphalt Leaching and Bacterial Degradation Experiments - D. A. Nelson

The leaching experiments have been conducted for about 5 months, with no sign of leachate coloration. No obvious signs of asphalt degradation have been observed during this time.

TABLE 26.8. Formulation and Results of Asphalt Emulsion-Aggregate Mixes

Emulsion	Formulation, wt%		Cure Time, days	Time in Helium Permeameter, days
	Water	Emulsion		
Slow-Set Anionic				
25-104A	0	25	>19	To be tested
25-99A	0	30	19	6
25-85C	0	35	17	4
Slow-Set Cationic 1				
25-104B	0	25	>19	To be tested
25-99B	0	30	17	6 ^(a)
25-85C	0	35	27	7
Slow-Set Cationic 2				
25-104C	0	25	>19	To be tested
25-99C	0	30	>21	To be tested
25-95E	0	35	17	6 ^(a)

(a) Leak occurred at joint after 5 days. Sealed joint with asphalt cement and placed back in permeameter.

TABLE 26.9. Effective Diffusion Coefficient for Radon Through Seal

Sample	Asphalt	Mix	Asphalt Content, wt%	Approximate Diffusion Coefficient, cm ² /sec.
25-84 A	Hot asphalt	Macadam	23.8	5.0×10^{-9}
25-84 B	Hot asphalt	Macadam	23.4	5.2×10^{-9}
25-84 C	CRS ^(a) emulsion	Macadam	21.1	2.2×10^{-8}
25-84 D	CRS emulsion	Macadam	20.3	Failed the leak test
25-125 C	Hot asphalt	Hydraulic	11	4.6×10^{-9}
25-125 D	Hot asphalt	Hydraulic	11	1.6×10^{-8}

(a) Cationic rapid-set

The bacterial degradation of asphalt is being investigated. Thin films of three asphalt emulsions were coated on petri dishes and flasks. These asphalts are exposed to gram-positive cocci bacteria known to degrade diesel fuel and heavy crude oil. The flasks contain sterile salt solution with no added nutrients except the asphalt. The growth rate of the culture is being measured by standard plate-counting procedures. The petri dish procedure is being developed as a faster assay method than the standard

flask method. Bacterial growth using asphalt as the carbon source has been quite slow so far.

The oxygen content (gaseous) available to the asphalt-overburden interface was investigated under laboratory conditions by polarography. Air diffusion through 3 ft of Grand Junction, Colorado, overburden was quite rapid. The oxygen level reached 21% within 30 to 45 min at the interface. The field conditions may be radically different,

depending upon the amount of overburden moisture and the presence of microorganisms.

An attempt was made to measure oxygen uptake by asphalt with a small sensitive manometer. Temperature and pressure changes, however, did not allow accurate measurements. The oxygen uptake, therefore, will be measured by a laser Raman spectroscopy technique. This should provide us with a means of measuring oxidation over a long period without environmental interference.

Two asphalt admix samples were investigated by x-ray fluorescence for their elemental composition. We were particularly concerned with vanadium and molybdenum since they can catalyze oxidation. The vanadium (54 to 85 ppm) and molybdenum (200 to 300 ppm) were quite low, but iron (1.26 to 1.30%) was unexpectedly high. A total of 52 elements were quantitatively analyzed.

Several asphalt samples are being analyzed by the infrared spectroscopic techniques of Claive Petersen (Laramie Energy Technology Center). The information obtained from this work will allow us to monitor oxidation quantitatively via the end products of that reaction (ketones, acids and anhydrides). Field samples from Grand Junction will be similarly examined to correlate oxidation with time.

Cyclic Freeze-Thaw Analysis -

P. L. Koehmstedt

The cyclic freeze-thaw experiments were completed. Based on the results of the experiments to date, the following conclusions can be made.

- The freeze-thaw test developed by Plancher et al., Laramie Energy Technology Center, is not directly applicable to the admix seal specimen, but the specimen preparation and freeze-thaw exposure conditions can be modified to closely simulate field

conditions. With these modifications the Plancher test simulates field seal specimens and provides very severe exposure conditions.

- All specimen failures were caused by specimen slumping. No specimen failure was related to freezing. Since there is a high enough asphalt content to bridge the particles to provide a radon gas-tight seal, no water permeation occurs and therefore no subsequent freeze damage.
- The specimens fabricated from emulsion containing the higher viscosity asphalts remained unchanged in 19 freeze-thaw cycles.
- Specimens fabricated from emulsions containing solvents all failed the test on the initial thaw cycle due to excessive slumping.
- The specimens with higher asphalt-rubber concentrations did not crack in 12 cycles. However, all assumed a tan color and expanded with progressive cycles. The specimens with low asphalt-rubber concentrations slumped or fell apart on the initial thaw cycle.
- Specimens with higher asphalt cement concentrations (15 to 20 wt% asphalt) remained intact as far as the test had progressed (7 cycles). Lower concentrations (5 to 10 wt% asphalt) slumped or fell apart on the initial thaw cycle.
- All incompletely dried samples, simulating premature field compaction, failed on the initial thaw cycle due to excessive slumping.

The problem of slumping would not occur in field application since the seal would not undergo the 60°C thaw temperature used in the laboratory experiments. The effects of frosting the surface of selected specimens were not totally conclusive. No apparent effects were observed when water

was allowed to accumulate on the surface of the specimen and then was frozen and thawed.

Stability Analysis of Asphalt Emulsion
Seal and of the Compacted Tailings -
 C. F. Voss

An elasticity analysis was performed to determine the stability of the asphalt seal in the event of localized subsidence in the underlying tailings pile. Results indicate the seal to be capable of withstanding loss of support up to 1 m without failure of the seal and a safety factor of five. The safe span length is dependent on the stiffness modulus, E_a , of the asphalt seal; the stiffness, E_c , and depth, d_c , of the cover material; and the support rigidity provided by the tailings at the subsidence location. The safe span, L_{safe} , decreases with 1) decreasing stress-strain modulus (stiffness)

of the cover material, 2) increasing depth of the cover material, and 3) increasing stiffness of the asphalt seal (Table 26.10). If the asphalt seal formulation is considered optimal, design criteria should attempt to minimize the depth of the cover material needed and to obtain optimum compaction of the material.

The analysis assumes the asphalt seal to be a homogeneous, isotropic and elastic mass. The void space beneath the seal resulting from subsidence is considered to be formed instantaneously with the remaining tailings providing rigid supports. These assumptions are necessary to use elastic beam analysis, the asphalt seal/overburden being treated as laminated beams bridging a span, L . Viscous behavior is not considered in this analysis due to the absence of data concerning the time-dependent behavior of asphalt. Temperature and loading rate of

TABLE 26.10. Calculated Values of δ_{max} , σ_{max} , L_{safe}

E_a , x 10^5 psi	E_c , x 10^3 psi	d_c , in.	q , psi	δ_{max} , x 10^{-5} in.	σ_{max} , psi	L_{safe} , in.
10	0	0	0.207	40.2	14.9	88.5
10	0.5	36	1.115	216.8	80.3	38.1
10	1	36	0.72	148.2	54.9	46.1
10	2	36	0.47	90.7	33.6	50.9
10	5	36	0.22	41.9	15.5	86.7
5	0	0	0.207	80.5	14.9	88.5
5	0.5	36	0.762	296.3	54.9	46.1
5	1	36	0.467	181.4	33.4	58.9
5	2	36	0.263	102.2	18.9	78.5
5	2.6	36	0.208	80.9	15.0	88.2

E_a = stiffness modulus of asphalt.

E_c = stress-strain modulus of cover material.

d_c = thickness of cover material.

q = transverse load on seal.

δ_{max} = maximum deflection of seal.

σ_{max} = maximum tensile stress in outermost seal fiber.

L_{safe} = safe span.

the asphalt affect the visco-elastic response. Laboratory testing is necessary before the more accurate analysis can be performed. Core samples of the Grand Junction test seal have been collected for testing at the R&D laboratory at Kirkland Air Force Base in Albuquerque, New Mexico. Standard asphalt tests will be conducted to determine the mechanical properties of the asphalt under expected conditions. Results of these tests will be used to perform a visco-elastic analysis of seal stability next quarter.

A possible method of altering the response of the asphalt seal using synthetic fabrics was also considered. Additional support of a geotextile fabric beneath the asphalt seal could prevent ductile failure of the seal by limiting the deformation across a subsidence zone. Further analyses are planned for next quarter, and a small test area using geotextile fabric will be constructed at Grand Junction this summer.

An analysis of the Grand Junction tailings materials was performed to estimate their ultimate bearing capacity. This information is useful to determine whether paving equipment can be operated directly over compacted tailings or the minimum road base requirements are needed. The results indicate adequate bearing capacities for power operation directly over the tailings if the tailings are compacted to 95% of the ultimate dry density. Areas where compaction is <95% could allow the power wheels to penetrate the surface, reducing the efficiency of the paver and the asphalt seal. The lavender slime material was shown to be the most likely material to fail. Penetration of the tailings by the bogies is particularly likely during loading of the hopper when the impact from the aggregate causes the ultimate pressure to be exceeded.

Controlled loading using a conveyor system in tandem with the paver to deliver aggregate would eliminate this problem. Use of a geotextile fabric for roadbed stabilization could result in an increased bearing capacity with lesser amounts of road base material.

The ultimate bearing capacity calculations were based on work by Bell and Terzaghi. Soil properties for Grand Junction tailings materials were taken from Colorado State University's July 1980 - September 1980 Quarterly Report, Inactive Uranium Mill Tailings Sites Analysis of Stability. Material properties from GJ-4 (fine sands), GJ-5 (lavender slime) and GJ-8 (cover material) were used. Loading conditions of a fully loaded Midland Mix Paver were used to calculate the factor of safety for operation on the tailings materials at different levels of compaction (Table 26.11).

The cost of using an asphalt seal could be significantly reduced if the need for a road base stabilization could be eliminated. Field testing at Grand Junction this summer will allow the feasibility of direct asphalt application to be evaluated.

FIELD STUDIES

Application Technology

Equipment Modifications - D. J. Esterl

Modifications needed to increase the production rate of the cold-mix paver (CMP) were identified. A screening test to evaluate a modified CMP was planned with Blackrock Construction, Holbrook, Arizona. The test is scheduled for April 21-23 at Holbrook, where operating conditions for the CMP will be determined.

TABLE 26.11. Factor of Safety Calculated from Loading Conditions for Midland Mix Paver

Location	Compaction, %	Density, lb/in. ³	Ultimate Bearing Capacity, psi	Applied Bearing Pressure, psi	Factor of Safety
GJ-4	100	0.063	123	15.8	7.8
	94	0.060	56.1	15.8	3.6
	90	0.057	37.3	15.8	2.4
GJ-5	100	0.049	32.1	15.8	2
	95	0.047	28.6	15.8	1.8
	90	0.044	12.4	15.8	0.8
GJ-8	100	0.059	116.5	15.8	7.4
	95	0.056	41.9	15.8	2.7
	90	0.053	17.4	15.8	1.1

Economic Evaluation - J. L. Buelt

An economic evaluation of asphalt emulsion covers is being performed by comparing the anticipated costs for earthen cover and asphalt emulsion covers. The earthen cover requirements have not yet been identified for the proposed disposal sites of the four high-priority tailings piles. Therefore, the criteria for choosing the cover system from an economic standpoint are being developed as a function of various earthen cover depths, overburden availability and costs, transportation modes, and disposal site locations.

A preliminary comparison was performed for a generic case in 1981 dollars. Figure 26.1 compares the cost of an asphalt emulsion cover with overburden as a function of required depth. Case 1 uses the assumptions of NRC's Final Generic Environmental Impact Statement (1980), which states that the overburden is free and available at the tailings disposal site. However, when overburden is not available at the site, additional transportation costs are incurred. Cases 2 and 3 illustrate the costs for overburden available at 4 and 22 km, re-

spectively. These estimates are based on a small sampling of industrial experts. The cost for the asphalt emulsion cover is based on a compacted seal 8 cm thick, containing 25% residual asphalt. The type of asphalt is the least expensive grade of cationic medium-set (CMS) emulsion.

Although this cost comparison is preliminary, the comparison already points out the cost effectiveness of asphalt emulsion, especially if more than 3 m of overburden is required to meet the proposed radon flux of 2 pCi/m²/sec.

Radon Flux Measurement System - H. D. Freeman

The radon flux measurement system is being redesigned to make it more accurate and easier to operate. A mathematical model is being used to evaluate the effect of concentration buildup under the tent. The tents will be evaluated in the laboratory to validate the mathematical model. Calibration of the tents is also planned with input from Argonne National Laboratory.

The use of activated coconut charcoal instead of Pittsburgh Carbon Co. (PCC) carbon to collect radon has been investigated.

FIGURE 26.1. Preliminary Cost Comparison of Radon Covers

Results of the investigation (Table 26.12) show that PCC is more efficient at higher temperatures and, therefore, is the carbon that will be used in the measuring system.

Joint Field Test - J. N. Hartley and
H. D. Freeman

Funds were allocated for the joint field test that will include evaluating three radon barrier systems: 1) asphalt emulsion systems, 2) earthen cover system, and 3) multilayer system, which is a separately funded PNL project.

The field test is to be held on the Grand Junction tailings pile from June 1 through September 30, 1981. The basic field test schedule is as follows:

TABLE 26.12. Radon Collection Efficiencies for PCC Carbon and Coconut Charcoal

Temp., °C	Radon Collection Efficiency, %	
	PCC	Coconut
20	>99.9	100
40	99.9	99.4
60	94	85.2

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

A 2.5-acre test plot will be used, with 1 acre allocated to the asphalt and multilayer systems and ~0.5 acre for the earthen cover tests. The asphalt emulsion radon barrier system will consist of an admix seal ~7.6 cm (3 in.) thick containing ~20 wt% residual asphalt and 2 ft of overburden. The earthen cover test plot will consist of four separate test areas each ~60 x 100 ft and one test area 10 x 100 ft: 1) 10 ft overburden cover type 1; 2) 10 ft overburden type 2; 3) 2 ft clay type 1 plus 8 ft overburden type 1; 4) 2 ft clay type 2 plus 8 ft overburden type 2; and 5) 6 to 8, 6-ft column tests. The types of clay and overburden to be used have not yet been chosen. Those available near the Grand Junction tailings

pile will, however, have high priority. A joint field test plan is being prepared and will be sent out in May.

REFERENCE

Final Generic Environmental Impact Statement on Uranium Milling. 1980. Nuclear Regulatory Commission, NUREG-0706, Washington, D.C.

27. LINER EVALUATION FOR URANIUM MILL TAILINGS

J. L. Buelt - Project Manager

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

SUMMARY

The exposure conditions have been identified to which the eight selected liner materials will be subjected in 0.6-m-dia exposure columns. These conditions were chosen to chemically and physically accelerate the degradation of the liners. Because degradation mechanisms differ for clay liners and processed material liners (asphalts and synthetics), different acceleration techniques were used for these materials.

ASPHALT AND SYNTHETIC LINERS - J. L. Buelt

The degradation mechanisms for asphalts and chlorosulfurated polyethylene being addressed in this study are autooxidation (the diffusion and reaction of oxygen in the asphalt, causing hardening and embrittlement), salt solution attack, radiation damage, and physical stresses from ground subsidence. Since no time was available to determine the reaction kinetics empirically for autooxidation, the liners were assumed to behave identically to pavement asphalts in the absence of light. Van Oort (1956) and Blokker and van Hoorn (1959) determined the reaction kinetics for pavement asphalts empirically, but disagree on how oxygen and temperature

accelerate the reaction rate. By exposing the liners to 7.8 atm of pure oxygen at 60°C for 3 months, the equivalent time exposure is 2500 years according to Van Oort's studies, but it is 90 years following Blokker and van Hoorn's relationships. The actual equivalent time exposure for the liner materials will have to be determined empirically in future studies.

The other degradation mechanisms for asphalts and the synthetic material have also been accelerated. The oxidizing strength of the salt solutions has been accelerated by elevating the temperature to 60°C and increasing the H⁺ concentration. The equivalent time exposure is between 320 and 3100 years. Separate liner samples will be subjected to 1000 years of equivalent radiation dose. Also the physical stresses incurred by subsidence of the subsoil from the weight of the tailings will be simulated by a collapsible membrane beneath the liners in the exposure columns.

CLAY LINERS - V. Q. Hale

Since chemical degradation is not a factor with clay, the critical conditions are those that remove exchangeable sodium from the exchange complex. These conditions are

the concentration of other cations, chiefly calcium, in the contacting solution and the volume of the solution that passes through the liner. The simulated tailings solution with which the liners are to be tested contains a "worst case" concentration of salts as they were shown to be present in the tailings. Thus the concentration of cations is constant and the only condition that can be varied is the volume of solution passing through the liner.

To estimate the effective life of a clay liner, the exposure conditions must be accelerated to cause liner failure. For relating the failure to time, the most accurately measurable parameter identified is pore volume. From the pore volume of the liner and the measured volume of solution passing through the liner the number of pore volumes required to make the liner fail can be determined. In the laboratory tests, the clay-soil liners are 2.5 cm thick, considerably less than the field thickness. Pressure is applied above the liner to accelerate the rate of flow of solution through the liner. When the rate of flow exceeds 10^{-7} cm/sec., the liner will be assumed to

have failed, and the number of pore volumes of solution required for failure will be determined. By relating the number of pore volumes to a liner of field thickness and by relating the applied pressure in the columns to the maximum water head pressure expected in the field, the life expectancy of the clay liner can be calculated.

DIRECTION

The eight liners installed in the exposure columns will be monitored for permeability during their 3-month exposure period. The liners will then be comparatively evaluated, and the most promising liner will be installed in the field.

REFERENCES

- Blokke, P. C. and H. van Hoorn. 1959. Durability of Bitumen in Theory and Practices. Fifth World Petroleum Congress, New York, New York.
- Van Oort, W. P. 1956. Durability of Asphalt - Its Aging in the Dark. Koninklyke-Shell Laboratorium, Amsterdam, The Netherlands.

28. 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

Significant results obtained during the quarter can be summarized as follows:

- A review of geomorphic processes indicates that stability of multilayer covers will depend largely upon the magnitude and effects of three major geologic factors: erosion, seismic events and subsidence. Proper placement of tailings piles and adequate drainage and compaction of tailings will ensure maximum protection against cover rupture.
- Simulation of water retention in a multilayer cover during dry years indicates that the clay/gravel layer will retain water indefinitely when considering liquid flow only. When vapor flow was considered, it was estimated that 20 years would elapse before the clay/gravel layer would dry appreciably.
- Transient radon flux modeling indicates that as long as 30 days after cover placement is required before radon flux measurements attain maximum, steady-flux values. Monitoring of covers at earlier times will underestimate the radon flux.
- Field test data show radon flux values are highly variable both in time and space. Average surface flux in February

on plots with a compacted clay/gravel layer ranged from 11 to 73 $\text{pCi m}^{-2} \text{sec}^{-1}$ compared to 196 pCi m^{-1} on plots without a compacted layer. Flux reductions due to cover placement ranged from 93 to 97% on the multilayer plots.

- Field study plans for tests at Grand Junction, Colorado, were prepared and subsequently presented for review at the UMTRAP (Uranium Mill Tailings Remedial Action Program) Cover Task Group meeting in Albuquerque in March.
- Cost comparisons favor multilayer earth cover systems over single-layer systems.
- A cost optimization code, RAECO, that determines the minimum cost of multilayer cover systems has been developed and documented by Rogers and Associates (RAE).
- Multilayer cover diffusion test columns have been assembled in the RAE laboratory for use in verifying the radon diffusion part of RAECO.
- Field measurements of moisture distributions at five mill tailings disposal sites are continuing.

COVER STABILITY - J. T. Zellmer

A task report on the stability of multilayer earth barriers used to isolate uranium

mill tailings has been prepared and was circulated for review at the March UMTRAP Cover Task Group meeting. The report addresses the long-term geologic and geotechnical considerations of cover stability. It identifies erosion, seismic events and subsidence as the three major geologic factors affecting cover stability. Geotechnical evaluation of the covers for tailings piles will require site-specific information. For the Grand Junction pile, using available and assumed data on tailings properties and site characteristics, it was determined that a theoretical maximum of 1.5 m subsidence could occur on the pile if the tailings material ultimately settled to their maximum density. If this magnitude of settling occurred relatively uniformly over the pile, no cover rupture would occur. Differential settlement could be a possible cause for rupture, but more detailed sampling of tailings would be required to evaluate the magnitude of this problem. However, the Grand Junction tailings have drained for over 10 years and remain unsaturated except near the base of the pile. Hence the theoretical maximum settlement is unlikely, and, based on present observation, the pile should be considered stable, with little if any further settlement expected. If the Grand Junction tailings are eventually moved, proper engineering considerations of compaction and dewatering should ensure optimum stability for tailings and cover.

MODELING - C. S. Simmons and D. W. Mayer

Radon gas movement through earth (soil) covers is controlled by both the soil material and the water present in the soil. Radon gas travels mainly by diffusion through the air filled voids in the soil. The air-filled voids in turn are governed by soil

compaction and soil water content. The amount and distribution of water in the soil then is an important parameter in assessing the effectiveness of a soil cover for radon diffusion. Simulation of water flow and retention in soil covers was carried out using UNSATV, an unsaturated water flow model with the capability of simulating the long-term (multiyear) water balance of a soil cover system. A task report documenting these simulations has been completed and is currently being reviewed. The simulations indicate that a multilayer cover system using as its radon control layer, a compacted, wet clay/gravel layer can be constructed in such a way that it maintains its wetness for extended time periods. Simulations using Grand Junction, Colorado, climate data for wet (23 cm precipitation) and dry (13 cm precipitation) years indicate that the wet clay/rock does not change water content even after successive dry years. When water vapor losses were considered, it was estimated that over 20 years of continuous dry weather (drought) would be required to dry the layer significantly. In normal or wet years, there would be sufficient water addition to maintain the wet clay/gravel indefinitely. The simulations have demonstrated the capability and the limitations of making long-term predictions of water flow and retention in soil covers. The more data available on climatic and soil conditions the better the simulations are expected to be in predicting soil-water distributions in the cover and hence in predicting the effectiveness of the cover for long-term radon control.

Modeling radon diffusion through cover materials has allowed for detailed analysis of the requirements needed in design of multilayer earth (soil) covers to control radon to prescribed limits. Efforts both at

Pacific Northwest Laboratory (PNL) and by Rogers and Associates (RAE) have centered on tests and uses of both steady-state and transient, one-dimensional, radon diffusion models to assess the effectiveness and economy of multilayer or composite cover systems and to aid in the analysis of the field test data. Figure 28.1 shows the multilayer cover system designed and tested by PNL at the 1980 Grand Junction test site.

The plot of surface radon flux versus clay/gravel thickness, for the multilayer system shown, indicates that a $2 \text{ pCi m}^{-2} \text{ sec}^{-1}$ radon flux can be achieved by $< 2 \text{ m}$ of cover. In contrast, for a similar tailings material and typical top soil characteristic, a single-layer cover, to meet the $2 \text{ pCi m}^{-2} \text{ sec}^{-1}$ radon flux limit, would require over 4.5 m of soil. It should be noted that in analyzing the radon diffusion through cover materials we observed a time dependence on the radon flux. Table 28.1 tabulates the calculated time dependence of the radon flux in reaching a steady state through the multilayer system shown in Figure 28.1 for several thicknesses of clay/gravel layer and for several radon diffusivity values assigned to this layer. The results indicate that measurement of radon flux earlier than 30 days after cover place-

ment underestimates the actual radon flux from the multilayer cover system.

FIELD MEASUREMENTS - G. W. Gee,

R. R. Kirkham, M. E. Dodson, and B. E. Opitz

Field test data show that radon flux values have been attenuated by 93 to 97% on the multilayer cover test plots at Grand Junction. Table 28.2 describes the features of the clay/gravel mixtures, and Table 28.3 gives plot characteristics for the cover tests. The data show that the radon flux values on individual plots vary considerably. Calculated coefficients of variation ranged from 36 to 115%. Water added directly to the surface of the clay/gravel layers on plots 1, 2, and 3 in December did not appreciably change the radon flux readings measured in February on these plots. Laboratory measurements on the clay/gravel mixtures indicate that water drainage from, and possibly gravel segregation in, the mixtures may explain why radon flux levels did not change significantly and why they are higher than expected. More thorough mixing of clay and gravel prior to application, greater proportions of added fine material, and thicker layers should all contribute to improved radon flux control on the test plots. In

TABLE 28.1. Calculated Equilibrium Time Required To Reach 99% of Final Steady-State Radon Flux Value for a Multilayer Cover System with a Variable Thickness Clay/Gravel Layer, Having Different Radon Diffusivity Values. Tailings radon content assumed to be 1600 pCi/g . Multilayer cover design as shown in Figure 28.1.

Clay/Gravel Thickness, m	Clay/Gravel Diffusivity, cm^2/sec	Final Radon Flux, $\text{pCi m}^{-2} \text{ sec}^{-1}$	Equilibrium Time, days
0.15	$1.0 \text{ E}-2$	192.1	26
0.15	$1.0 \text{ E}-4$	34.0	28
0.15	$1.0 \text{ E}-5$	2.9	30
0.30	$1.0 \text{ E}-4$	16.4	29
0.45	$1.0 \text{ E}-4$	9.4	30

FIGURE 28.1. Surface Radon Flux as a Function of Control Layer (Clay/Gravel) Thickness for Multilayer Earthen Cover System

TABLE 28.2. Clay/Gravel Mixtures Used as Radon Control Layer at 1980 Grand Junction Field Test

Plot	Mixture Code	Material	Wt%
1	A-	-3/4 Road fill	86
		Fill soil (silty clay)	14
2	A+	-3/4 Road fill	86
		Bentonite	14
3	B-	Pea gravel	29
		Concrete sand	29
		Fill soil (silty clay)	42
4	B+	Pea gravel	29
		Concrete sand	29
		Fill soil (silty clay)	28
		Bentonite	14

addition, isolation of individual plots from adjacent plots and from exposed edges containing high radon source materials should aid in identifying the radon leaks apparent in some of the plots. The interconnection

of all plots by clean rock used as the capillary barrier (Figure 28.1) obviously has some influence on the final radon flux values observed on each plot. This influence should be most pronounced on plot 4, which is closest to the plot (5) containing no clay/gravel layer. The degree of this lateral flow is yet to be quantified. Two-dimensional modeling of the cover system will assist in evaluating the influence of lateral flow on measured radon flux values on the individual plots.

Field plans for next summer have been developed. In cooperation with J. N. Hartley of PNL, an exhaustive study of three cover systems composed of "standard" earthen covers, multilayer cover systems and asphalt covers has been planned. This work is scheduled to begin in Grand Junction in June and will be completed in late September or October. The initial plan for the joint field study was presented to the UMTRAP Cover Task Work Group in March.

TABLE 28.3. Plot Characteristics and Surface Flux Measurements at Grand Junction Test Site

Plot	Mixture	Radon Control Layer		Radon Flux, $\text{pCi m}^{-2} \text{sec}^{-1}$		Flux Reduction, %	Flux Reduction, % Required to Meet $2 \text{ pCi m}^{-2} \text{sec}^{-1}$ Limit
		Thickness, m	Density, g/cm^3	Initial	160 Days		
1	A-	0.17	2.05	385(± 137)	11(± 17)	97	99.5
2	A+	0.17	1.97	374(± 186)	15(± 12)	96	99.5
3	B-	0.19	2.00	537(± 589)	38(± 40)	93	99.6
4	B+	0.18	1.66	1178(± 597)	73(± 88)	94	99.8
5	None	0	--	1628(± 203)	196(± 157)	88	99.9

Cost estimates have been developed based on actual cover material and application costs and calculated thickness requirements to achieve $2 \text{ pCi m}^{-2} \text{sec}^{-1}$ flux levels on the Grand Junction tailings. Table 28.4 shows the cost associated with both single and multilayer cover systems needed to reduce the radon bare surface flux at the Grand Junction test site to $2 \text{ pCi m}^{-2} \text{sec}^{-1}$. The costs for the multilayer cover for plots 1, 2, and 3 are less than one-half the cost of a single-cover earth fill (cover depths from 4.5 to 5.6 m). In all cases, the costs for multilayer systems are less than those for single layer earthen covers.

COVER OPTIMIZATION - Rogers and Associates (RAE)

A computer code, RAECO, that determines the minimum cost of a multilayer cover (under user-specified constraints) has been developed by RAE. The documentation of this code has been drafted and reviewed and will be published during the next quarter. Test columns have been assembled in the RAE laboratory for use in verifying the radon diffusion portion of the RAECO code. RAE has developed a time dependent technique that allows for rapid determination of radon diffusivity of soil cover materials. This

TABLE 28.4. Cover Thickness Requirements and Costs To Meet $2 \text{ pCi m}^{-2} \text{sec}^{-1}$ Radon Flux Limit at 1980 Grand Junction Test Site

Plot	Average Bare Surface Flux, $\text{pCi m}^{-2} \text{sec}^{-1}$	Single Layer Thickness, m	Single Cover Cost, \$/acre	Control Layer Thickness, m	Multilayer Cover Cost, \$/acre	Multilayer Cover Cost, \$/m ²	Cost Ratio, Multi/Single
1	385	4.5	146K ^(a)	0.2 ^(b)	55K	13.6	0.38
2	374	4.5	146K	0.2	55K	13.6	0.38
3	573	5.6	181K	0.3	85K	21.0	0.47
4	1178	7.4	240K	0.4	120K	29.6	0.50
5	1628	8.0	259K	0.5	150K	37.1	0.58

(a) Based on $\$4/\text{yd}^3$ and a 1.3 bulking factor.

(b) Assumes an air-filled porosity of <0.02 can be achieved.

technique is being used to determine cover diffusivity coefficients on cover materials taken from sources near the priority tailings sites at Salt Lake City, Utah; Shiprock, New Mexico; Durango, Colorado; Grand Junction, Colorado; and Riverton, Wyoming. Field

measurements of moisture distributions and temperature at depths to 3 m in soil cover materials are being taken periodically. These data will be correlated with climatological data to aid in assessment of long-term moisture distributions in cover materials.

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

J. F. Cline - Project Manager

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

SUMMARY

The major effort of this quarter was spent in determining the final combination of polymer, pellet size and trifluralin loading to be used in the field trial at Grand Junction this year. The soil concentrations of trifluralin necessary to inhibit root elongation in eight additional plant species were determined to be ~7 ppm.

Prairie dogs were placed in animal enclosures that were built over a rock barrier at Grand Junction. Observations showed that the prairie dogs excavated considerable quantities of rocks and soil cover.

DEVELOPMENT OF PCD SYSTEMS AND DETERMINATION
OF HERBICIDE RELEASE RATES FROM PCD SYSTEMS -
W. E. Skiens and F. G. Burton

A major effort this quarter was spent in determining the final combination of polymer, pellet size, and trifluralin loading to be used in this year's field trial at Grand Junction, Colorado. Previously fabricated pellets (3 to 5 mm dia and 5 to 7 mm long) had a maximum effective zero-order lifetime to ~14 years. Using the fact that surface area increases as the square of the diameter while volume increases as the cube of the

diameter, we can predict that larger devices will have a much longer lifetime. Theoretical calculations based on the release rate and loading of the previously fabricated pellets suggest that a pellet 9 mm in diameter and 9 mm long will have lifetime in excess of 100 years. This pellet size also allows the use of conventional equipment for spreading in the field.

The previously fabricated pellets contained 10 parts per hundred of trifluralin. Increasing this to 30 to 50 parts per hundred, we were also able to increase the effective lifetime of the device. Since the amount of trifluralin that can be retained in a polymer depends on the polymer type, we attempted to mix various concentrations of trifluralin with a number of polymers. Once the pellet or sheet containing the trifluralin was fabricated, a weighed piece was extracted to determine the amount of trifluralin contained. Fillers such as carbon black were added to some polymers to determine whether the filler would increase the amount of trifluralin retained. Some resulting data are shown in Table 29.1. Based on these analyses, we were able to eliminate several polymers, e.g., polyurethane and polyethylene-vinyl acetate as potential reservoirs for the delivery system.

TABLE 29.1. Methods Used To Increase Amount of Trifluralin Within Several Polymers

Polymer	Targeted Loading, pph	Analyzed Loading, pph
Polyvinyl	10	10.1
	30	22.1
	50	48.6
Poly (butadiene-estyrene) rubber	10	9.0
	30	20.6
	50	36.6
Polyurethane	30	4.3
Polyethylene-vinyl acetate	30	9.5
	50	15.7
Polyethylene, no carbon black	30	16.0
Polyethylene, 25 pph carbon black	30	18.8
Polyethylene, 40 pph carbon black	30	13.1
Polyethylene, 40 pph carbon black	50	31.3

During April we will be looking at release rates from some of the other polymers, with the object of making the final choice of polymer for use in the Grand Junction field trial.

PHYTOTOXICITY AND DEGRADATION STUDIES - D. A. Cataldo

During this quarter, studies were conducted in the following areas: 1) eight additional plant species were screened to determine soil concentrations of trifluralin that will inhibit root elongations; 2) studies were continued to determine soil trifluralin concentrations when equilibrium was achieved within the soil around the implanted PCD devices; 3) studies were extended to determine the effective diffusion path length for trifluralin in soil after release from PCD devices; and 4) studies were initiated to evaluate the effect of soil moisture content on trifluralin release from PCD systems and on accumulation in soil.

Previous lysimeter studies to determine the concentrations of trifluralin in soils

required to stop root elongation showed a wide range in plant sensitivity to the toxin. Russian thistle stopped elongation at 1.0 ppm, while crown vetch and tansy mustard continued growth until concentrations of ~7 ppm were reached. It was noted that lateral roots of the crown vetch and tansy mustard passed the treated zone along the lysimeter wall. Plant species exhibiting this tendency were added to a list of plants previously tested for evaluation. These results are shown in Table 29.2; they show that soil trifluralin levels ~7 ppm will be needed to inhibit root elongation.

Determinations of the equilibrium soil concentrations of trifluralin resulting from implanting PCD devices in the soil in November have continued. A Profax PS-1600® PCD device placed in soil at three loading rates (0.5, 1.0, and 3.0 g pellet/400 g soil) behaved predictably, based on in vitro test systems. Equilibrium soil concentrations,

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TABLE 29.2. Soil Concentrations of Trifluralin Required To Inhibit Root Elongation

Plant Species	Soil Concentration, ppm
Russian thistle	0.3 - 0.5
Tansy mustard	4.1 - 5.7
Fourwing saltbush	1.8 - 3.5
Gardner saltbush	4.2 - 6.1
Winterfat	0.2 - 0.5
Crown vetch	5.8 - 6.5
Rocky Mountain penstemon	0.9 - 1.5
Palmer penstemon	1.4 - 2.1
Whitmar beardless	
Bluebunch wheatgrass	0.5 - 0.8
Thickspeike wheatgrass	0.6 - 1.1
Russian wild rye	0.5 - 1.1
Blue flax	1.4 - 2.5
Bitterbrush	0.4 - 2.0

where steady-state release from the device and decomposition rates were constant, were found to be 0.7, 1.5 and 4.5 ppm in soil for the three loading rates, and were obtained after 80 days of incubation. These analyses will continue over the next quarter.

The larger pelletized PCD devices proposed for placement into field studies in the summer of 1981 are being analyzed. These studies will evaluate the following:

- 1) trifluralin release rates from the device,

soil accumulation rates, and time to reach equilibrium in the soil; 2) effect of soil moisture content on the equilibrium trifluralin concentrations; and 3) diffusion profiles necessary to determine the ultimate depth of the PCD systems.

GREENHOUSE AND FIELD STUDIES - J. F. Cline

The greenhouse experiment using polymeric/trifluralin pellets placed in a thin layer below the soil surface was completed. Plant roots passed through the barriers containing 1 and 4 pellets/in.², and about 50% of the roots passes through the layer of 16 pellets/in.², as shown in Table 29.3. Two reasons for roots passing the barrier were: 1) these first-attempt pellets were too small and had inadequate trifluralin delivery rates because the concentration of trifluralin in the soil above the pellets was <3 ppm after 90 days in the soil and 2) plants were planted immediately after the placing of pellets in the soil; since the trifluralin had a 50-day effective half life, the soil did not have adequate time to reach equilibrium. Instead, time should be allowed for the trifluralin to be released slowly from the polymer and to build up in soil.

TABLE 29.3. Results of (PCD) Pellets and Radon Seals as Plant Roots Barrier in Plant Containers in Greenhouse

Pellet Spacings, Pellets/in. ²	Seal Type	Roots Passed Pellet Barrier, %	Roots Passed Seal, %
0	Asphalt	100	0
0	Clay layer	100	0
0	None	100	-
1	None	100	-
1	None	100	-
4	None	100	-
4	Asphalt	100	0
16	None	50	-
16	Clay layer	50	0

These problems have been corrected in three ways: 1) by increasing the pellet size from ~3 mm to 9 mm in diameter by 9 mm long; 2) increasing the trifluralin loading in the pellets from 10% to 25%; and 3) in subsequent experiments, allowing sufficient time between placing the pellets and planting for the soil concentration of trifluralin to reach ~6 ppm. In preliminary studies, the soil concentration 1 cm above the layer reached 5 ppm 20 days after placement of the larger pellets in the soil. We have also determined that we can overcome the equilibrium problem in the field by spraying liquid trifluralin onto the soil at the time the pellets are placed. The liquid trifluralin will maintain the concentration in the soil until the buildup from the pellets is adequate. In our experiment, plant roots did not penetrate the asphalt emulsion seal or the rock layer placed over the clay/aggregate layer seal (Table 29.3). Roots touched the asphalt, then grew horizontally along the seal, indicating that the asphalt was not toxic and that the roots could enter the seal if a crack or void presented itself. Likewise, roots grew to the rock layer placed over the clay seal, but horizontal growth was less.

A small spreader has been developed to place PCD pellets on the experimental plots (20 x 50 ft) over radon seals at the Grand Junction site.

ANIMAL INTRUSION STUDY - K. A. Gano

A visit was made to the Grand Junction uranium tailings site to build three en-

closures over a rock barrier. The rock layer had been placed over the southeast corner of the asphalt emulsion plot. Prairie dogs were placed in each of the pens to test their burrowing ability against the rock layer. After 1 week, one animal had escaped by burrowing under a shallow corner of the fence. Visual observations showed that the prairie dogs had excavated considerable quantities of the rock and the soil cover. The extent of the burrowing and excavation of the cover will be measured and documented in June.

The excavations of the ground squirrel enclosures were postponed from February until April to allow more time for burrowing.

PUBLICATIONS

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

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

30. 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

Current and planned test plot studies will evaluate vegetation establishment as affected by sealant/barrier systems and planting methods. Construction of the Grand Junction test plot was completed. Tentative plans for future test plots were established.

Sampling methods for gathering site-specific data were identified and sampling procedures determined. A summary of the type of site-specific data collected to date is presented.

Task definition for riprap studies was completed and work began. The goal of this task is to describe the effects of vegetation, rock cover (riprap) and climate on erosion and soil water dynamics via mathematical models. FY 1981 work will concentrate on selecting and evaluating appropriate existing models.

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

The general purpose of the Test Plot Task is to evaluate how planting methods and sealant barrier systems might affect re-

vegetation establishment. The response of vegetation to sealant/barrier systems is being tested at the Grand Junction Test Site. Effects of planting methods on plant establishment will be studied on future test plots.

Details of the experimental design for the Grand Junction Test Site were discussed in the previous quarterly report. Progress during this quarter consisted primarily of establishing an irrigation system on the site. This system will provide supplemental moisture to aid in seed germination and establishment of the vegetative cover.

Tentative plans were made this quarter to construct a test plot. Here plant establishment will be correlated with planting methods, soil stratification and irrigation intensity. Based on state-of-the-art knowledge of revegetation research, five treatment variables were identified as being pertinent to the stabilization of mill tailings. These treatments will be incorporated into the plot design:

- Irrigation - Varying amounts of water will be applied to the plots to determine the optimum for plant establishment.
- Mulch - Effects of applying organic and rock mulches will be compared to unmulched treatments.

- Plant propagules - Direct seeding, seeds in planting blocks, and container-grown plants will be compared.
- Soil stratification - A layer of sandy soil will be placed over the resident soil to increase water infiltration. This will be compared to untreated soil and to soil with rock mulch.
- Species composition - Seed mixtures and application rates will be compared and evaluated for their effects on plant establishment and plant community composition. The effects of herbaceous vegetation on shrub establishment will also be evaluated.

The following criteria were established for the location of the test plot:

- The location must be as representative as possible of the 25 inactive tailings sites.
- The location must be reasonably accessible.
- Water must be available for irrigation.
- Test plot studies at this location should contribute information needed in reclamation research.
- The plot should be located on a surface mined area, and the mine operator must be cooperative.
- Material for rock mulching should be available.

Based on these criteria, three potential locations were suggested:

- Farmington, New Mexico
- Grand Junction, Colorado
- Gallup, New Mexico.

Farmington was the preferred area.

In addition to the major test plot, low-intensity test plots (screening plots) will be established near three inactive mill tailings locations: Falls City, Texas; Lakeview, Oregon; and Lowman, Idaho. The purpose of these plots is to test the revegetation po-

tential of selected plant species that will be identified following site sampling. The areas were chosen because information about revegetation is lacking for those regions of the country, and because they present environmental conditions different from the majority of sites.

These low-intensity test plots will be designed to test the following:

- the effects of direct seeding at high and low application rates on plant establishment
- the success of establishing container-grown shrubs planted along with grasses and forbs seeded at high and low densities
- the effect of seed mix (the ratio of herbaceous to woody species) on plant establishment.

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

The focus of the Species Selection Task during the second quarter of FY 1981 was on defining the objectives of the site sampling subtask and designing the methodology needed to meet these objectives. Sampling in the vicinity of each tailings pile will accomplish the following:

- identify species for use in revegetation
- determine climatic and edaphic influences on plant community structure (cover, density, rooting profile)
- provide necessary data to estimate revegetation potential
- provide data needed for erosion modeling
- provide information on local soils suitable for use in covering the tailings pile.

The inventory of information available from the Soil Conservation Service, the Bureau of Land Management, and the U.S. Forest Service will be used to select

several sampling sites. These sites will have suitable cover soils and will represent soils and associated vegetation in the areas of the tailings piles.

Vegetation sampling in the selected sites will include: the percent of the vegetative cover, the height, the diameter, and the rooting depth for dominant species. Voucher specimens and photographs will be taken for documentation. Two to three standard soil cores will be collected from each site, taken as deep as possible. The soils will be characterized by depth using standard SCS analyses (structure, particle size, electrical conductivity, saturation index, bulk density, etc.). Other site characteristics that will be described are: wildlife use, slope, aspect, range condition, and erosion potential.

Along with a growing bibliography on revegetation of mine spoils, the Revegetation of Inactive Uranium-Tailings Sites Project has also acquired much information on conditions at each U-tailings site. Table 30.1 summarizes this information.

RIPRAP STUDIES - P. A. Beedlow, D. W. Mayer, W. Walters, R. L. Skaggs, and T. J. Bander

At present, the scope of this task is to initiate the construction of models describing the effects of vegetation, rock cover and climate on erosion and soil water dynamics. Specific objectives are as follows:

- determine the climatic, topographic and edaphic conditions under which rock cover (riprap) should and should not be used to stabilize tailings covers
- estimate changes in soil water resulting from rock/vegetation stabilization methods
- estimate the stability of vegetation covers through time.

Established models of soil erosion and water flow will be adapted for use at tailings sites. The FY 1981 work will use data collected from the Grand Junction area and the tailings pile. Subsequent work is planned to verify the models using site-specific and regional data from other uranium mill tailings sites.

Three models will be explored for possible use in estimating erosion due to overland water flow. The simplest is the Universal Soil Loss Equation (USLE). It is an empirical equation that estimates long-term average annual soil loss. The USLE is easy and expedient to apply and can provide useful information. It does not, however, account for the potentially catastrophic effects of extreme rainfall events.

The Agricultural Runoff Management (ARM) Model is a more complex model. It simulates the hydrologic processes which convert precipitation to overland, subsurface, and ground-water flow and the erosion of soil materials due to rainfall impact and runoff. The major components of the model, LANDS and QUAL, individually simulate the hydrologic response of the watershed and sediment production and transport, respectively. Basically, LANDS is an accounting procedure for surface and subsurface moisture. It simulates all flow components (overland, subsurface, and ground-water flow) and moisture storages by representing the processes of interception, infiltration, percolation, evapotranspiration, and snow accumulation and melt. QUAL simulates the accumulation and removal of sediment, and the erosion of soil particles by rainfall detachment and transport by overland flow. ARM requires considerable amounts of detailed hydrologic and meteorologic data and information on watershed characteristics and land use. ARM continuously simulates the rain/runoff and

TABLE 30.1. Site-Specific Data Currently on File for the Revegetation of Inactive Uranium-Tailings Sites Project

U-Tailings Sites	Priority	Ford, Bacon and Davis Report	Soils Information	Climatological Information	PIN Information
Salt Lake City (Vitro)	High	M-17 ^(a)		M-128	
Cannonsburg, PA	High	M-32	M-203	M-130	
Durango, CO	High	M-23	M-202	M-129	+
Shiprock, NM	High	M-24	M-46	M-129	
Grand Junction, CO	High	M-25	M-47	M-129	+
Riverton, WY	High	M-21	M-201	M-130	+
Gunnison, CO	High	M-30	M-48	M-129	+
Old Rifle, CO	High	M-28	(b)	M-129	+
New Rifle, CO	High	M-28	(b)	M-129	+
Mexican Hat, UT	Medium	M-37		M-130	
Lakeview, OR	Medium	M-22		M-13	
Falls City, TX	Medium	M-27	M-51	M-130	
Tuba City, AZ	Medium	M-35	M-43	M-129	+
Naturita, CO	Medium	M-19		M-129	+
Ambrosia Lake, NM	Medium	M-31	M-45	M-129	+
Green River, UT	Low	M-20		M-130	
Slick Rock (NC), CO	Low	M-16	M-200	M-129	+
Slick Rock (UC), CO	Low	M-16	M-200	M-129	+
Maybell, CO	Low	M-29		M-129	+
Monument Valley, AZ	Low	M-36	M-44	M-129	+
Lowman, ID	Low	M-2b	M-40, M-39 ^(c)	M-129	+
Converse, Co., WY	Low	M-18	M-38 ^(c)	M-130	+
Baggs, WY	Low		M-38 ^(c)	M-130	+
Bellfield, ND	Low		M-42 ^(d)	M-129	
Bowman, ND	Low		M-41	M-129	+

(a) Information can be obtained by these reference numbers in the project's computer data retrieval system.

(b) Advanced copy (unpublished) available only. Unnumbered.

(c) State map only.

(d) Available for Slope County only.

soil erosion process. Therefore, it provides a means of analyzing the effects of sequential rain/runoff events.

An alternative to ARM is a single-event, high-resolution model for overland water and sediment routing known as WASED. The model is termed high-resolution because it uses a finite difference solution technique to solve

the water-continuity and soil-erosion equations. Such a scheme provides the capability for describing the surface slope and shape in detail and eliminates possible errors due to the assumption of uniform slope made by ARM. WASED can be used to analyze the consequences of extreme events, both observed and hypothetical in detail. Also, since the

model is more deterministic in nature than ARM, it is less reliant on calibration. However, it too requires a significant amount of information for its operation.

The wind erosion model developed by W. S. Chepil has been used to estimate erosion from mill tailings and will be employed in this project. The model is based on wind tunnel and agricultural field measurements. Meteorological parameters and those describing the physical properties of the tailings site are used as input data. Soil loss by wind in tons/acres/year is the output.

To evaluate the impacts of stabilization methods on soil water, an unsaturated flow model will be used. This model (UNSAT) is currently in use on other UMTRAP projects.

The UNSAT computer model was originally developed to describe vertical, one-dimensional unsaturated water movement under usual agricultural conditions. It was designed as a model for isothermal water flow in the liquid phase. Most unsaturated flow models are alike in that they depend critically on the quantity and quality of site-specific input data.

By using models of soil erosion and soil water dynamics in conjunction with the results from the test plots, appropriate stabilization methods can be determined for specific tailings sites. Appropriate methods are those that ensure, in a cost-effective manner, the integrity and proper functioning of the sealant/barrier system.

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