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Nuclear Waste Management Quarterly Progress Report April Through June 1980

A. M. Platt
J. A. Powell

September 1980

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

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
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NUCLEAR WASTE MANAGEMENT
QUARTERLY PROGRESS REPORT
APRIL THROUGH JUNE 1980

Compiled by
A. M. Platt and J. A. Powell
Nuclear Waste Technology Program

September 1980

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

Pacific Northwest Laboratory
Richland, Washington 99352

FOREWORD

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

These reports are issued quarterly. The prior one in this series is Nuclear Waste Management Quarterly Progress Report January Through March 1980, PNL-3000-5.

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1. HIGH-LEVEL WASTE IMMOBILIZATION

D. E. Larson - Program Manager
T. A. Golding - Program Administrator

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

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

Work Element 1.3.1 Waste Form Development and Characterization

Work Element 1.3.2 Process and Equipment Development

SUMMARY

Recovery from radiation damage evidenced by density change in glass samples of widely different composition was found to occur at closely similar temperatures.

Studies of phase separation in waste glasses indicate that separation is increased with the addition of molybdate and results in increased leach rates.

As candidate materials for engineered barriers, Titanium Grades 2 and 12 show outstanding corrosion resistance in simulated low-oxygen brine and moderate-oxygen Hanford ground water.

Screening leach tests of ceramics and the exposure of polymers to ground water and radiation show that graphite and alumina, ethylene propylene rubbers, polyphenylene sulfides, filled epoxies and ethylene-tetra fluoroethylene copolymers also are worthy of continued consideration as engineered barrier materials.

Crucible melt tests and joule-heated melter tests show that melt foaming is dependent on the oxidation states of the multivalent ions of manganese, iron, and nickel in the waste.

Studies show that use of microwave energy is a feasible method of boosting feed rate processing in liquid-fed melters.

Corrosion of the calcine-fed ceramic melter after long-term operation is attributed to experimental operation at extreme temperatures.

Preliminary safety analyses of the liquid-fed ceramic melter process show that releases for all postulated accidents fall within limits of regulatory guidelines.

Data from spray calciner operation led to development of an equation correlating calciner capacity with temperature and dimensions.

WASTE FORM DEVELOPMENT AND CHARACTERIZATION

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

Recovery from radiation damage evidenced by density change in five waste glass samples of widely different composition was found to occur at closely similar temperatures. The experiment was performed on curium-doped glasses allowed to achieve saturation damage at doses of 6 x 10^{18} dis/cm^3. Recovery, monitored by heat release during annealing, proceeded smoothly as the temperature increased and was complete at 360°C.

Comparison of leaching behavior of high-zinc borosilicate glass over 4 years in a static environment and in a quasiflowing environment (IAEA test) showed that total release in the IAEA test is about 5 to 6 times greater than in the static test. The IAEA procedure simulates flowing conditions by periodically replacing the leach solution with fresh water. The initial dynamic leach rate was a factor of 3 greater than the rate at 3-1/2 years.

Study of the effects of molybdate on phase separation in some waste glasses shows that they separate into two phases, one rich in alkali borate, the other in silica. Leach tests indicate that if phase separation occurs in nuclear waste glasses a lowering of chemical durability cannot be avoided, unless the SiO_2 content is very high and the alkali borate-rich phase is dispersed as droplets.

For the corrosion screening of candidate metallic engineered barrier materials, U-bend specimens containing simulated welds are exposed to two environments, both at 250°C: NaCl - $MgCl_2$ Waste Isolation Pilot Plant (WIPP) brine and a Hanford basalt ground water. The oxygen level of the WIPP brine is 50 ppm; the Hanford ground water tests have been run at two oxygen levels: ~1 ppm and 50 ppb. After 24 days in the WIPP brine, the cupronickel, copper, and cast iron specimens were badly corroded and removed from the test. After 72 days, samples of 405 SS and 410 SS were cracked and showed high weight losses (350 mg/cm^2). The remainder of the materials, i.e., specimens of various 300 series stainless steels, Inconel 625, and alloys of titanium and zirconium, showed little weight change, and no cracks were evident.

In the Hanford ground water tests, the cast irons showed high, but not catastrophic, weight changes. After 89 days in water of ~1 ppm oxygen, the irons showed weight losses in the range 180 to 450 mg/cm^2, with deep pitting on a grey iron specimen. The titanium 50A and titanium Code 12 alloys showed outstanding corrosion resistance, with weight changes of +0.4 and +0.2 mg/cm^2, respectively. The nickel-copper, zirconium-base alloys, and 300 series stainless steels showed intermediate behavior; interestingly, no U-bend specimens cracked in the Hanford ground water studies.

In the further evaluation of titanium Grades 2 and 12 as candidate materials for engineered barriers, tensile, impact, static and dynamic fracture toughness, and fatigue-crack-growth tests have been performed. Tensile and impact tests were done over the range 20 to 250°C. The ductility of both alloys increases significantly with temperature. Yield and tensile strengths decrease by 50% between 20 and 250°C. The Grade 12 alloy exhibits higher strength and lower ductility over all temperatures studied. The static and dynamic fracture toughness of Grade 12 is significantly lower than that of

Grade 2 over the entire temperature range. The toughness of both materials increases significantly with temperature. Instrumented impact studies show that this is due primarily to propagation energy rather than initiation energy, indicating a high resistance to failure under severe accident conditions.

Center-cracked tension specimens and compact tension specimens were used for fatigue-crack-growth-rate testing of the alloys. The fatigue-crack-growth-rate of Grade 12 is much higher than that of Grade 2 under ambient conditions.

The ceramic leaching studies in connection with engineered barriers led to the conclusion that graphite and high-purity alumina offer the best resistance to ground water attack/dissolution. Titania and zirconia could be considered candidates, though their performance was inferior to that of alumina and graphite.

Polymers selected for study as barrier materials were polyamide-imide, polyarylene, polyimide, polyolefin, polyphenylene sulfide, polysulfone, fluoropolymer, silicon, epoxy, and ethylene-propylene copolymer (EPDM) rubber. Some materials were tested as the neat polymer such as the polyolefins or fluoropolymer, while others tested were composites containing fiber glass or other fillers (e.g., polyimides and polyphenylene sulfide) to enhance properties.

After testing at 150°C a number of polymers appeared to retain their properties: polyphenylene oxide, polymethylpentene, polysulfones, and glass-fiber reinforced polymides. After 7 days at 200°C, only EPDM rubbers (ethylene propylene elastomers), polyphenylene sulfide, a metal-filled epoxy and fluoropolymer samples were found to have retained good mechanical properties. Only the EPDM rubbers, polyphenylene sulfides and the fluoropolymer materials survived the 250°C test. Polymers that appeared to be little affected by exposure to 5×10^8 rads of gamma radiation were polyphenylene sulfide, polyimide, and metal-filled epoxy. EPDM rubber samples, although suffering considerable loss in elongation, still retained reasonable tensile strengths after the radiation exposure while the fluoropolymer, although dropping in impact strength, retained much of its initial tensile strength and elongation. The leading polymeric candidates for use in engineered barrier systems after this initial evaluation are EPDM rubbers, polyphenylene sulfides, filled epoxies and ethylene-tetra fluoroethylene copolymer.

PROCESS AND EQUIPMENT DEVELOPMENT

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

Crucible melt tests investigating foaming in glass melts show that foaming is dependent on the oxidation states of the multivalent ions of manganese, iron and nickel present in significant quantities in Savannah River Plant waste. The manganese oxides appear to be the major contributor to the problem. Foaming was minimized by reducing the oxidation states of these multivalent ions by the addition of reducing agents such as cornstarch, Na_4 EDTA and urea to the liquid waste.

A test in which simulated Savannah River waste was slurry-fed into a liquid-fed, joule-heated melter demonstrated a glass production rate up to 40 kg/hr over a period of 44 hr with steady-state operation at a feed rate of 80 ℓ/hr for 14.5 hr. Feed was a slurry of 72 wt% glass-forming frit to 28 wt% waste oxides spiked with trace elements for volatility studies. Cornstarch effectively controlled foaming, and Bentonite was added to improve particle suspension. The formation of a spinel-type precipitate during melting was reduced by about 50% over the results acquired in previous calcine-feeding tests. This improvement was attributed to the superior mixing of the waste with the glass formers. Volatility of the tracer elements during steady-state operation was determined. The volatilities of antimony and cesium were unexplainably high: 31 wt% and 10 wt%, respectively. Less than 4 wt% of the tellurium and <2 wt% of the ruthenium volatilized. No volatility, other than the physical carryover, was detected for strontium. Levels of antimony and tellurium were found to be lower in the off-gas line than in the melter plenum, indicating that these elements may be condensing on the lid and the off-gas line. Particulate entrainment was found to be 0.1 wt%.

Studies indicate that the use of microwave energy is feasible as a method to boost the rate of feed processing in liquid-fed melters. By this technique the additional power required to dry and calcine the liquid feed can be introduced without direct contact with the waste. Experimental work will be done in a laboratory-scale joule-heated melter to develop engineering data. An investigation is under way to identify suitable ceramics to insulate the melter yet not absorb microwave energy excessively.

Disassembly and inspection of the liquid-fed ceramic melter were completed, and reconstruction is proceeding on schedule. Restart is expected to occur near the end of August. Inspection data and results will be formally reported next fiscal year.

Preliminary analysis of postulated accidents for the safety assessment of the prototypic, liquid-fed ceramic melter process shows that the releases for all accident groups within the design bases meet regulatory guidelines for reactors. The analysis is for accident groups defined for the generic power waste flowsheet, and because of the lower activity of defense wastes, shows that accident consequences for the defense waste flowsheet are even less severe.

Post-operation examination of the calcine-fed ceramic melter revealed significant internal corrosion attributed to operation at excessive temperatures. The melter had processed more than 6000 kg of glass since April 1978, some of which was produced in foaming tests at extreme conditions (>1200°). The refractories on walls and lid were severely attacked as were some metal surfaces; the floor was somewhat protected by a layer of sludge. The glass freely penetrated the refractory joints but did little damage to the backup materials. Corrosion to the Inconel 690 electrodes was negligible as they were maintained at 900 to 1050°C at all times.

The calcine-fed ceramic melter is being rebuilt. It will be used in continued experiments directly coupled to a spray calciner or in tests to evaluate direct liquid feeding with boosting techniques such as plasma torch, fuel combustion and microwave heating, but will not be operated at temperatures exceeding 1200°C.

Data produced in long-term full-scale and pilot-scale spray calciner runs under equilibrium operating conditions led to development of an equation correlating capacity of the calciner to spray chamber height, diameter and wall temperature. Capacity (ℓ/hr) =

$7.477 \times 10^{-11}\ T(°C)^{2.83} \times \text{dia (cm)}^{1.41} \times \text{height (cm)}^{0.705}$.

Cold operations of the in-cell spray calciner/in-can melter were begun. Initial problems with plugging of the calciner spray nozzle and loss of prime to the feed pumps were corrected by changes to operating procedures. The operational safety requirements have been approved by PNL, HEDL and DOE; and permission has been requested of DOE to begin hot operations.

The final draft of the spray calciner/in-can melter Technical Manual has been reviewed by General Electric and distributed for internal review and approval preparatory to issue in September (DOE-HQ monitored milestone).

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

Hot isostatic pressed (HIP) samples of PW-9 calcine and SPC-5B supercalcine were fabricated and characterized. Leaks developed during fabrication, resulting in very little compaction. Open porosity was calculated at 25% for PW-9 and 45% for SPC-5B. Weight loss during 3-hr volatility tests (700°C-1300°C) ranged from 6 to 20 wt% for PW-9 and 0.3 to 1 wt% for SPC-5B.

Initial results indicate that hot pressing of supercalcine SPC-4 in graphite may provide a superior product to that obtained by cold pressing and sintering. Densities obtained for hot-pressed supercalcine ranged from 4.38 to 4.48 g/cm^3, whereas densities of 3.93 to 4.01 g/cm^3 were obtained for cold-pressed and air-sintered supercalcine. Element retention was highest for hot-pressed samples followed by cold-pressed and Ar-4%H_2-sintered samples. Poorest element retention values were obtained for pellets sintered in air.

Pyrolytic carbon (PyC) chemically vapor deposited (CVD) fluidized-bed coatings were deposited on UO_2 stand-in substrates at Battelle Columbus Laboratory (BCL) and quartz substrates at PNL at 445 and 430°C, respectively. In both tests, a mixture of ~1.5 mole% C_2H_2, ~0.01% $Ni(CO)_4$, and 98.49 mole% H_2 gases were used. Dissociation of propylene in a radio frequency (rf) field was identified as a possible method to deposit PyC at 350°C.

A metallic screw-agitated coater (SAC) 10-cm dia by 46-cm long has been successfully demonstrated at BCL on 6 mm Al_2O_3 balls and 13 mm simulated waste glass marbles. The best-appearing PyC coatings were applied at a bed temperature of ~500°C, using ~0.02 mole% $Ni(CO)_4$, ~3.0 mole% C_2H_2 and the remainder H_2.

Titanium, glass, graphite, and ceramic castables have been identified as highly promising barrier matrix materials. Borosilicate glass beads and supercalcine pellets have been sent to General Atomic Company (GAC) for encapsulation in graphite. Mixtures of graphite, nickel, and sulfur have been cold pressed and heat treated at PNL. Scanning electron microscope (SEM) examination of metal matrix encapsulated waste forms, prepared and heat treated at PNL,

have been completed at the Hahn-Meitner Institute.

Comparative study leach resistance tests were completed on the celsian glass ceramic samples. Elements generally considered to be the most mobile (cesium, sodium, molybdenum, boron) seem to be less affected by surface area to volume ratio than by time. The celsian glass ceramic has the best leach resistance at 90°C in deionized water of all the comparative study samples studied to date.

The lab-scale hot-cell equipment development milestone for crystalline waste from fabrication was completed. Major equipment includes a hydraulic pellet press and a sintering furnace. Accommodations were made to hot press using a furnace on the hydraulic press.

Leaching studies on partially metamict and nonmetamict zircons are in progress. Single crystals of thorite and huttonite (average size 0.6 mm) were grown from $Na_2Mo_2O_7$ flux at 1100 and 1300°C, respectively. Studies on the preparation of polycrystalline thorite and huttonite were completed.

The marbles in lead encapsulation (MILE) process milestone was successfully completed ahead of the scheduled September date. A canister 41 cm dia by 2.1 m tall was initially filled with 300 kg of marbles produced from Savannah River Plant glass composition. Then the contents were completely encapsulated in molten lead which was subsequently cooled and solidified starting from the bottom of the canister. Several tests are planned to determine the quality of the casting.

Seventy-nine kg of precisely formulated supercalcine SPC-4 and 51 kg of precisely formulated SPC-5 were produced. Thirty-two kg of the SPC-4 will be delivered to Rockwell Hanford Operations, fulfilling subcontract requirements. Both the pin mixer and disc pelletizer are now in operation and will be used to produce supercalcine and other substrates for coating studies.

A sample of PW-4b-7 simulated nuclear waste solution was prepared and sent to Lawrence Livermore Laboratories (LLL). A sample of simulated Savannah River calcine was also prepared and shipped to North Carolina State University (NCSU). Samples sent to both sites will be used in SYNROC studies.

A second in-can sintering run without Al_2O_3 carrier was performed to supply sintered SPC-4 supercalcine pellets for metal matrix encapsulation. About 76 liters (57 kg) were produced. Quality was good although some pellets had fused together. In future runs, an Al_2O_3 carrier will be used. Alternative sintering methods are being investigated.

The lab-scale PyC fluidized-coater system has been assembled and tested at PNL as part of the technology transfer from BCL. Design of an engineering-scale PyC-coating system is nearly complete. This system will employ a screw-agitated coater as developed by BCL.

Six papers have been presented and one paper published during this quarter.

WASTE FORM DEVELOPMENT AND CHARACTERIZATION

Ceramic Development - R. O. Lokken and C. N. Wilson (Hanford Engineering Development Laboratory)

The remaining two samples for the comparative studies have been received and evaluated. These are samples of PW-9 calcine and SPC-5B supercalcine produced by hot isostatic pressing (HIP). The samples were prepared for HIP by uniaxially pressing denitrated and dried powder into stainless steel cans 5.4 cm dia at 28,000 psi. A mild steel plug 6 mm thick was placed atop the compacted powder, and a lid containing a filtered vacuum stem was welded to the can. The cans were evacuated while heating to 150°C, sealed by crimping and welding the tube, and placed in a HIP chamber. The assemblies were pressurized to ~10,000 psi with argon at room temperature, heated to 900°C (PW-9) or 1000°C (SPC-5B) at 20,000 psi, and held for 2 hr under these conditions. During the HIP cycle, leaks apparently developed in the welds, resulting in internal pressurization and consequently little compaction. Immersion densities of the samples were 2.89 and 1.62 g/cm^3, respectively, for PW-9 and SPC-5B. Open porosity was calculated at 25 and 45%, respectively.

Volatility measurements were conducted on the HIP samples at temperatures of 700°C, 900°C, 1100°C, 1200°C, and 1300°C; each sample was held at temperature for 3 hr. The weight loss from HIP PW-9 increased from 6 wt% at 700°C to 19.9 wt% at 1200°C. The PW-9 samples spalled in the attempted 1300°C test. SPC-5B demonstrated much better stability losing 0.3 wt% at 700°C and 1 wt% at 1300°C. The material melted at the highest temperatures.

Hot-pressing studies are being conducted to determine if hot pressing offers any significant advantages over cold pressing and sintering for the preparation of supercalcine and ceramic waste forms. Five hot-pressing tests were completed using varied temperature, time, and die-design parameters. Characterization of the hot-pressed pellets includes density, element retention, oxidation state, die reaction, microstructure, and leaching. Initial results indicate that hot pressing in graphite may provide a superior product to that obtained by cold pressing and sintering.

Rapid densification during hot pressing was initiated at ~1080°C in all five test runs. Metallographic and SEM examination indicated that near-complete densification had occurred by 1100°C. No open porosity was observed, and small ($\leq$1 μm dia) pores observed by SEM were estimated to account for <1% of the pellet volume. Final density values, measured by both geometric and immersion methods, ranged from 4.384 to 4.555 g/cm^3. Geometric densities obtained by cold pressing and sintering in air and in flowing Ar-4%H_2 are compared to the values obtained by hot pressing in Table 2.1.

X-ray fluorescence analysis was conducted on diamond-sawn cross sections from pellets sintered in air, sintered in flowing Ar-4%H_2, and hot-pressed pellets. Assuming zirconium to be a nonvolatile element present in the oxide matrix phase of SPC-4, characteristic x-ray count rates for all elements of atomic mass 14 (Si) or greater were ratioed to the Zr Kα count rate. The same peak-to-Zr ratios were also derived from a cold-pressed SPC-4 pellet to provide a green pellet standard.

Elements that appeared to show significant loss under one or more of the processing conditions were cesium, rubidium, barium, strontium, molybdenum, and ruthenium. Calculated retention values for these elements, along with gadolinium (which showed a small peak-to-Zr ratio error and should be stable), are given in Table 2.2 for 1200°C air sintered, 1180°C Ar-4%H_2 sintered, and hot-pressed pellets at 1100°C and 1210°C. Hot pressing at 1100°C resulted in the best element retention, followed by sintering under reducing conditions. Worst element retention values were obtained for pellets sintered in air.

TABLE 2.1. Supercalcine SPC-4 Geometric Densities

Sintered 2 hr(a) in Air		Sintered 2 hr(a) in Flowing Ar-4%H_2		Hot Pressed 30 min(b) 4500 psi in Graphite	
°C	g/cm^3	°C	g/cm^3	°C	g/cm^3
1015	3.91	940	2.64	1100	4.451
1200	3.93	1180	3.84	1150	4.457
1250	4.01	1255	3.32	1210	4.384(c)

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a. Based on single pellet, temperature accuracy unknown.
b. Three-pellet average (except 1210°C) ±5°C.
c. Two-pellet average, irregular pellets due to surface reaction.

TABLE 2.2. Supercalcine SPC-4 Element Retention by X-Ray Fluorescence

Element	Peak Zr Ratio Error, %	Air Sintered 2 hr at 1200°C	Ar/H_2 Sintered 2 hr at 1180°C	Hot Pressed 30 min	
				1100°C	1210°C
Cs	2	66	92	101	94
Rb	2	86	99	100	95
Ba	4	81	84	99	89
Sr	1	96	103	99	90
Mo	1	78	106	97	69
Ru	3	79	97	98	104
Gd	1	103	102	100	99

Coating Development - R. W. Kidd (BCL), M. F. Browning (BCL), J. L. Kaae (GAC)

Impervious PyC coatings have been applied at BCL to UO_2 substrates (stand-in substitute for waste particles) at 445°C in a fluidized-bed coater. A mixture of ~1.5 mole% C_2H_2, ~0.014 mole% $Ni(CO)_4$, and ~98.49 mole% H_2 was used. The coating rate was ~4 μm/hr. A micrograph of the coated particles is shown in Figure 2.1.

A metallic screw-agitated coater (SAC) 10-cm dia by ~46-cm long has been designed, fabricated, and tested at BCL. Figure 2.2 is a schematic of the system. It has been used to apply PyC coatings to 6 mm Al_2O_3 balls and 13-mm simulated waste glass marbles.

In efforts to reduce gas-phase nucleation, $Ni(CO)_4$ and C_2H_2 are currently being introduced into the bed through separate feed tubes. When $Ni(CO)_4$ was introduced through the holes in the cone, the holes plugged, probably with nickel. No problem occurred in introducing the C_2H_2 through the feed tube that also serves as the bottom retainer/bearing for the auger. The pointed tip of the auger merely rotates in this feed tube. Because of the $Ni(CO)_4$ plugging the inlet holes on the side of the cone, it was decided to introduce the $Ni(CO)_4$ through the feed tube that serves as the bottom retainer for the auger and introduce the C_2H_2 through the holes in the side of the cone. It was reasoned that the auger retainer maintained a slightly lower temperature than the side holes and that this would reduce the tendency to decompose the $Ni(CO)_4$. In addition, the tip of the auger could be expected to abrade

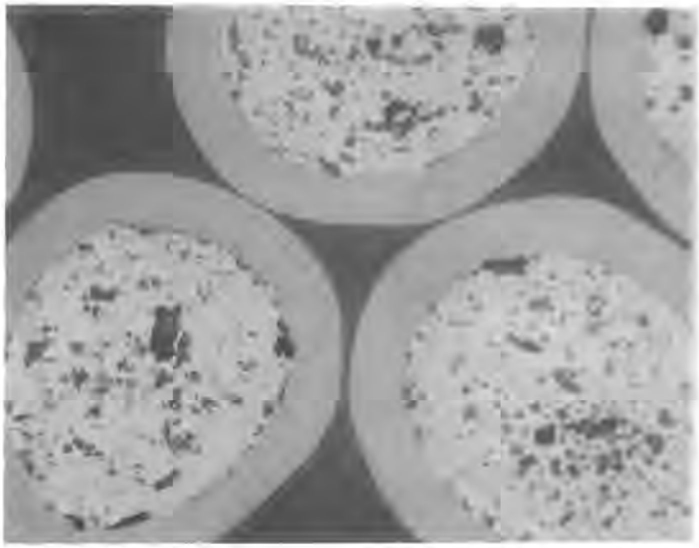


FIGURE 2.1. Nominal 17-μm PyC Coating on Mesh Uranium Dioxide

off any nickel deposited in the upper portion of the feed tube. In runs of 4 to 5 hr duration, this approach to introducing the reactants was successful. Some modifications, such as having a longer tip on the auger, may be required for longer runs or higher $Ni(CO)_4$ concentrations than currently found to be useful.

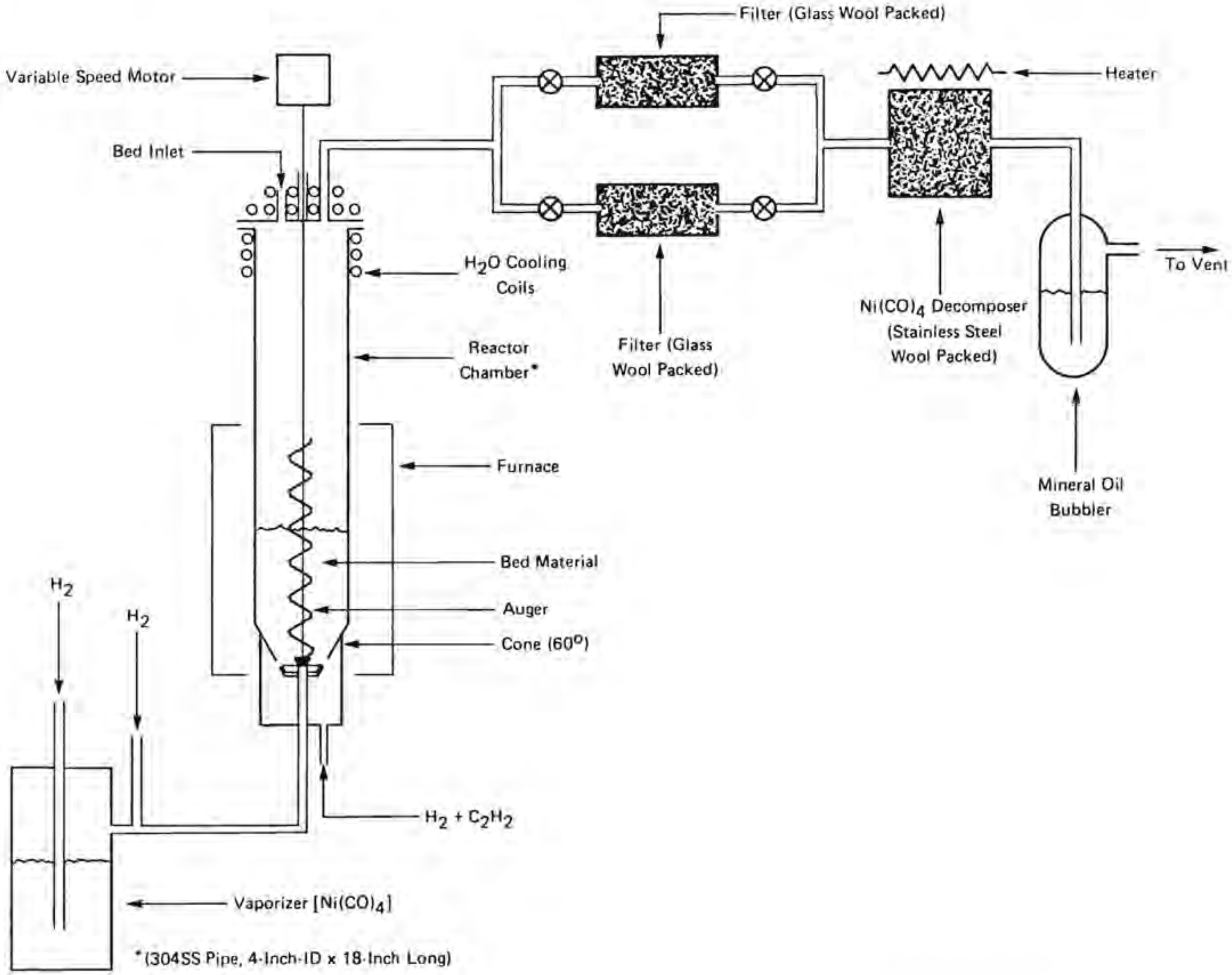
No apparent problem was encountered in coating PNL substrate. During a heat treatment of PNL glass marbles, it was noted that the glass marbles begin to soften at ~540°C. The best-appearing PyC coatings were applied using the following conditions: ~0.02 mole% $Ni(CO)_4$, ~3.0 mole C_2H_2, and balance H_2 with a bed temperature of ~500°C. However, the coating rate was only 1 to 2 μm/hr.

The deposition rate decreased as the total flow was increased, suggesting that the reactant gases required preheating. An expedient approach to preheating the gases was tried by positioning the reactor further up in the hot zone of the reactor furnace. Efforts to increase the coating rate by preheating the gases have not been very successful due to premature $Ni(CO)_4$ decomposition.

Literature reviews on feasibility of coating particles with diameters >4 mm and low-temperature PyC coatings have been initiated at the General Atomics Co. A coating process used to deposit carbon at 350°C was identified. This process uses a rf field to cause dissociation of propylene at a pressure of 10 torr. Deposition rates of 20 μm/hr were obtained.

Matrix Development - W. E. Gurwell, J. W. Wald and J. L. Kaae (General Atomics Co.)

Matrix survey work was essentially completed by the issuance of the first rough draft of a report entitled A Survey of Matrix Materials for Solidified High Level Waste. The three features of a barrier matrix are discussed in the report: 1) an outer envelope of pure matrix material that encapsulates and protects the entire waste form;



*(304SS Pipe, 4-Inch-ID x 18-Inch Long)

FIGURE 2.2. Schematic Diagram of the 4-in. Screw-Agitated Coater (SAC) and Associated Equipment

2) a web of matrix material that encapsulates and protects the individual waste cores; and 3) a bond between the matrix and waste core that limits the waste core area exposed to leach waters. Titanium, glass, graphite, and castables are highly promising barrier matrix materials. Matrix radiation levels need to be defined to evaluate the potential of polymers.

SEM examination of metal-matrix-encapsulated waste forms, prepared and heat treated at PNL, have been completed at the Hahn-Meitner Institute. Glass samples, cast in 100% lead and heat treated at 550°C (close to the glass transition temperature), have shown the greatest extent of reaction. After 150 hr at 550°C, the reaction zone thickness is 250 µm for 76-68 glass and 60 µm for MOD-102, a Hahn-Meitner Institute glass. Characterization of these samples is continuing, and detailed results will be reported next quarter.

Samples of 3-mm and 6-mm borosilicate glass beads and 2 mm supercalcine beads have been sent to GAC for encapsulation in graphite matrices. Mixtures of graphite, nickel, and sulfur have been cold pressed and heat treated. An exothermic reaction was observed at 240°C, which resulted in temperatures in excess of 600°C.

Leaching - J. W. Shade

Comparative study static leach resistance tests were completed on the celsian glass ceramic samples. The comparative study samples were leached according to a previously designed parametric leach study matrix. The matrix includes three surface area-to-volume ratios (0.6, 0.06, and 0.006 cm^{-1}), three temperatures (30, 90, and 200°C) and three times (1, 3, and 9 days). This matrix was designed, in part, to determine the effects of leaching parameters on the leach behavior of individual elements and also to compare the durability of different waste forms. The results are shown in Tables 2.3 and 2.4 for the celsian glass ceramic.

The data in Tables 2.3 and 2.4 are presented in units of normalized grams per square meter of surface area and were calculated as follows:

$$\frac{\text{normalized grams}}{\text{meter}^2} = \frac{Ci \times SV}{1000 \times SA \times Fi}$$

where:

Ci = the concentration of element i in mg/l as reported from ICP analysis of the leach solutions

SV = solution volume used in the leach tests in liters

SA = surface area (geometric) of the sample in square meters (m^2)

Fi = the weight fraction of element i in the waste form.

The data of Table 2.3 show the leach results from celsian glass ceramics as a function of time and surface area to volume ratio. Although both parameters affect leaching, these data suggest that the effect on specific elements is not equal. Elements that are generally considered to be the most mobile (i.e., cesium, sodium, molybdenum, boron) seem to be less affected by SA/V than by time. On the other hand, elements such as barium and calcium seem to be affected more by SA/V than by time as compared to the more mobile elements. This observed behavior could be partly a function of the distribution of elements among polyphase material and should not be construed to apply to all waste forms. Table 2.4 illustrates both the time and temperature dependence of leach behavior. At a constant SA/V ratio, sodium, cesium, and boron seem to be the most

TABLE 2.3. Results of Leaching Celsian Glass Ceramic in Deionized Water, Normalized g/m^2

	90°C, 1 day		90°C, 9 days	
Element	SA/V 0.6 cm^{-1}	SA/V 0.006 cm^{-1}	SA/V 0.6 cm^{-1}	SA/V 0.006 cm^{-1}
Cs	1.68	6.66	4.14	44.2
Na	2.25	5.76	5.77	57.9
Ba	0.90	5.35	0.68	21.5
Ca	1.17	11.64	1.69	46.8
Mo	9.45	21.20	13.29	74.7
Si	0.62	5.05	0.95	30.5
Al	0.20	-0-	0.27	4.9
B	3.60	16.72	9.69	103.5

TABLE 2.4. Results of Leaching Celsian Glass Ceramic in Deionized Water as a Function of Temperature, Normalized g/m^2

	SA/V = 0.06 cm^{-1}				
Element	1 day 30°C	9 days 30°C	3 days 90°C	1 day 200°C	9 days 200°C
Cs	0.6	1.7	10.9	36.2	92.7
Na	1.84	1.96	13.3	52.1	107.5
Ba	0.73	1.67	4.5	9.4	3.8
Ca	0.93	1.58	8.7	27.6	24.7
Mo	6.4	10.1	26.5	31.7	80.2
Si	0.3	0.94	6.1	21.4	38.0
Al	-0-	-0-	2.9	11.4	12.1
B	1.26	3.77	22.8	86.2	187.2

temperature dependent. It is interesting to note, however, that molybdenum is affected by both and, in fact, the data for molybdenum at 90°C/3 days is almost identical with those for 200°C/1 day.

Table 2.5 depicts some leaching results of celsian glass ceramics in comparison with some previously studied alternate waste-form materials.

Leaching studies are continuing on pyrolytic carbon and Al_2O_3-coated supercalcine pellets. Most of the effort has been confined to SEM (scanning electron microscopy) studies of polished cross sections of these materials. SEM studies of the high-temperature PyC-coated spheres previously reported as not preventing the release of cesium have been emphasized. SEM/EDAX (energy-dispersive x-ray analysis) scans revealed high concentrations of cesium in the PyC coatings. Volatilities in supercalcine at coating temperatures of 1200°C is ~2%/hr. The volatile cesium probably was trapped in the PyC during coating. This was also observed in the Al_2O_3/PyC duplex coatings, but the Al_2O_3 outer coating did not contain cesium.

<u>Radiation Effects</u> - D. W. Brite, R. C. Ewing and R. E. Haaker (University of New Mexico)

The milestone for development of lab-scale hot cell equipment for crystalline waste form

TABLE 2.5. Leach Resistance of Comparative Waste Forms[(a)]

Element	Normalized Concentration in Solution, g/m^2 Sintered PW-9	Cement 10% PW-9	Sintered Glass Frit +50% PW-9	Super Calcine SPC-5B	Glass 76-68	Celsian Glass Ceramic 20% PW-9
Na	6800	2370	91	33	25	5.8
Si	NA	0.4	9	4	6	1.0
Mo	6800	30	74	33	25	13.3
Cs	3800	1800	4	0.4	6	4.1

a. Leached 9 days at 90°C; SA/V = 0.6 cm^{-1}.

fabrication was completed with the procurement and cold testing of equipment for pressing and sintering crystalline ceramic waste form pellets. The major equipment items include a hydraulic pellet press and a sintering furnace. Calcine will be produced by the laboratory-scale spray calciner in D-cell. Cell space assignment was completed with allocation of one-half of the north half of 324 D-cell for crystalline waste form fabrication.

A 12-ton press with motorized hydraulic power supply was selected for sample pressing. The motorized hydraulic system can be placed in the cell, or it can be located out of the cell and connected to the press with a single hydraulic hose penetrating the cell wall. The pressing system has been tested and operates satisfactorily to the full-rated 12-ton capacity.

A pellet die with remote handling features has been designed and fabricated for use with the hydraulic press and has now been tested with simulated sludge calcines. It appears that die lubricant will not be necessary if the die is cleaned after each pressing. This will simplify the pressing operation.

A furnace was purchased for pellet sintering, capable of operation with an air atmosphere at temperatures to 1500°C. Furnace controls and power supply will be located out of the cell, with power and thermocouple wires penetrating the cell wall. The furnace was tested to 1400°C and found to operate satisfactorily.

Hot pressing is under consideration as an alternative technique for in-cell fabrication of crystalline waste forms. The hydraulic press was selected for hot cell work partly because it provides sufficient working height (18 in. between platens) to accommodate hot pressing equipment. A preliminary design has been prepared of a hot pressing system for use in-cell in the hydraulic press. The system includes a graphite die with supporting hardware and a shop-built furance using a commercially available Kanthal® heating element for 1350°C operation in air, inert or reducing (5% H_2-argon) atmospheres. Atmosphere control is obtained by purging. This furnace can be operated with the same power supply and controller used for the sintering furnace. Components required for construction of the hot-pressing furnace have been purchased or are on order.

Cold pressed and sintered and/or hot-pressed pellets will be evaluated for density, leaching behavior, volatility, chemical

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composition, compressive strength, and microstructure. A micrometer with electronic digital readout and an electronic balance with digital readout readable to 0.1 mg are available for making the measurements required for calculating pellet densities. Leaching behavior will be measured using the Materials Characterization Center (MCC) or Waste/Rock Interactions Technology (WRIT) in-cell facilities if available. If they are not available, a commercially available water bath will be procured and placed in the hot cell for leach testing.

Volatility of crystalline waste pellets will be measured by simple weight loss techniques. A cold finger technique will be used to collect volatile species, which will be measured for composition and concentration. Chemical composition of both pellets and volatiles will be measured by the HEDL analytical laboratory using radiochemical methods.

Pellet compressive strength will be measured by HEDL using an available diametral compressing test hot cell facility. Microstructures will be examined visually after ceramographic sample preparation by the HEDL radiometallurgy facility. X-ray diffraction (XRD) analysis of waste pellets will be conducted on the MCC hot XRD equipment.

Leaching studies on partially metamict and nonmetamict zircons are in progress. The degrees of crystallinity of the zircons are characterized by density measurements and Debye-Scherer powder diffraction photographs. Elemental compositions of the zircons are being determined by electron microprobe analysis. Zircon samples for leaching have been cut into cubes with ~2-mm edges to allow accurate measurement of apparent surface areas. Initial leaching runs have been done under the following experimental conditions: One zircon cube and 16 ml of H_2O containing 2 wt% $KHCO_3$ in a 25 ml acid digestion bomb. The bombs are held at 100°C for 7 days. The leachate will be analyzed for thorium, uranium and zirconium by neutron activation at LASL. Limits of detection for these elements by this method are in the 0.1 ppm range.

Crystals of thorite and huttonite with an average size of about 0.6 mm were grown from a $Na_2Mo_2O_7$ flux at 1100° and 1300°C, respectively. Thorite and huttonite crystals were prepared from two different molar ratios of refractory oxides: 0.90 ThO_2:0.10 CeO_2 and 0.95 ThO_2:0.05 CeO_2. These crystals are being mounted and polished for quantitative analysis by electron microprobe. Unit cell constants for crystals of both types and compositions are being determined by the single-crystal diffraction technique using a Syntex R3 diffractometer.

Studies on the preparation of polycrystalline thorite and huttonite have been completed. Pellets of thorite and huttonite with molar ratios 0.90 ThO_2:0.10 CeO_2 and 0.925 ThO_2:0.075 CeO_2 are being polished for quantitative analysis by electron microprobe. Conclusions that can be drawn from x-ray diffraction data include:

1. Thorite cannot be prepared with any degree of reliability by annealing 324-mesh huttonite powders in the thorite stability field (1100°C - 124 hr). The kinetics of the huttonite to thorite phase change are sluggish and complex.
2. When cerium-doped huttonite is prepared in air in the temperature 1500-1650°C, a second phase as yet unidentified is also formed. This may indicate that some Ce^{+4} is being reduced to Ce^{+3}.

PROCESS AND EQUIPMENT DEVELOPMENT

Ceramics - C. L. Timmerman and J. G. Carter

Installation of the disc pelletizer and the pin mixer agglomerator is nearly complete. Both the pin mixer and disc pelletizer are now electrically operable. An improved exhaust hood was also designed, built, and installed on the disc pelletizer. A pressurized binder system was obtained so that liquid binders other than water can be tested during the pelletizing. The dust containment building now lacks only the water and air services and the fire sprinkler system to be fully operational. Operating procedures for the disc pelletizer and pin mixer were prepared and approved. The pelletizing equipment is expected to be in service in July.

Precise formulations of SPC-4 and SPC-5 (see Table 2.6) supercalcines were produced. Seventy kilograms of SPC-4 and 40 kg of SPC-5 were to be produced in the pilot-scale spray calciner. Effluent sampling was performed during both production runs. This effluent data will be used to provide decontamination factor information on ruthenium, palladium, cesium and other elements for spray calciner operation.

The SPC-4 run yielded 79 kg, of which 32 kg were delivered to Rockwell Hanford for use in their engineered-barriers studies. The run required ~18 hr, feed rate was 31 ℓ/hr, and temperatures ranged from 565-655°C. The SPC-5 run yielded 51.5 kg over an operating time of 6 hr. Feed rate averaged 35 ℓ/hr, and temperatures varied from 500-625°C. Both the SPC-4 and SPC-5 runs experienced lower than normal calciner temperatures, which will cause a higher residual nitrate concentration in the supercalcine due to the incomplete calcination. Upon completion of the runs, both the SPC-4 and SPC-5 were barrel rolled to provide homogeneous products. Both of these supercalcines will be used in characterization studies.

In addition to the PW-4B-7 calcine previously sent to LLL and North Carolina State University, an acid waste solution was prepared and shipped to LLL. This solution, with appropriate additives, will be spray dried by LLL to produce SYNROC for characterization studies. A sample of simulated Savannah River calcine was also prepared and shipped to NCSU.

A second in-can sintering run was performed to supply sintered SPC-4 supercalcine pellets for metal matrix encapsulation. Approximately 76 liters (57 kg) of the supercalcine pellets were loaded into an Inconel canister 41-cm dia by 2.1-m tall. A simple plate fin assembly, air purge line, and thermocouple were placed in the canister prior to the pellet loading.

During the heating, the air purge line slowly trickled air into the canister for oxidation and off-gas removal throughout the run. The air purge line maintained a pressure of 2 psi and a flow of 1 scfh to prevent any effects from fluidizing. The heating rate of the in-can furnace was 200°C/hr to a maximum temperature of 1200°C. The furnace was maintained at 1200°C for ~8.5 hr, and all pellets were heated at 1200°C for at least 4 hr. The total run time from startup to shutdown of the furnace was 12.5 hr. This time is much improved over the first in-can sintering run due to the smaller quantity of material in the canister and the addition of the fin assembly to improve the internal heat transfer.

Removal of the pellets was difficult because they had fused together. In future runs, alumina granules will be mixed with the pellets to prevent this. Other methods

TABLE 2.6. Formations of SPC-4 and SPC-5 Supercalcines

	SPC-4			SPC-5		
Component	Molarity		g/ℓ Oxide	Molarity		g/ℓ Oxide
Ag	.002		.2317	.002		.2317
Ba	.027		4.1402	.033		5.0602
Cd	.002		.2568	.003		.3852
Cr	.012		.9120	.012		.9120
Cs	.054		7.6086	.063		8.8767
Fe	.100		7.9850	.050		3.9925
H	2.000			4.000		
Mo	.095		13.6743	.110		15.8334
Na	.010		.3100	.499		15.4690
Ni	.005		.3736	.005		.3736
PO_4	.100		7.0970	.025		1.7743
Rb	.010		.9347	.012		1.1216
Ru	.059		7.8482	.007		.9311
Sr	.027		2.7977	.031		3.2122
Zr	.106		13.0613	.120		14.7864
Tc	--			--		
Te	.012		1.9152	.014		2.2344
Rh	--			--		
Pd	.032		3.9168	.043		5.2632
Rare earth						
Ce	.051		8.7781	.062		10.6714
Gd	.155		28.0938	.006		1.0875
Nd	.071		11.9450	.086		14.4686
La	.053	.078	13.6500	.065	.097	16.9750
Pr	.012			.015		
Y	.004			.006		
Pm	--			--		
Sm	.007			.008		
Dy	.001			.002		
Ho	--			--		
Eu	.001			.001		
Supercalcine additives						
Al	.148		7.5480	1.148		58.5480
Ca	.124		6.9440	.155		8.6800
Si	.489		29.3840	1.477		88.7529
Sr	.041		4.2484	--		--
			183.6545			279.6411

for sintering large quantities of pellets are being investigated. These include a vertical kiln and shuttle kilns.

Glass Marbles - S. C. Slate and R. G. Nelson

The marbles-in-lead encapsulation process was successfully demonstrated, resulting in a milestone completion 3 months ahead of schedule and under budget. In the demonstration, a canister having a diameter of 41 cm and a height of 2.1 m was initially filled with 300 kg of glass marbles produced from a simulated Savannah River waste composition, TDS-211. The marbles were contained inside a screened basket centered inside the canister. They were completely encapsulated in 1400 kg of lead by first melting lead shot inside the canister and then by slowly cooling and freezing the molten lead beginning at the bottom of the canister. Final weight of the canister is 1963 kg. It will be used in a full-scale impact test.

The marbles were produced using the vibratory marble machine directly connected to a continuous ceramic melter. Premelted TDS-211 glass frit was used as the feed material. About 700 kg of glass was produced at a maximum melting rate of 35 kg/hr. Rates higher than this are expected for the TDS-211 glass feed because the melter is not being operated at maximum power. The rebuilt marble machine is working very well. The new speed range has resulted in much better control over the marble size and quality. The redesign emphasized making operation of the machine easier and more reliable. The maximum rate demonstrated so far is 35 kg/hr of marbles. Higher rates are expected to be possible because of the new cooling hoods that have been added. A separate 10 hr-run was made using TDS calcine and 211 frit as the feed material. Production rate varied from 28 to 35 kg/hr. Over 1000 kg of glass marbles have been produced on the marble machine.

The marbles were encapsulated in lead using the shot method illustrated in Figure 2.3. The canister assembly containing the marbles was preheated in an in-can melt furnace to 450°C. Lead shot was then poured into the canister assembly, requiring 2-1/2 hr for complete filling. Slow cooling from the bottom took a total of 7 hr.

Coatings - K. H. Oma and J. F. Nesbitt

A lab-scale pyrolytic carbon, PyC, fluidized coater system has been assembled and tested at PNL as part of the technology transfer from BCL. This system is illustrated in Figure 2.4. Major components include a gas distribution system, a nickel tetracarbonyl catalyst bubbler, a 27-mm-ID quartz fluidized-bed reactor, Pyrex wool filter, catalyst destructor, and oil trap systems. Quartz particles (32 x 48 mesh) were coated with PyC at 430°C using a mixture of 98.49 mole% H_2, 1.50 mole% C_2H_2, and 0.01 mole% $Ni(CO)_4$ at a total flow rate of 6.2 ℓ/min. Quality of the coating appears good, and characterization tests are now being performed on the material.

Design of an engineering-scale pyrolytic carbon coating system is nearly complete. This system will employ a screw-agitated coating vessel capable of coating glass marbles or ceramic pellets of up to 1 cm in diameter. Purchase orders have been placed for the process hoods, process programmer, gas control panel, and mass flow controllers. The coating and off-gas system will be placed in a large, custom-built, walk-in fume hood. The catalyst bubbler system will be placed in a standard bench fume hood.

PAPERS AND REPORTS

A presentation, "Alternative Waste Forms: Process Feasibility," was made by J. F. Nesbitt and R. L. Treat at the 82nd Annual Meeting and Exposition of the American Ceramic Society, Inc., on April 29, 1980. It compared the complexity, demands, limitations, state of development, and safety concerns of nine high-level waste solidification processes. The results of that comparison are shown in Table 2.7. Other papers given at the meeting were "Evaluation of Basalt-Based Waste Forms," by R. O. Lokken and J. M. Rusin, and "Effects of Fabrication Parameters on Sintered and Hot-Pressed Crystalline Waste-Form Durability," by J. W. Shade and C. N. Wilson. A typical result from the latter paper is shown in Figure 2.5 which illustrates the effects of sintering temperature and atmosphere on leach

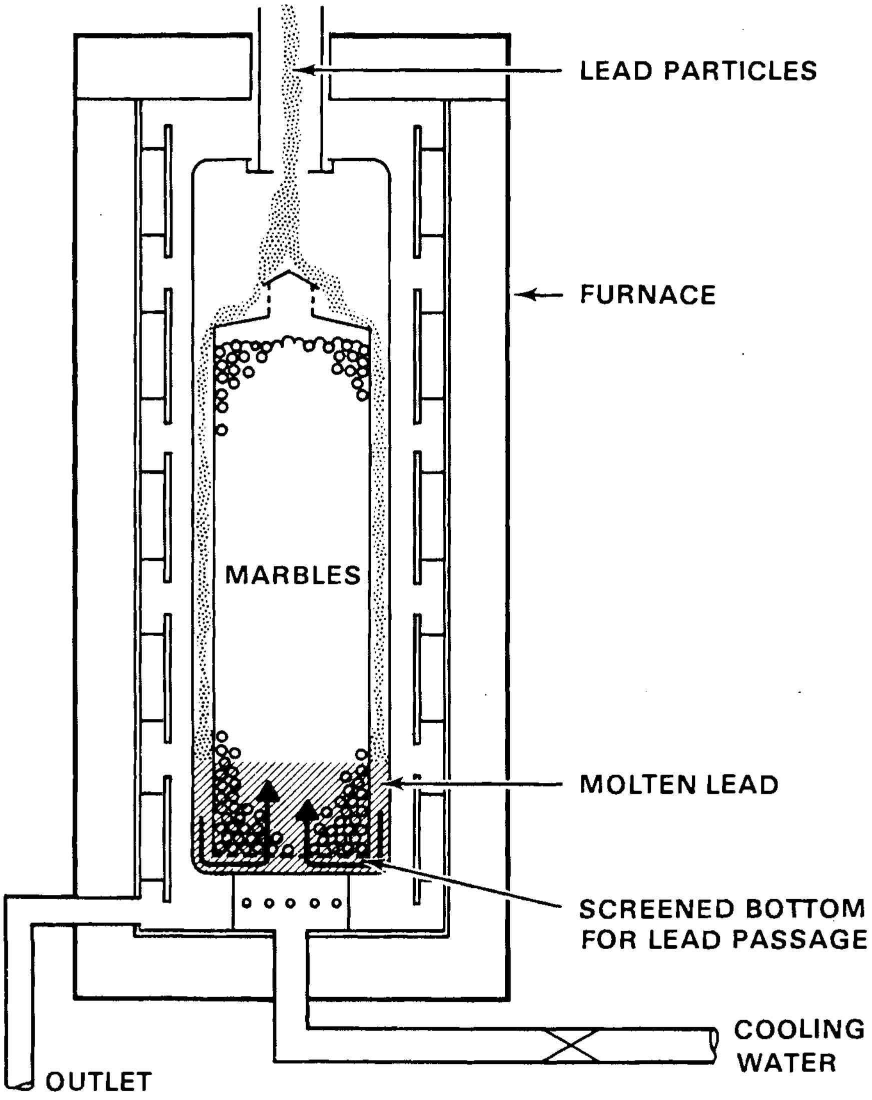

FIGURE 2.3. Shot Melting Encapsulation

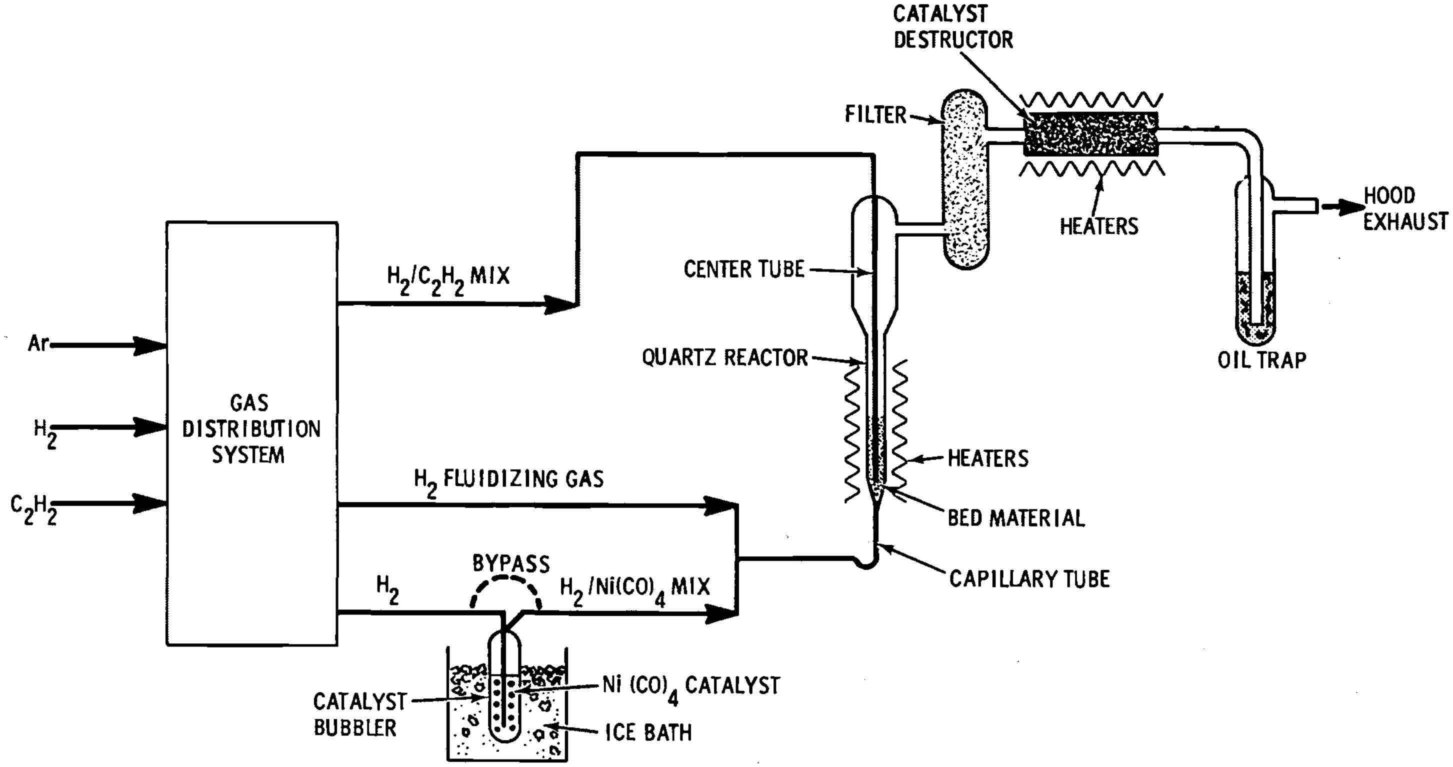

FIGURE 2.4. Lab-Scale PyC Coater System

Table 2.7. Summary of Process Feasibility Study

Process	Feasibility Factors Rating Complexity	Demands and Limitations	State of Development	Safety Concerns	Total
In can glass melting	2	1	1	3	7
Joule-heated glass melting	2	1	1	2	6
Glass ceramic	2	2	2	2	8
Marbles-in-lead matrix	4	3	3	2	12
Coated supercalcine pellets in lead matrix	6	5	4	4	19
SYNROC	8	4	5	3	20
Titanate	10	3	5	4	22
Concrete	6	1	2	2	11
Cermet	6	3	5	4	18

resistance in deionized water and on density for supercalcine SPC-4.

Two papers were presented at the Workshop on Alternative Nuclear Waste Forms and Interactions in Geologic Media held at Gatlinburg, TN, June 13-15, 1980. These were "A Review of Glass Ceramic Waste Forms," by J. M. Rusin, and "Chemically Vapor Deposited Coatings for Multibarrier Containment of Nuclear Wastes," by J. M. Rusin et al. "A Review of Waste Forms" was also presented by J. M. Rusin at the 1980 Annual Meeting of the American Nuclear Society in Las Vegas June 8-11, 1980.

W. J. Gray published a paper, "Reaction of Graphite with Water and Its Implications for Radioactive Waste Storage," in Radioactive Waste Management: An International Journal, 1(1):105 (1980).

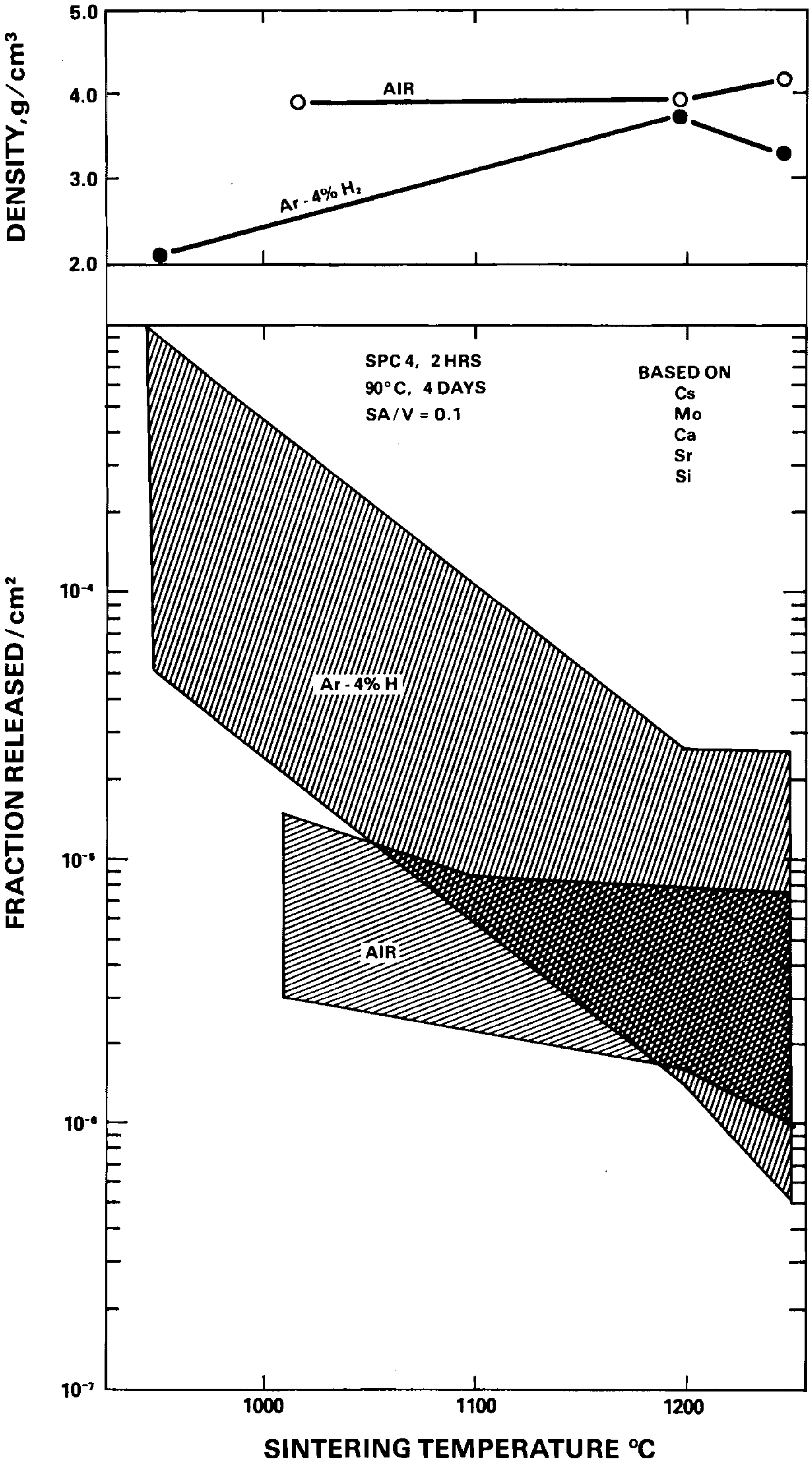

FIGURE 2.5. Effects of Sintering Temperature and Atmosphere on Leach Resistance in Deionized Water and on Density of SPC-4

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

Two of the three test methods submitted to the Chairman of the MRB have been reviewed, and the static leach test method is being revised based on his comments. A second workshop on leaching was held and has resulted in an increased emphasis on testing in simulated ground waters. The workshop on the standard test for alpha-recoil effects was planned, and two review papers were written. Alpha recoil in nuclear waste glasses and crystalline materials changes their properties as a function of dose until saturation limit is approached. A draft procedure for a diametral compressing test has been written. In addition, first drafts have been written to describe support methods used in MCC characterization studies. Test procedures have been reviewed for corrosion testing, stress-corrosion testing, fatigue testing, and drop-tower impact testing of candidate metallic materials for barriers.

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

High-level waste, TRU waste, transportation, and waste isolation lead contractors and subcontractors have been contacted to continue interfacing MCC activities with them. The organization and purpose of the MCC has been publicized by presentations at the annual meetings of the American Ceramic Society, the American Nuclear Society, and European Communities Conference on Radioactive Waste Management and Disposal. The Chairman of the MRB has reviewed two of the three test methods submitted to him and has discussed the content and organization of the static leach test method with the MCC staff. The test method is being revised based on his comments; it will be resubmitted August 1, 1980.

WASTE FORM MATERIALS CHARACTERIZATION (1.3.1) - R. P. Turcotte and J. E. Mendel

Experimental activities have continued on all test methods except for those on radiation damage. There the work has been limited to the drafting of several review papers and preparing for the workshop to be held July 29-30, in Seattle.

Chemical Durability

A second workshop was held in Denver to discuss various aspects of leaching mechanisms. As a result, some small changes have been made in the proposed test methods, including an increased emphasis on testing in simulated ground waters. For example, the static leach test (MCC-1), which will be formally submitted to the MRB August 1, 1980, will require testing in a salt brine, a silicate ground water, and pure water. The MCC has also decided to adopt as one of its tests (MCC-5) the proposed ISO-Soxhlet leach test with additional required analyses of the leachate.

Work on the other test methods is proceeding satisfactorily with an emphasis on use of Teflon in all work up to 200 C. A statistically designed experiment at 40 C using the low-flow leaching apparatus has been completed. It will be repeated at 90 C to evaluate questions about flow rate consistency, leachant volume/sample surface areas, and post-leach treatment/analysis of solutions.

Radiation Stability

Two review papers have been drafted dealing with alpha-recoiling damage in nuclear waste glasses and in crystalline materials, including single-phase and waste ceramic studies. Alpha recoil in nuclear waste glasses and crystalline materials changes their properties as a function of dose until saturation limit is approached. This behavior helps justify the ^{244}Cm doping method used at PNL, which the MCC plans to formally adopt. A closely related test has already been proposed by ISO and may be adopted, depending on discussions at the Radiation Damage Workshop.

Thermal Stability

Work on several glasses has been completed to demonstrate and evaluate the proposed method of defining so-called TTT curves for glass devitrification. Experiments with Portland cement have been initiated to evaluate possible application of this general method to thermal-induced phase changes in concretes.

In volatility studies, a high-pressure apparatus has been designed to evaluate possible canister pressurization by noncondensable gases in a thermal excursion. A quadrupole mass spectrometer will be coupled to this system and to a recording TGA unit to provide on-line gas analyses. High-temperature volatility studies have been temporarily suspended until comments are received from the MRB on the procedure already submitted.

Mechanical Properties

A draft procedure for a diametral compression test has been written. Data have been collected on simulated waste glass and soda-lime glass. Further measurements on glass, concrete, and supercalcine are being conducted to establish tighter specifications for surface finish and pad materials. Impact tests are being developed through a subcontract to Effects Technology. They will report on a recommended method by August 1, 1980.

Analytical Facilities and Methods

First drafts have been written describing support methods 'routinely' used in MCC characterization studies. These include the following: ICP emission spectroscopy, atomic absorption, x-ray diffraction, x-ray fluorescence, metallography, SEM/EDX microprobe and Auger/ESCA/SIMS surface analyses. These methods descriptions will provide a basis for discussion at the planned Analytical Methods Workshop, November 1980, in Seattle.

In other activities, suitable hot cell space for sample preparation has been identified as well as space for the shielded x-ray diffractometer, scanning electron microscope and ICP systems. The x-ray diffraction system design, including the cask, has been completed. Four offsite fabrication bids have been received and are currently under review.

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

The major activities have been to obtain reviews of pertinent test procedures for corrosion testing, stress-corrosion testing, fatigue testing, and drop-tower impact testing of metallic candidate materials for barriers. Radiation effects related to long-term stability of metallic materials have been reviewed, and no damaging effects are reported for the radiation levels being considered. Phase transformations in metastable alloys, however, are a possible problem, and damage in ceramics and polymers will require further study. An approach to corrosion testing is being defined, and preparations are under way for the Metal Corrosion Workshop to be held in August.

In other activities, MCC staff visited Sandia Laboratories to gather information on corrosion testing and the transportation problems associated with shipping casks. A subcontract was placed with the University of Washington to review delayed failures associated with hydrogen and welding. Also, three autoclaves for use in a gamma radiation field are being constructed.

4. TRU WASTE IMMOBILIZATION

C. R. Palmer - Project Manager

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

SUMMARY

The comparison model based upon utility theory for use in the system assessment was partially developed and documented during the quarter. Currently the methodology is being developed for gathering utility information from a large group.

Chemical analysis of chemical process sludge at two generating sites is nearing completion. Simulation analysis for incinerator ashes was completed, yielding reference ash characteristics to be assumed in preparing candidate waste forms.

Experimental development of sintered crystalline ceramics containing clay additives, cast and pressed hydraulic cements, and recrystallized basalt glass ceramics containing a blend of sludge and ash progressed during the quarter. Also, evaluation of spinel formation in borosilicate glasses began. The first glass samples containing plutonium-bearing waste were prepared, and static leach tests are beginning.

Preliminary process descriptions and flowsheets for six immobilization processes were completed during the quarter. Several problem areas in various unit operations were identified for engineering analysis.

DATA ANALYSIS - A. D. Chockie

The primary activities of this task during the quarter dealt with the completion of a task status report and the development of a data-gathering methodology. The status report provided a stimulus for individuals not directly involved with the program to contribute their comments on the task methodology. The other activity, development of a data-gathering approach, is a critical portion of the decision analysis task and, as such, has required careful planning to ensure that proper data are obtained.

Task Status Report

The program milestone report entitled "Comparative Evaluation Methodology: TRU Waste Immobilization Status Report" was also circulated to other interested individuals for their review of the model and methodology being used by this task. It describes the program's need for formal decision analysis, the structure of the analysis methodology being employed, and our present status. Included are detailed definitions of the six attributes (evaluation criteria) selected for evaluating the systems' performance. These six attributes, which were determined to incorporate all the major features of the immobilization processes and products are the following:

- gas generation
- quality assurance
- radionuclide confinement
- processing safety

- handling, transporation, and storage safety
- economic costs.

Along with having elicited numerous useful comments from individuals outside the program, the report should also provide a basis for the final evaluation methodology report to be completed by the end of September.

Data Gathering Methodology

Efforts were started to develop a questionnaire to gather information needed for the decision analysis model. This information will consist of the importance weights various individuals assign to the attributes and the utility or importance these individuals associate with the different levels of attribute achievement. To ensure that this information can be obtained with the least difficulty yet still represent the actual judgments of the individuals surveyed will require initial planning. To this end, Battelle Human Affairs Research Center (HARC) in Seattle was contracted to assist in this questionnaire planning operation. They are to aid the decision analysis task by helping define the sample of respondents who will provide judgments and by helping establish the data-collection procedure.

Incorporating the comments of individuals at HARC and recent experiences of other decision analysis programs, a preliminary questionnaire and interview approach was developed. The questionnaire will soon be pretested several times to ensure that it elicits the desired information within a reasonable time. The attempt will be made to require less than 1 hr per interview session to gather all necessary data.

A major factor influencing the interview technique's structure is the type of individuals to be contacted. Individuals to be contacted eventually for their judgment values were listed. The list is expected to be modified several times as the criteria for inclusion are completed.

TRU-Test Sensitivity Analysis

The sensitivity analysis was completed on the attribute weightings associated with the test case entitled TRU-TEST (described in last quarter's report). The results indicated that one of the three systems considered would be of least value in the immobilization of TRU waste independent of the importance assigned to the selected evaluation attributes. This effort provided verification of the suitability of the multiattribute decision analysis computer model in identifying those systems of significantly lower or higher utility in immobilizing TRU waste.

WASTE CHARACTERIZATION - G. H. Bryan

The program to quantify the compositional variations in the process sludges produced by the Rocky Flats Plant (RFP) is nearly complete. A similar program at the Los Alamos Scientific Laboratory (LASL) is partially complete. Sludge samples were taken at 2-week intervals during steady-state operations so as to minimize transient anomalies. Each sample was analyzed by various wet chemical and instrumental techniques for the cations and anions present in excess of 1 wt%. Residual water content was also determined and Pu, Am and U contents ascertained. Tables 4.1 and 4.2 show preliminary results of these determinations from each site. The results are reasonably similar except for phosphorus, which is present in

TABLE 4.1. Preliminary Results of Analysis of Six Rocky Flats Sludge Samples

Element	Range, ppm Low to High	Average
Al	5,000 to 20,000	9,000
Ca	70,000 to 190,000	130,000
Fe	40,000 to 62,000	47,000
K	6,000 to 6,000	6,000
Mg	10,000 to 18,000	13,000
Na	50,000 to 110,000	70,000
Si	76,000 to 100,000	94,000
NO_3^-	42,000 to 91,000	74,000
$CO_3^=$	4,000 to 51,000	17,000
Cl^-	2,000 to 15,000	6,000
H_2O	190,000 to 610,000	510,000
Pu	4 to 39	16
Am	1 to 32	8
U	1 to 1,700	410
Density	0.7 to 1.3 g/cm^3	1.0 g/cm^3

TABLE 4.2. Preliminary Results of Analysis of Two Los Alamos Scientific Laboratory Sludge Samples

Element	Range, ppm Low to High	Average
Al	5,000 to 50,000	28,000
Ca	30,000 to 300,000	170,000
Fe	10,000 to 100,000	55,000
K	1,000 to 30,000	11,000
Mg	3,000 to 30,000	17,000
Na	3,000 to 30,000	17,000
P	3,000 to 50,000	22,000
Si	20,000 to 500,000	190,000
H_2O	680,000 to 720,000	700,000
Pu	3.3 to 5.2	4.4
Am	0.2 to 0.3	0.3

the LASL sludge. This is explained by the fact that the RFP does not at present process its phosphate-bearing sludge; however, this waste will be processed when their new waste treatment facility is completed.

Characterization of "typical" incinerator residues was completed during the quarter. Following additional quantitative analyses of residues from oxidation of various combustible materials, the data file for the ASHCMP algorithm was revised. Subsequently, several incinerator feed mixtures were simulated via ASHCMP, producing ash compositions having the characteristics shown in Table 4.3. These characteristics will be assumed for our blended sludge/ash waste form experiments.

CRYSTALLINE CERAMIC WASTE FORM DEVELOPMENT - R. O. Lokken

Three types of alternate waste forms are being evaluated for the immobilization of plutonium-contaminated TRU wastes. These include sintered ceramics, cement-based, and basalt-based waste forms. All the waste forms contain blended TRU waste with a sludge-to-ash weight ratio of 3 to 1.

Sintered Ceramics

Fixation of TRU blended waste (TBW) in crystalline ceramics has been studied using various chemical and mineral additives.(1-4) In principle, waste solids are mixed with network additives, pressed into a pellet, and sintered at high temperatures into a ceramic (oxide) matrix. The network additives may serve two main functions. First, they may interact with certain species of the waste to form crystalline reaction phases. Second, they may form a matrix surrounding the waste particles, thereby physically isolating them

TABLE 4.3. Characteristics of Incinerator Ash Based upon ASHCMP Simulation of 46 Typical Incinerator Feed Mixtures

Compound	Composition, Wt% Average	Standard Deviation	Low	High
Al_2O_3	15.0	4.5	2.0	20.1
BaO	0.8	0.6	0.3	3.1
CaO	3.3	1.1	1.7	8.2
Fe_2O_3	0.4	0.1	0.2	0.9
K_2O	0.8	0.3	0.3	1.6
MgO	4.4	1.9	0.6	10.9
Na_2O	1.5	1.0	0.6	4.0
PbO	8.0	16.0	0.1	61.7
SiO_2	21.0	5.0	4.0	27.0
TiO_2	20.0	7.0	2.5	29.0
ZnO	1.0	1.0	0.5	2.4
C	8.0	4.0	3.6	21.9
S	0.3	0.2	0.1	0.9
P_2O_5	5.0	5.0	0.4	25.2
Other	11.0	1.0	9.3	14.4

from the biosphere. Recent studies(1,4) have shown that mixing TRU waste with bentonite clay has produced ceramic products with favorable properties. The products for the current study are prepared by ball milling bentonite and other clay minerals with TBW (2:1 by weight), pressing the powder into cylindrical pellets at ~9000 psi, and sintering for 2 to 12 hr at 900°C to 1100°C. Density measurements and static leach tests are currently in progress to determine optimum sintering conditions.

Cement-Based Waste Forms

The use of normal hydraulic cement is perhaps the most simple means of containing TBW. The sludge/ash mixture is simply blended with cement and water and cast into a drum or canister. However, the hygroscopic nature of the sludge complicates the processing in that excess water is needed to produce a paste that can be readily cast. As the TBW content increases, more water is required to form a paste with acceptable consistency. This increases porosity and reduces mechanical strength.

One way to reduce the detrimental effects of excess water is to uniaxially press the paste into a solid pellet, extruding all the water except for that remaining within the pellet interstices.(5) At a given pressure, the initial amount of water present in a paste does not, to any great extent, affect the amount in the final pressed pellet. Pellets containing 40 wt% TBW in high-alumina cement (HAC) and in Type II portland cement were produced by uniaxially pressing slurries at 23,000 psi. Half the pellets were cured in air, while the others were immersed in distilled water for 2 days, removed, and dried in air. The pellets that were "wet" cured developed a white scale on their surfaces. After 7 days of curing, bulk density measurements were conducted. The method of curing had no apparent effect on the density of the Type II portland cement samples, indicating that the pressed pellets contained sufficient water for hydration. The density of the pellets averaged 1.92 g/cm^3. The HAC samples showed increased densities for the "wet" cured samples--2.16 g/cm^3 compared with 2.00 g/cm^3. This indicates that the pressed pellets did not contain sufficient water to completely hydrate the cementicious constituents when cured in air. Wet curing, however, supplied the additional water needed for hydration and resulted in weight gain and increased density. These observations are supported by results of experiments conducted to determine the "stoichiometric" water/cement ratio of HAC and Type II portland cement, which were determined to be 0.236 and 0.170, respectively.

Basalt-Based Waste Forms

TRU blended waste is similar in composition to Pomona basalt, which is being tested as a repository media. Basalt has been shown to produce a homogeneous glass, and upon subsequent heat treatment, a fine-grained, chemically resistant glass ceramic can be produced.(6) By incorporating TBW into a basalt glass or glass ceramic and placing it into a basalt repository, close equilibrium between the waste form and intruding ground water can be maintained. Three approaches have been employed to produce basalt-like products. Each involves melting followed by controlled recrystallization. The first approach used natural basalt melted with 20 to 30 wt% TBW at 1350°C. The material was recrystallized by a two-stage heat treatment consisting of a nucleation temperature of 670°C followed by a crystal growth period at 920°C. A second approach involved the use of chemical oxide additions, which resulted in a product with an "exact" composition of basalt with only a minor contamination of chromium, nickel, and zinc. This material contained 18 wt% TBW and was processed exactly like the previously mentioned material. The third approach uses the similarity between basalt and TBW compositions to produce a glass comprised of 100% TBW. The TBW was melted at 1300°C for 2 hr and cast into a steel bar mold. Upon cooling, a scaly surface film developed on the exposed surface. During recrystallization at 920°C, the material softened and deformed, most likely due to the high sodium content. Static leach tests and microstructural examination will be used to select a waste form for further investigation.

GLASS DEVELOPMENT - G. B. Mellinger, K. D. Richardson, and R. E. Thornhill

Glass development during the quarter has concentrated on quantifying the tendency for TRU glasses to form spinel devitrification phases.

Crystalline precipitates having a spinel structure have been observed in PNL waste glasses containing significant amounts of ferric oxide and alumina. Table 4.4 indicates Al_2O_3 and Fe_2O_3 levels in three of our borosilicate glasses which are at the solubility limit of spinel. Increases in the level of either component produce additional crystals. In contrast, the reference glass known as 76-68(7) has about 9 wt% ferric oxide but no alumina, and does not form spinel at processing temperatures.

TABLE 4.4. Iron and Aluminum Oxide Levels in Glasses Tending to Form Spinel

Glass No.	Fe_2O_3, mole%	Al_2O_3, mole%
TDS-211	6.1	2.4
80-51	5.2	3.9
78-32	3.9	7.8

In the glasses shown in Table 4.4 the spinel has the composition $(Ni,Mn)Fe_2O_4$. In other waste glasses containing spinel the compositions vary from almost pure Fe_3O_4 to those spinels containing zinc, nickel, and chromium.(8) As aluminum is not found in the spinel, it appears that aluminum atoms preferentially occupy certain sites in the glass structure that are also occupied by iron. As aluminum is introduced, these sites become less available to iron, which then precipitates in spinel crystals.

A series of melts was prepared for study of the effects of Fe_2O_3 and Al_2O_3 concentration on spinel formation. To the base glass compositions shown in Table 4.5 the two compounds were added at varying levels. The glasses were cooled slowly to enhance crystallization and were then analyzed by

TABLE 4.5. Composition of Base Glass to Which Al_2O_3 and Fe_2O_3 Were Added to Produce Spinel

Component	Wt%	Mole%
SiO_2	44.6	44.3
B_2O_3	13.0	11.2
Na_2O	14.1	13.6
Li_2O	3.0	6.0
CaO	14.0	14.9
MgO	2.1	3.1
K_2O	0.7	0.4
MnO_2	3.0	2.1
NiO	3.2	2.6
TiO_2	2.1	1.6
ZnO	0.4	0.2
	100.0	100.0

x-ray diffraction to determine the approximate crystalline content. The resulting data have been plotted in Figure 4.1, with apparent isocrystallinity curves indicated. Whether formation of spinel is undesirable in glasses containing plutonium-bearing sludge and ash is not yet known. We plan parallel glove box experiments with contaminated waste to observe the plutonium behavior in the solid matrix as well as during leaching reactions.

RADIOACTIVE WASTE FORM CHARACTERIZATION - G. H. Bryan and T. R. Myers

Plutonium-bearing incinerator ash and sludge have been received from the Rocky Flats Plant and are currently being used to produce glass waste forms. Samples of cement-based and crystalline ceramic forms will be prepared next quarter. The glass samples prepared thus far contain 30 wt% TBW (i.e., three parts simulated sludge to one part ash). The ash is a 50:50 mixture of nonradioactive rotary kiln ash and plutonium-bearing ash from RFP. The glass frit composition (prior to the addition of the waste) is shown in Table 4.6.

The glass frit and TBW were blended and homogenized in a motorized mortar and pestle. The resulting mixture was placed in a ceramic crucible and heated to 1150°C for 2 hr. Subsequently, casting and annealing for several hours at 500°C provided samples having a surface area of ~500 mm^2. These samples were then subjected to static leaching conditions using a procedure being drafted by the Materials Characterization Center. While initial samples are being run to "shake down" the procedure for use in our glove box and

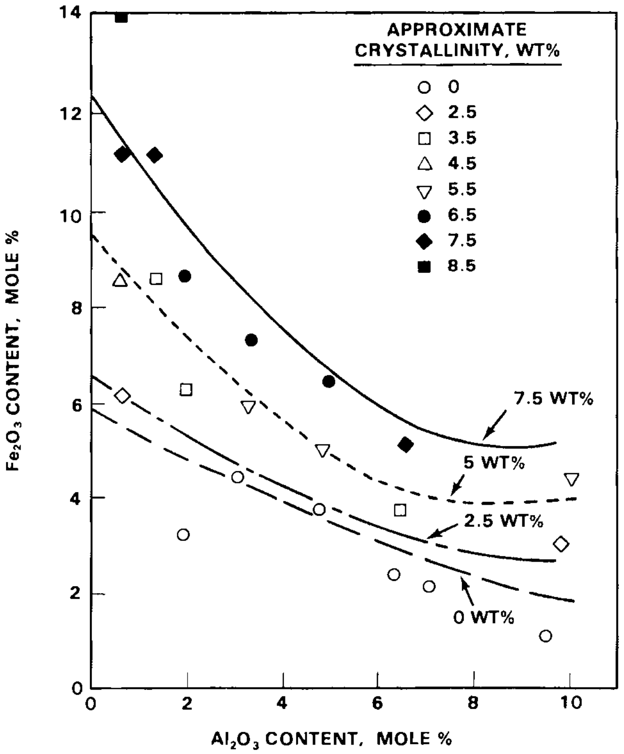

FIGURE 4.1. Isocrystallinity Curves for a TRU Waste Glass as a Function of Fe_2O_3 and Al_2O_3 Content

TABLE 4.6. Glass Frit Composition

Oxide	Wt%
SiO_2	50
B_2O_3	14
Na_2O	14
CaO	9
MgO	5
TiO_2	6
Li_2O	2

hood facilities, the first sample exhibited an apparent normalized plutonium loss of 2.8×10^{-5} kg/m^2 during the first 7 days (at 90°C in distilled water). This finding is viewed as qualitative, however, since the surface area was only approximately known.

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

Preliminary process descriptions and flowsheets were completed this quarter. Six basic processes were included for the initial assessment, as follows:

1. in-can glass melting
2. joule-heated glass melting
3. glass marbles
4. normal cast hydraulic cement
5. cold-pressed hydraulic cement
6. cold-pressed sintered ceramic.

The process flowsheets included for these processes also indicate the mass flowrates under normal operating conditions. For each process, the following operations were identified for consideration in developing the process flowsheets: feeding, blending, and grinding requirements; material transport; temperature; off-gas processing; recycle; load-out; decontamination; and interim waste storage. Unit operations common to all processes include blending of the sludge, ash, and other additives, along with the post-treatment steps of cooling, container closure, decontamination, and storage.

The in-can glass melting (ICGM) process is basically a containerized melting process that encapsulates the TRU wastes into a glass monolith as shown in Figure 4.2. Divergence of material to get the sludge/ash/glass frit blend into the two operating in-can furnaces is a prime consideration for this process. Also the melting temperature of 1050°C leads to some considerations regarding high temperature.

The joule-heated glass melting (JHGM) process illustrated in Figure 4.3 is like the ICGM process except that the glass/waste melting procedure is performed in a joule-heated ceramic melter instead of a specially designed canister. The glass product is poured from the melter into a 55-gal drum that will require a jacket for temperature control to prevent devitrification of the glass monolith. This processing scheme can be used to produce a borosilicate, aluminosilicate or basalt glass waste form. The JHGM process will have many of the same high temperature considerations as the ICGM process.

The glass marble process is an addition to the JHGM process in that spherical glass marbles are produced instead of a glass monolith. Figure 4.4 diagrams the process and shows the additional considerations given to marble making, recycle, material transport, and product loading. The benefits of this process include ease of sampling for quality assurance, little (if any) devitrification, and ease of product recycle.

The cast cement process is a simple incorporation of the transuranic sludge and ash waste into a wet cement mixture to form a cured (nonaggregate) cement. The process diagram of Figure 4.5 identifies a batch

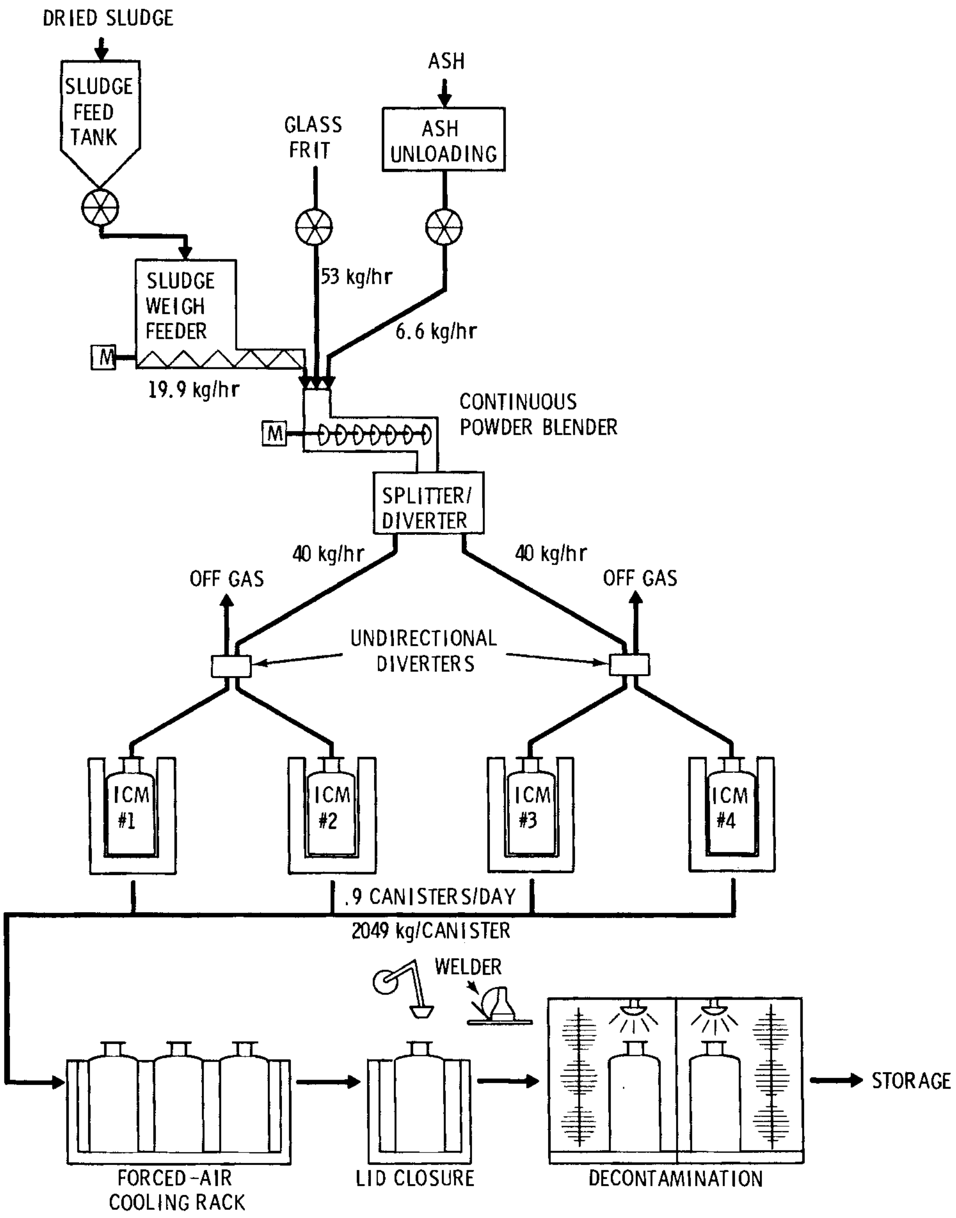

FIGURE 4.2. In-Can Melting Process

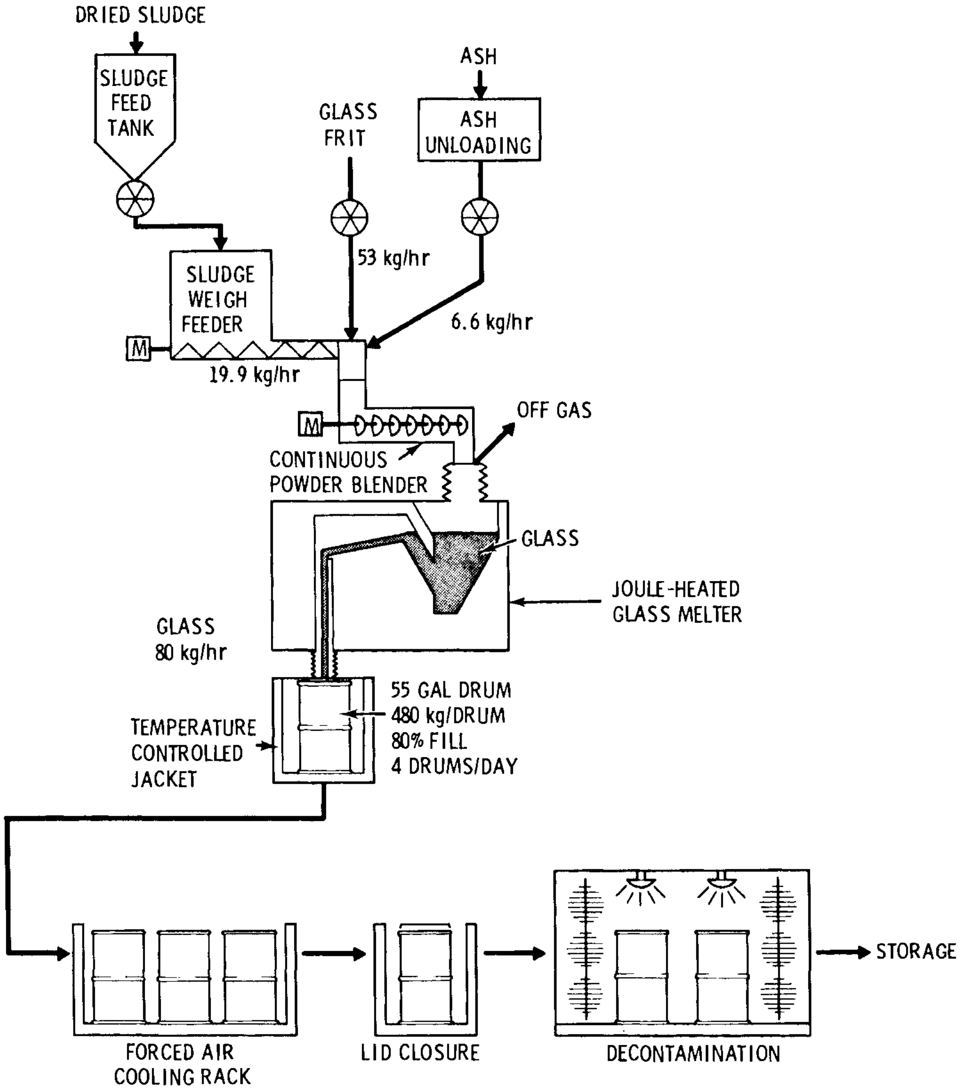

FIGURE 4.3. Joule-Heated Glass Melting Process

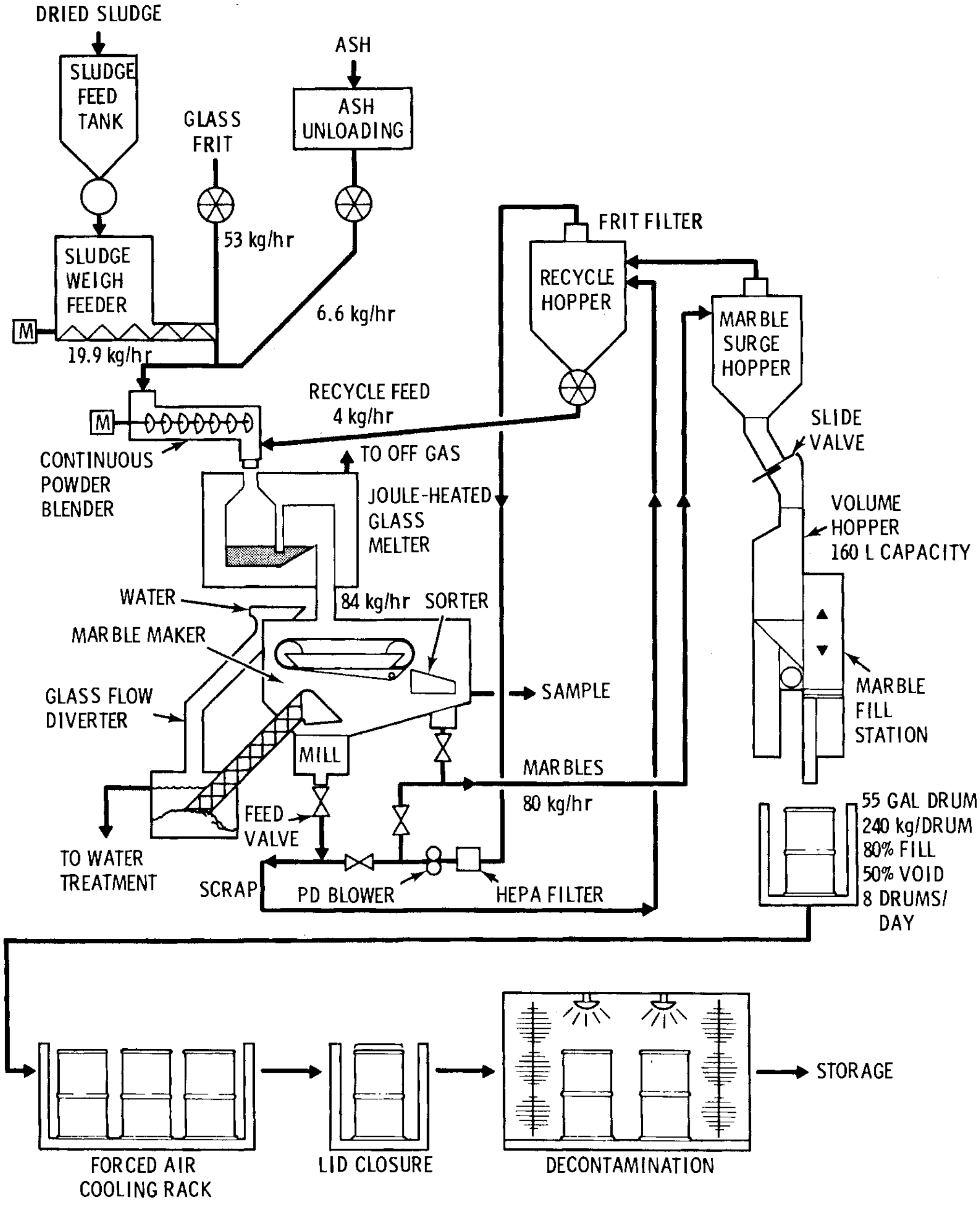

FIGURE 4.4. Glass Marbles Process

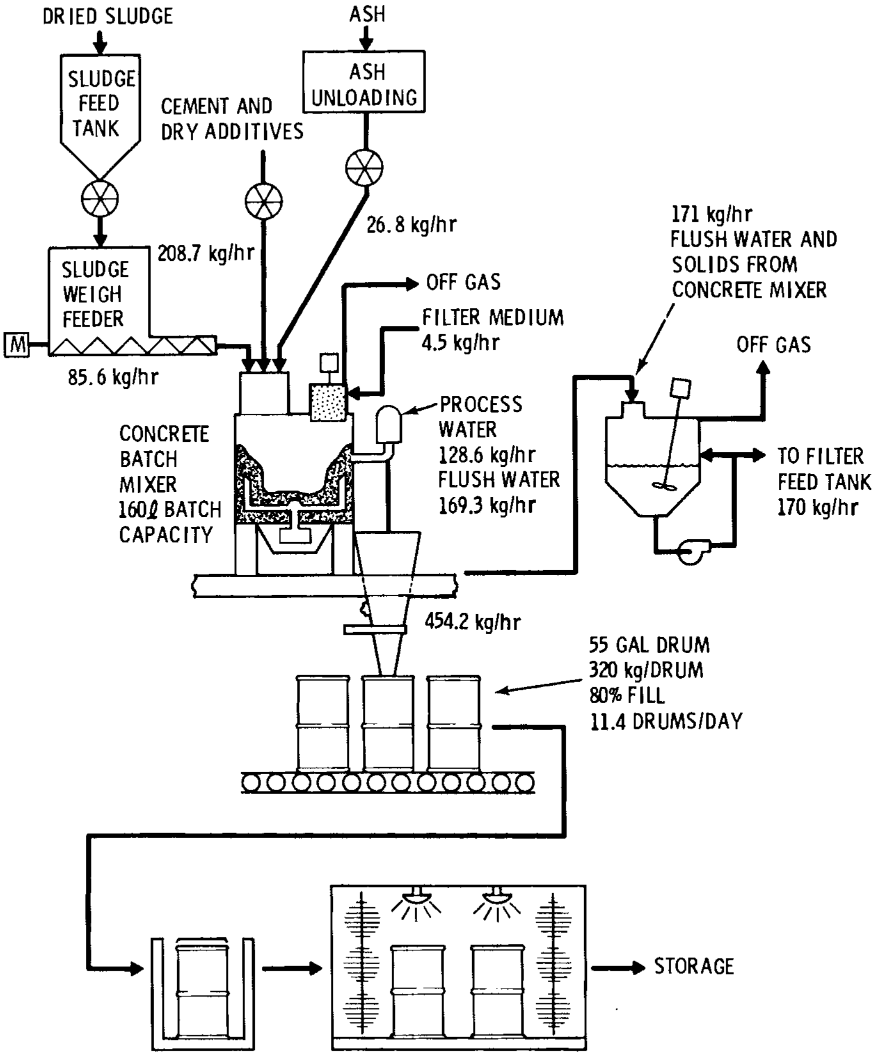

FIGURE 4.5. Cast Cement Process

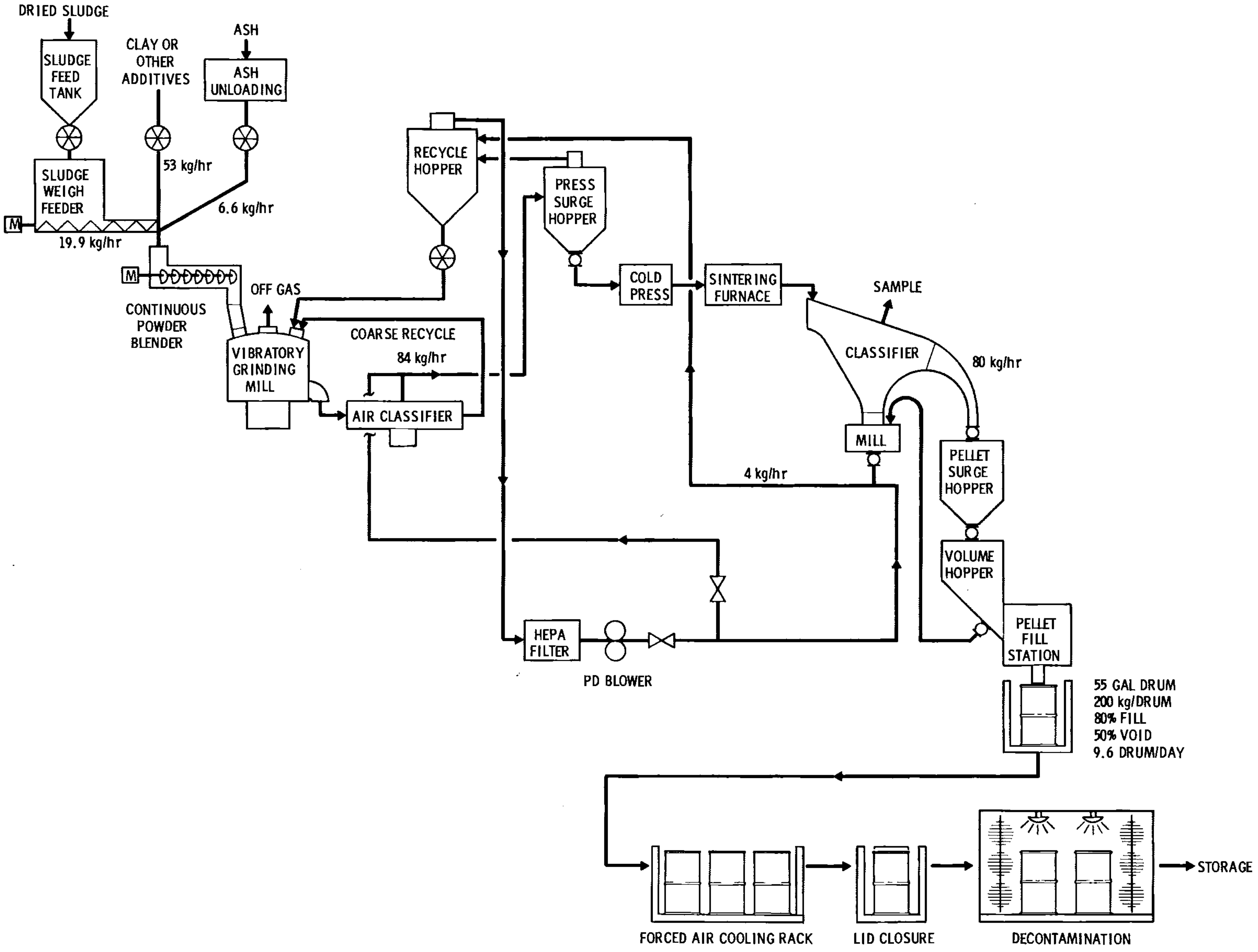

FIGURE 4.7. Cold-Pressed Sintered Ceramic Process

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

Onsite modification and installation of the high-production vibratory finisher were completed. The modifications included lowering the working height of the vibrating tub, repositioning the cylinder that operates the unloading gate, and repositioning the compound tank inlets and the pump intakes. A glove box line is partially installed that will be used with the vibratory finishing decontamination system. Installation of an electrostatic air cleaner for the plasma arc torch sectioning studies and a hydraulic lift table for manipulating glove boxes in the sectioning/pretreatment facility was completed. The system to transfer contaminated electrolyte and aqueous waste to the solution processing system was completed. Hot testing of a novel in-drum solidification apparatus was begun. Plans were completed for a public information meeting to be held on June 29 and 30. This meeting will provide information on vibratory finishing and other significant advances in TRU waste decontamination technology. Routine decontamination of sample recovery devices used at the Hanford tank farms was demonstrated.

DECONTAMINATION STUDIES

Vibratory Finishing

Installation of the high-production annular vibratory finisher and compound handling system was completed, and cold testing was begun. The vibratory finisher was modified slightly. These changes included shortening the vibratory finisher base for a more comfortable working height of the tub and moving the air cylinder that operates the unloading gate to allow more clearance for the compound tank. The compound handling system design was also modified. These design changes will result in moving the compound tank inlets to increase the clearance between the tub drains and the tank inlets and repositioning the pump intakes to optimize the recirculation of compound and the draining of the compound tank.

A glove box line is partially installed that will be used for sectioning material and moving material to the vibratory finisher. Figure 5.1 is the floor plan showing the positions of the glove box line and the high-production annular vibratory finisher. The glove box line will be

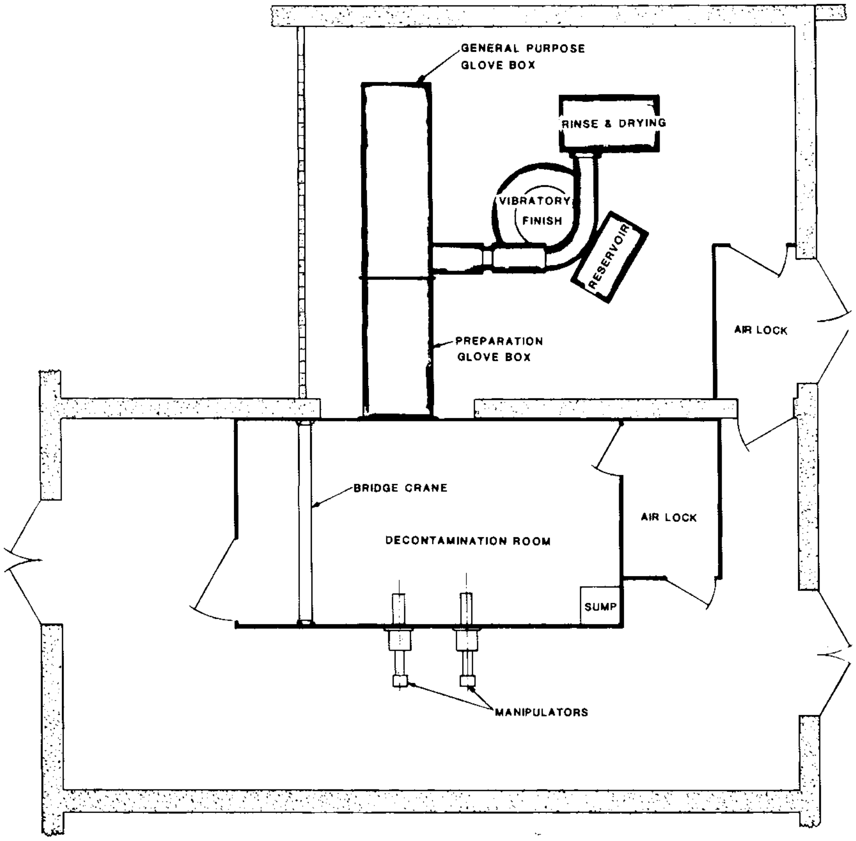

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FIGURE 5.1. Floor Plan of a Vibratory Finishing Decontamination System Being Installed in 231-Z Building. This system includes an annular high-production vibratory finisher, the existing walk-in sectioning/pretreatment facility, and a connecting glove box line.

connected to the sectioning/pretreatment facility. It will consist of a general-purpose glove box and a two-level sectioning glove box that will house the double-cut shear (Figure 5.2) currently in the sectioning/pretreatment facility. The glove box line will be connected to the vibratory finisher by a transition piece and flexible bellows.

This glove box line will provide space for hands-on sectioning with saws and nibbler without the need for time-consuming entries by personnel into the sectioning/pretreatment facility, as is currently done. Space for detailed disassembly of small components will also be provided. Furthermore, movement of materials from the sectioning/pretreatment facility to the vibratory finisher will be facilitated. Additionally, the transition piece will effectively separate the sectioning from the decontamination phase, reducing the cross-contamination from the sectioning phase to the less contaminated decontamination phase of the operation.

A work stoppage by construction personnel at Hanford has halted the installation of the glove box line. Progress made earlier included positioning of the glove boxes in the laboratory and welding the sectioning glove box to the sectioning/pretreatment facility.

80000578-10cn

FIGURE 5.2. Double-Cut Shear Used To Section Plutonium-Contaminated Metals Prior to Decontamination by Vibratory Finishing

PROCESS DEMONSTRATION

Preliminary production rate information was assembled based on past operating experience using small experimental equipment and facilities. Items such as TRU-contaminated glove boxes can be completely disassembled, sectioned, decontaminated, and packaged as low-level waste at the rate of 1 man-hr/ft^2 of material, with the actual decontamination step requiring <20% of the processing time. This information is based on the complete disassembly, sectioning, decontamination and packaging of two TRU-contaminated glove boxes, five 55-gal drums of plutonium-contaminated glove box material removed from a plutonium processing facility currently undergoing decommissioning at Hanford, and a plutonium-contaminated ventilation system for a fuel storage facility.

Vibratory finishing was the primary decontamination technique used, although electropolishing was also used occasionally to provide information for comparing the two decontamination techniques. A small 4-ft^3 tub-type vibratory finisher (Figure 5.3) was used for this decontamination. This vibratory finisher will accommodate only about 15 ft^2 of material per load; the optimum piece size is about 6-in. square. This vibratory finisher also requires time-consuming manual loading and unloading.

It must be stressed that this is preliminary information developed using a small research facility and does not represent production rates that could be achieved

7812272-6cn

FIGURE 5.3. Small Tub-Type Vibratory Finisher Installed in Sectioning/Pretreatment Facility. This vibratory finisher decontaminated plutonium-contaminated material during the process demonstration phase that established preliminary process rate data.

using a large automated production facility. A significant increase in the production rate is anticipated with improved materials handling systems and the use of even simple automation techniques such as the new vibratory finishing decontamination facility currently being installed in the 231-Z Building.

SECTIONING STUDIES

Previously noted problems(1) associated with plasma torch sectioning have been solved. Use of the torch produces copious amounts of smoke which, in the confined space of the sectioning facility, obscures vision and in <3 hr cutting time completely plugs HEPA filters. The addition of a coarse Fiberglas® prefilter, similar to a furnace filter, extended the life of the HEPA filter to about 5 hr of plasma torch cutting time.

The problem was completely solved by installation of an electrostatic air cleaner. This effectively removes the smoke from the

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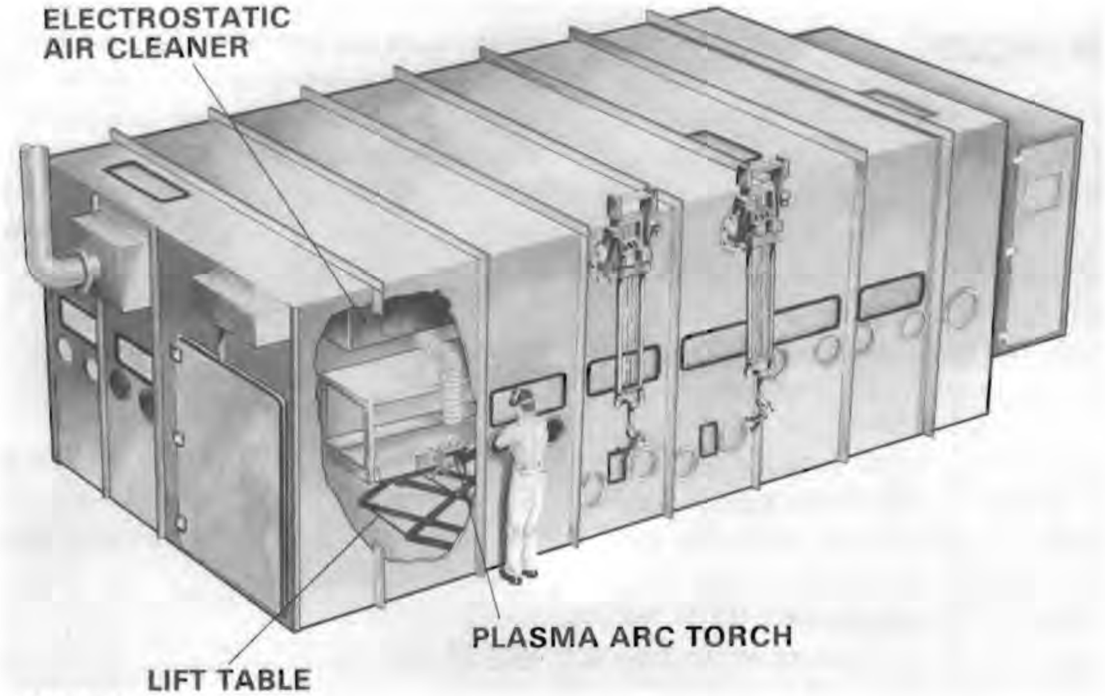
air inside the sectioning/pretreatment facility and allows continuous operation of the plasma torch without any smoke-related problems. The electrostatic air cleaner is an industrial, self-contained, two-stage electrostatic precipitator. Primary components are a mechanical prefilter, ionizer, collecting cell, and blower system. The prefilter removes large particles and spreads the air stream evenly across the ionizer area. The ionizer supports thin tungsten wires that carry a positive charge of 11 to 12 kV DC. The ionizer's function is to electrically charge the particles of smoke passing through the unit. The collecting cell contains plates alternately charged to a positive voltage of 5.5 to 6.0 kV DC. This collects ionized contaminants that have passed through the ionizer. The blower system consists of a blower and an electric motor with a variable speed drive system. The blower can move up to 800 cfm of air.

Tests of the electrostatic air cleaner with the plasma torch in the sectioning/pretreatment facility showed that positioning of the air cleaner inlet is critical for complete smoke removal. The inlet must be positioned so that the smoke plume from the plasma torch rises directly to the inlet. A plenum and flexible inlet duct were installed to provide greater flexibility to the air cleaner.

A hydraulic lift table (Figure 5.4) was installed in the sectioning/pretreatment facility. It is to provide a stable work platform and facilitate the positioning of



8008755-1

FIGURE 5.4. Artist's Conception of Plasma Arc Torch Sectioning in the Sectioning/Pretreatment Facility with Electrostatic Precipitator and Hydraulic Lift Table Installed

items weighing up to 4000 lb, such as glove boxes, for dissassembly and sectioning. The table top can be raised hydraulically to any height from 6 in. to 5 ft using controls located outside of the sectioning/pretreatment facility. The table top can also be manually rotated 360° so that all sides of an item placed on it are easily accessible.

The lift table was modified before service: A fire-resistant skirt was fastened to the table top to protect the lift mechanism, and a stainless steel sheet was placed on the table top to protect it from damage from use of the plasma torch on or near the table. In addition, all electrical components were waterproofed to protect them when high-pressure water sprays are used for cleaning operations in the sectioning/pretreatment facility.

SOLUTION PROCESSING

The transfer system for contaminated liquid waste was completed. This system, composed of welded stainless steel pipe, allows the direct transfer of contaminated liquids from their point of origin to the appropriate waste processing system (Figure 5.5). Two systems are in operation. The electrolyte transfer system connects the electrolyte tank in the 400-gal electropolishing facility to the acid processing unit. The other system is for aqueous waste and connects the rinse tanks in the 400-gal electropolishing facility and the sump in the sectioning pretreatment facility to the evaporator feed tank, where the wastes are stored until processed in the evaporator. Additionally, part of this system connects the evaporator with the liquid waste solidification unit to permit direct transfer of evaporator bottoms to that unit for solidification prior to disposal.

LIQUID WASTE SOLIDIFICATION

More than 100 gal of plutonium-contaminated liquid waste were solidified with portland cement. The apparatus used is shown in Figure 5.6. A 55-gal drum, precharged with portland cement, is placed vertically on the machine. The liquid waste is then added and the drum sealed. The machine tilts the drum containing the waste and cement to a horizontal position and rotates the drum. About 2 hr mixing is adequate time for the waste and cement. This system's chief advantage over traditional cement mixing techniques is that the drum remains sealed during the mixing process, avoiding any spread of contamination.

The optimum waste-to-cement mixing ratio was determined by preparing a series of drums using various amounts of noncontaminated liquid and portland cement and then sectioning the resulting solid masses. The maximum amount of liquid that resulted in complete, consistent solidification was 32 wt%. This ratio would allow the addition of 35 gal of liquid waste to a 55-gal drum. However, due to weight restrictions at Hanford, only 23 gal of liquid waste may be added, resulting in a 600-lb drum. Used filter cartridges can also be disposed of using this same process by adding them to the liquid-cement mixture. However, a 10% reduction in the amount of liquid waste that can be added to the drum is needed to ensure complete solidification.

RELATED PROJECTS

Five sample recovery devices, shown in Figure 5.7A, were successfully decontaminated using a citric acid solution to dissolve the contaminated salts and using electropolishing for spot decontamination. Rockwell Hanford

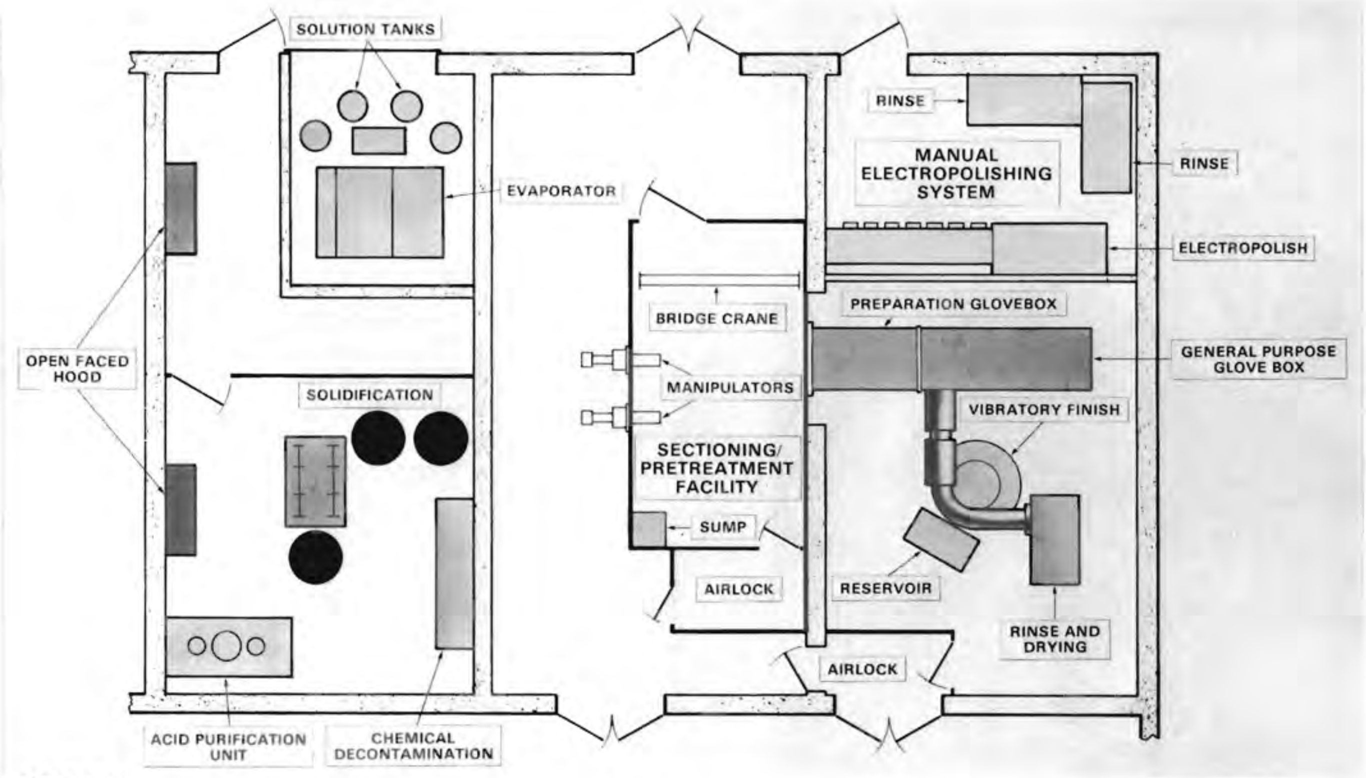


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FIGURE 5.5. Floor Plan of the 231-Z Building Decontamination Facility Showing Major Components Connected by the Liquid Waste Transfer System

8007436-8cn

FIGURE 5.6. Apparatus Used for In-Drum Solidification of Plutonium-Contaminated Liquid Waste Using Portland Cement

Operations uses these devices to recover sludge samples from the Hanford tank farms. The radiation level on these devices ranged from 500 to 5000 mrem/hr when received; all were decontaminated to <50 mrem/hr, which was the level desired by Rockwell.

The sample recovery devices, completely assembled, were submerged in a solution of 230 g of citric acid per liter of water for 1 hr to remove most of the gross contamination. The devices were then dissassembled (Figure 5.7B) and the components resubmerged in the same solution for an additional hour. Areas with radiation levels above the 50 mrem/hr limit were electropolished using in situ techniques until all accessible surfaces were <50 mrem/hr.

PUBLIC INFORMATION MEETING

Preparations are continuing for the Public Information Meeting and tour to be held July 29 and 30. More than 50 attendees are expected. This meeting will update and broaden the information presented at the successful public information meeting on electropolishing held at Hanford in April of 1978. Topics to be discussed include an in-depth review of electropolishing and vibratory finishing as decontamination techniques, sectioning methods, and the measurement of surface contamination. Decontamination technology development programs at Rocky Flats, Savannah River, Oak Ridge, and Rockwell Hanford Operations will also be described.

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FIGURE 5.7A. Assembled Sample Recovery Device Decontaminated Using Citric Acid Bath and In Situ Electropolishing Techniques

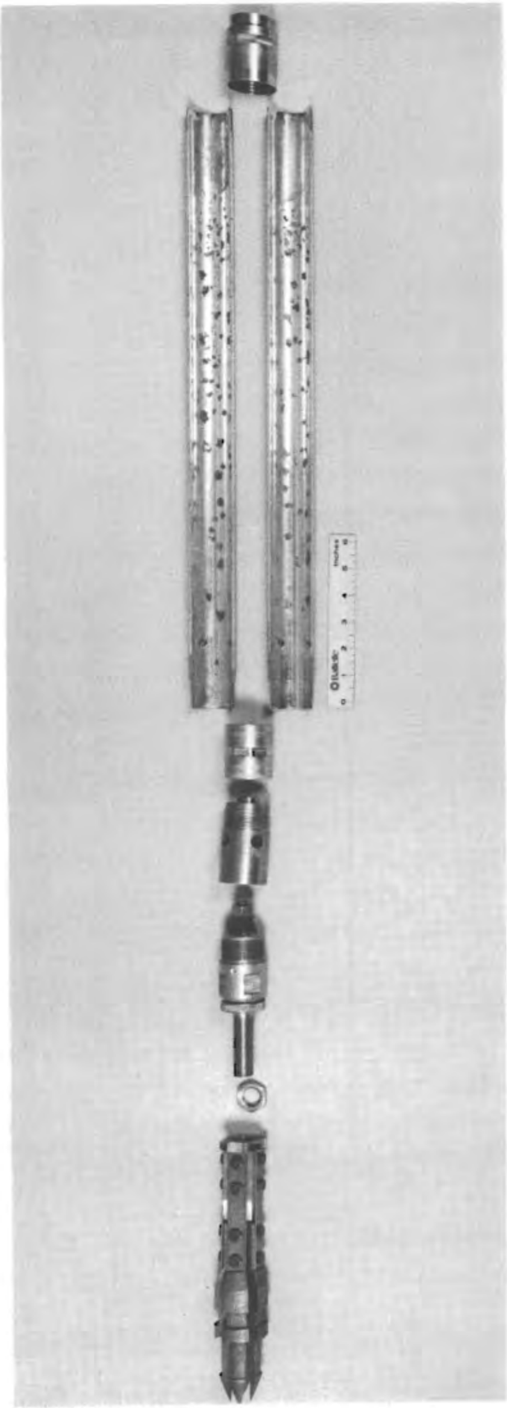

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FIGURE 5.7B. Disassembled Sample Recovery Device Showing Major Components

REFERENCE

1. Platt, A. M. and J. A. Powell, compilers, November 1979. Nuclear Waste Management Quarterly Progress Report July Through September 1979, p. 12.7. Pacific Northwest Laboratory, Richland, WA.

6. KRYPTON SOLIDIFICATION

G. L. Tingey - Project Manager

The objective of this program is to develop techniques for storing radio active krypton in a solid matrix. Two 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

A preliminary design of the facility and equipment for ion-implantation of krypton in sputter-deposited metals has been completed. This design incorporates ten sputtering chambers that are 3.6 times the size of our small laboratory chamber. Preliminary cost estimates indicate that the increased cost of sputtering over compressed bottles is more than offset by lower storage costs.

The first experiment using ^{85}Kr has shown no significant effect of the radioactivity on sputtering parameters. Some finely powdered contamination was present, however, and future work should address the problem of powder in any scheme for converting ^{85}Kr to a solid form.

Long-term release of krypton from amorphous sputtered metal and sintered porous glass has been measured after heating for periods up to 190 days. The data appear to fit a $t^{1/2}$ relationship similar to Fick's Law diffusion. Extrapolation of these data indicates that total krypton release should be limited to about 1% or less for $Fe_{0.79}Y_{0.12}Kr_{0.09}$ at 300°C and about the same value for $Fe_{0.76}Zr_{0.19}Kr_{0.05}$ or Thirsty Vycor® at 420°C.

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

System Requirements for Commercial Size Plant

A preconceptual identification of a production-size ^{85}Kr encapsulation facility and the equipment for the ion implantation-sputter deposition process has been developed. The system is sized to a 2000-MTHM (metric ton of heavy metal)/year fuel reprocessing plant that will generate 1.7×10^7 Ci/year of ^{85}Kr. At this stage, we have conservatively selected a sputtering chamber with only 3.6 times the capacity of our laboratory-scale equipment and only twice that of a larger apparatus already demonstrated in our laboratory. Ten of these chambers would be required to handle the krypton generated in a 2000-MTHM/yr plant. Larger size equipment could almost certainly be developed, but in order to consider a system currently near "state-of-the-art," we have selected the 3.6x scale for our systems study. Furthermore, at present we do not see a great incentive, either economic or technical, to go to very large sputtering chambers.

Figure 6.1 shows the general arrangement of the facility. Two sputter cells, each containing five sputtering chambers, are

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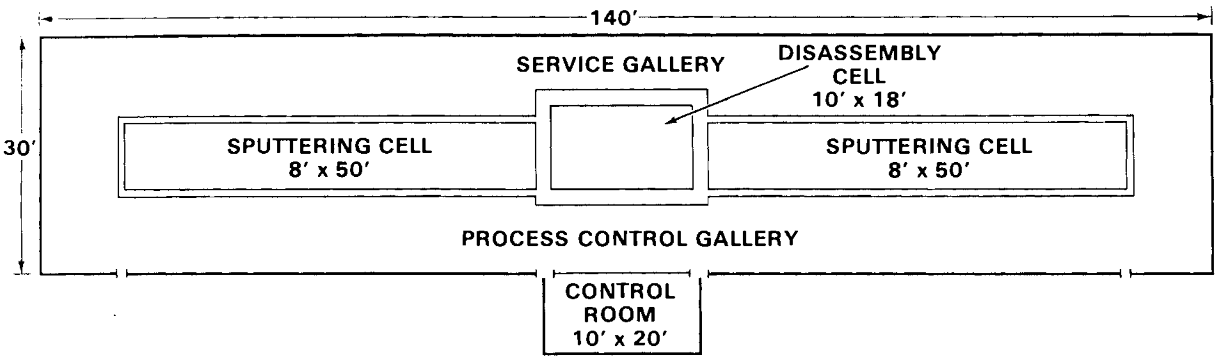


FIGURE 6.1. Facility for Ion Implantation of Krypton in Sputter-Deposited Metals

placed on each side of a control disassembly cell. Interim storage and electrical equipment will be housed on a level below the cells. Figure 6.2 indicates the general arrangement of the process cells. The sputtering chambers are located in two cells to allow more versatile access to the equipment. After the deposit is completed, the sputtering chamber is transported to the disassembly cell, where the deposit is removed and placed in a cask for transport and/or storage.

The thickness of the deposit, and thus the krypton loading, is yet to be determined. However, as the basis for this study, we have evaluated two thicknesses, 5 mm and 10 mm. The actual thickness achievable is dependent upon many parameters, including thermal conductivity of the sample and temperature dependence of the krypton sticking coefficient. Future work will be required to optimize the thickness, but at least 5 mm appears to be readily achievable.

This concept will lead to between 400 and 700 deposits/yr, depending on the deposit thickness. These deposits will then be stacked together and stored in 15 to 30 dry wells following the concept described by Klett.(1)

Preliminary cost estimates were also developed. Although the sputtering costs are considerably greater than those estimated for compressing the gas in pressurized storage bottles, the cost difference is more than offset by the high cost of monitored storage for the gas bottles.

Ion Implantation of Radioactive Krypton

All previous sputtering runs have been conducted using nonradioactive krypton. There are, however, several reasons to test the system using a gas of the approximate composition anticipated from the reprocessing of nuclear fuels. Among these reasons are 1) to evaluate the effect of radiation on the plasma and the sputtering process, 2) to evaluate the extent of radiation damage in the resulting deposit, 3) to determine gas release with improved sensitivity, and 4) to discover the potential for radioactive contamination during the process.

We have, therefore, designed a small sputtering chamber with a deposit surface 7.6 cm in diameter and 10 cm long in which to implant about 11 Ci of ^{85}Kr (5%) in stable krypton. In preparation for the radioactive run, several tests were run on the small apparatus using nonradioactive gas. The purpose of these preliminary tests was threefold: 1) to debug the new sputter

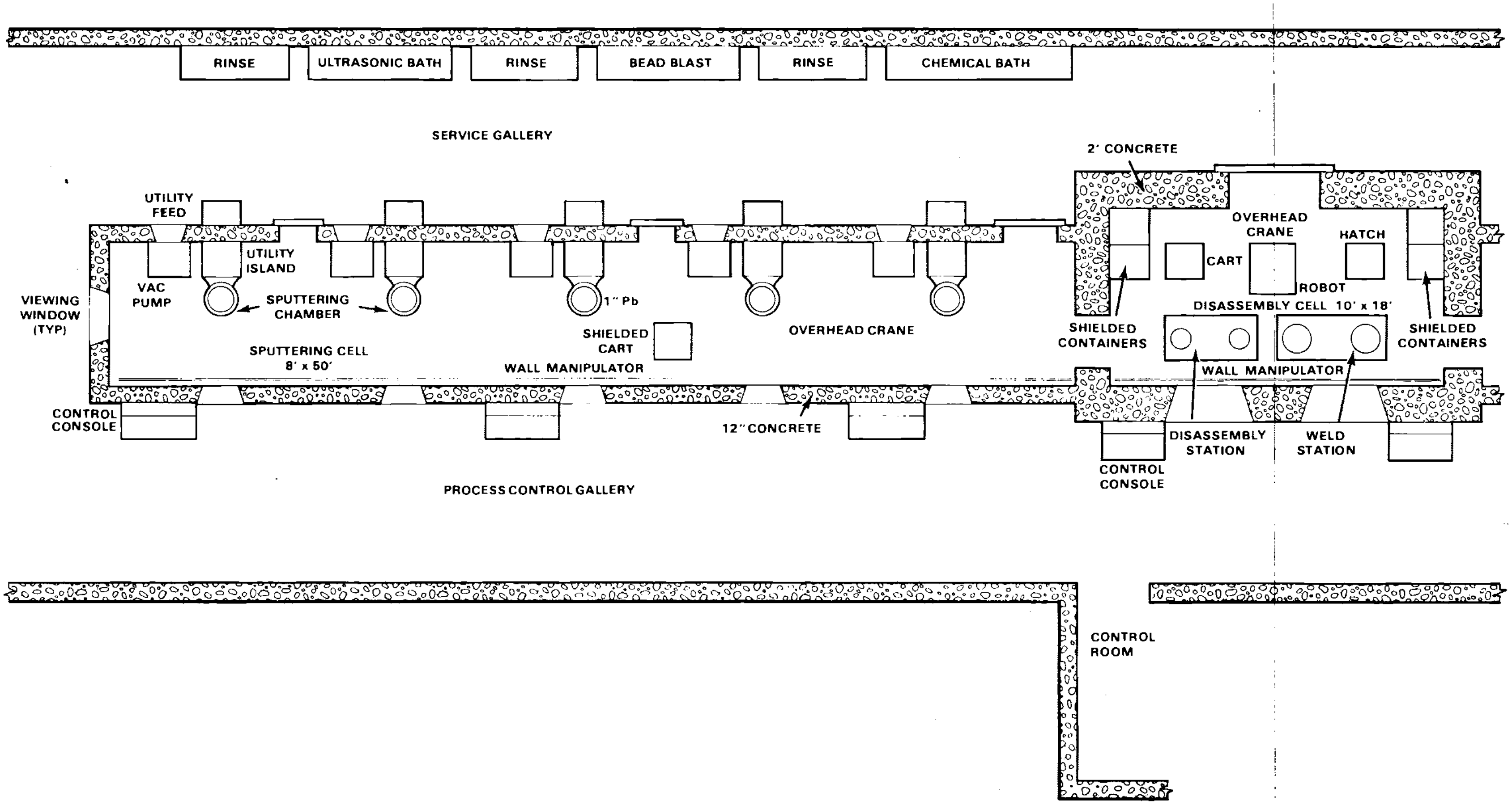
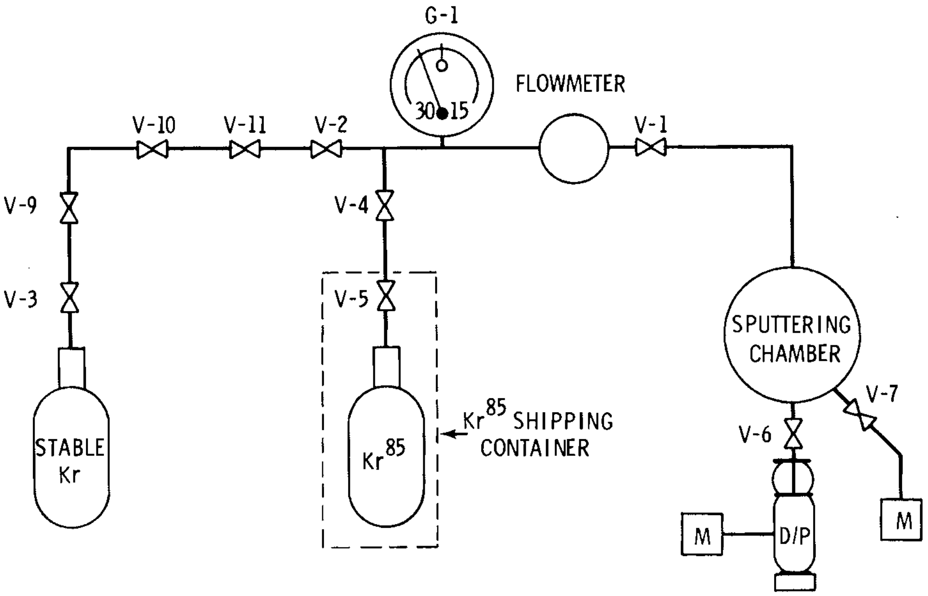


FIGURE 6.2. Process Cell for Sputtering Chambers

deposition apparatus and its instrumentation, 2) to measure the geometric plating efficiency (weight of deposit on the substrate/ weight removed from target), and 3) to evaluate the procedure for introducing ^{85}Kr into the sputtering chamber. During the runs, problems with target design, surface cleaning, and instrumentation were observed and corrected. The geometric plating efficiency was found to average about 80%; learning this enabled us to predict accurately the time required to implant all the krypton in the ^{85}Kr reservoir.

The experiment was then set up with the radioactive krypton using the valving arrangement shown in Figure 6.3. Two krypton sources, one containing ^{85}Kr and the other only stable isotopes of krypton, could be introduced into the chamber; this permitted us to start the experiment with nonradioactive krypton and to deposit a relatively gas-free "closeout" layer over the ^{85}Kr-containing layer. Before the experiment, an otherwise identical run was made using nonradioactive krypton to ensure that the test would perform as planned. This test (GT-75) ran smoothly, yielding an amorphous solid containing 34 cm^3 of Kr(STP)/g of deposit, or about 9 at.% krypton. The deposit appeared well bounded and very smooth except for a small area near the top of the substrate behind the shields, where the deposit was not well bonded and loose or poorly bonded flakes were observed.



V-1: VEECO LEAK VALVE
V-2: MANUAL SHUT-OFF
V-3: BOTTLE VALVE
V-4: MANUAL SHUT-OFF
V-5: BOTTLE VALVE
V-6: HI-VAC VALVE
V-7: ROUGH VALVE
V-9: REGULATOR
V-10: MANUAL SHUT-OFF
V-11: SOLENOID VALVE
G-1: COMPOUND GAUGE 30" Hg - 15 psi
M: MECHANICAL PUMP
D/P: DIFFUSION PUMP

FIGURE 6.3. Valving Arrangement for Introducing ^{85}Kr Into Sputtering Chamber

Despite this debonded area, we proceeded with the experiment using the 5 at.% ^{85}Kr in Kr(GT-76). This experiment proceeded identically to the blank, with the gas uptake as expected and the process running smoothly until the krypton gas was depleted. At this point the pressure decreased but did not pump down as thoroughly as expected. The radioactive krypton storage or delivery system appeared to have a "virtual" leak (a small amount of gas trapped somewhere within the system, perhaps in a weld bubble) that slowly supplied a small gas flow. This continued about 30 min, with the plasma being intermittent as the pressure fluctuated, and the decision was made to terminate flow from the ^{85}Kr reservoir. Nonradioactive gas was then introduced, and a 0.4-mm "closeout" layer was deposited.

The sputtering experiment showed clearly that radiation had no adverse effect upon the sputtering process and that stable krypton can be used to quantitatively establish the sputtering conditions. Another very important finding resulted from this experiment. When the sputtering chamber was opened and the deposit removed, some radioactive contamination of the system was observed that was mobile enough to be transported to the glove box and even into the room. This contamination was due to a small amount of finely divided metal powder containing ^{85}Kr. Its source is not definitely established at present but is likely due to the poor bonding on the top of the substrate where sputter cleaning was inadequate or to corrosion from a possible air leak at the close of the run. Since both of these effects are due to abnormal sputtering conditions, we believe that they can be readily corrected. However, the presence of powdered contamination containing ^{85}Kr points out an area of concern for solid-state storage of radioactive gases. Any waste form for krypton should have minimum potential for powder formation because the solid powders appear to be substantially more hazardous than the gaseous species. The solids are much more difficult to remove from the body or other biological system and thus could result in much more exposure than would otherwise occur. In addition, it is not sufficient to have a canister to contain the solid because the canister then becomes the primary barrier to the spread of the radioactive waste and the solid form only a secondary barrier.

In conclusion, ion-implanted krypton in sputtered metals appears to occur as expected from nonradioactive tests, but care must be taken to ensure that the waste forms have high integrity so that the potential for powder formation will be minimized.

LONG-TERM RELEASE OF KRYPTON FROM GLASS AND SPUTTERED METAL MATRICES - G. L. Tingey and J. M. Lytle

For storage of ^{85}Kr the most important property is the rate of release of the gas under storage conditions. It is desirable to limit the release to a few percent of the original krypton during the entire storage period. However, due to decay the total ^{85}Kr is continually decreasing, resulting in lower heat loading. We have, therefore, assumed that most of the ^{85}Kr release will occur during the first half-life (10.7 yr). To test the long-term release, we have initiated a test to investigate krypton release from three types of samples at the temperatures indicated:

• Sintered Thirsty Vycor	420°C
• Amorphous $Fe_{0.79}Y_{0.12}Kr_{0.09}$	300°C
• Amorphous $Fe_{0.76}Zr_{0.19}Kr_{0.05}$	420°C

These samples are sealed in pyrex ampoules and maintained in a furnace at the desired temperatures. After the test, the break seals are broken, the pressure measured, and the gas analyzed. Samples currently under test will extend the release data up to 2 years. At present, data have been extended to 190 days. Figure 6.4 shows the fractional release of krypton from the three samples as a function of square root of time ($t^{1/2}$). Although there is some scatter in the data, the release appears to increase linearly with $t^{1/2}$.

Several authors$^{(2)}$ have shown that for spherical geometry, the Fick's Law diffusion equation at low total release can be approximated by

$$\frac{Qt}{Q_\infty} = \frac{6}{r_0} \left(\frac{Dt}{\pi}\right)^{1/2}$$

where Qt/Q_∞ is the fractional release, D is the diffusion coefficient, and r_0 is the diffusing radius. A similar relationship, differing only in the value of the constant, also approximates diffusion for planar geometry. An evaluation shows that for Qt/Q_∞ up to 10% the error due to the

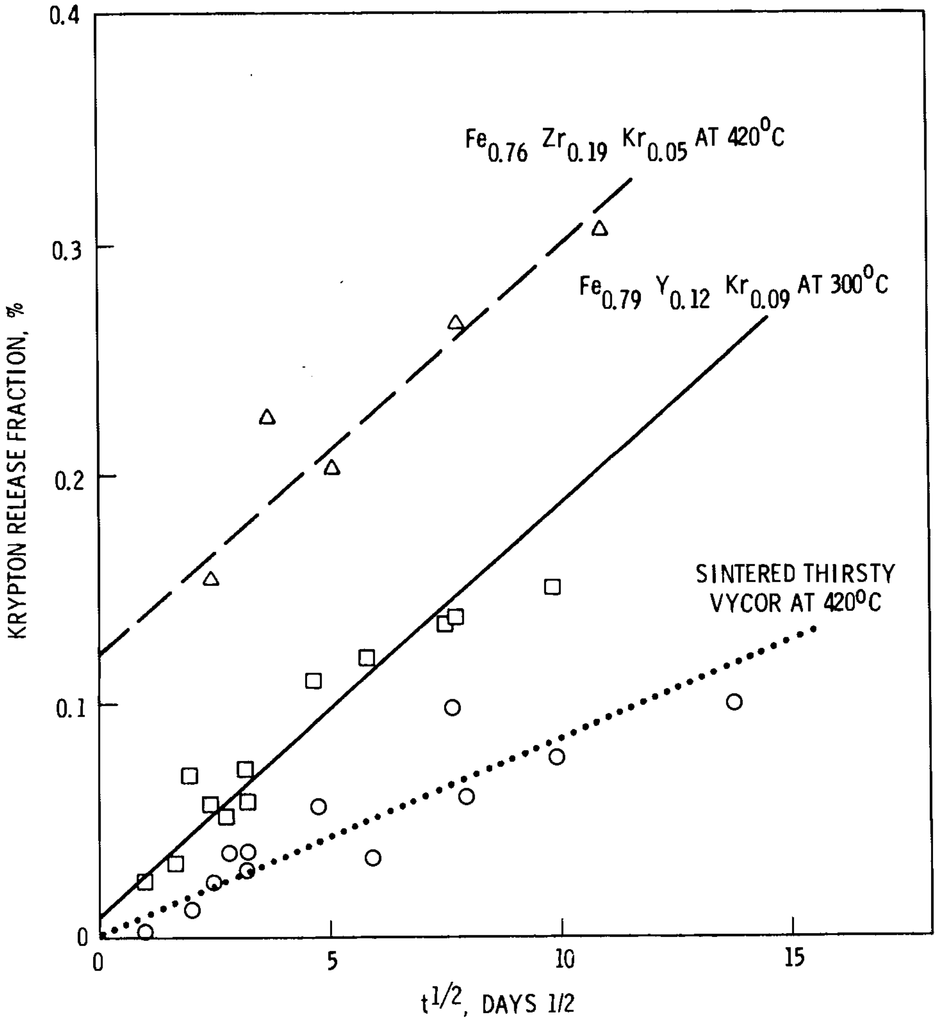


FIGURE 6.4. Long-Term Krypton Release from Krypton-Loaded Samples at Elevated Temperatures

approximate solution does not exceed 3% of the value.

The theoretical basis of the equation along with the $t^{1/2}$ fit of the experimental data provides the basis for an extrapolation of the release data shown in Figure 6.4 to 10 years.

Such an extrapolation of the data yields a total krypton release in the first 10 years as follows:

• $Fe_{0.79}Y_{0.12}Kr_{0.09}$	1.1% at 300°C
• $Fe_{0.76}Zr_{0.19}Kr_{0.05}$	1.2% at 420°C
• Sintered Thirsty Vycor	0.5% at 420°C

These samples clearly exceed the requirements for long-term storage of ^{85}Kr. Refinement of the data will occur as longer-term release tests are completed.

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7. THERMAL OUTGASSING

L. L. Burger - Project Manager

The objectives of this 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* ^{3}H, ^{14}C, ^{129}I, *and* ^{85}Kr.
3. *apply the information obtained from both experiment and theory to spent fuel reprocessing, interim and long-term storage, and to reactor safety.*

SUMMARY

The use of DOE facilities at the 327 Building, using equipment already developed by the Hanford Engineering Development Laboratory (HEDL) for studying reactor transients, was delayed until FY-1981 because of unexpected building modifications. No milestones were affected by this action. Funds for the HEDL portion of the program were set aside by verbal request from Exxon Nuclear Idaho Company.

Initial sweep-gas tests on Shippingport UO_2 fuel have been started. Equipment modifications were completed at the 325-B Hot Cell, and fuel has been cut into segments for analysis. The initial experiments at 1000 to 1500 C will include sweep gas compositions of He or He + 6% H_2.

The merits of applying sputter-deposition to the thermal outgassing program were reviewed. E. D. McClanahan has completed an initial literature review to determine the feasibility of using sputter-deposited UO_2 containing trapped fission gas to complement the more expensive irradiated fuel tests. His review shows that Navinsek(1) and Marlowe(1) have demonstrated that UO_2 can be sputter-deposited. Based on PNL experience with other oxides, the stoichiometry can vary from theoretical to several percent low in oxygen content. In the case of UO_2 it may be possible to exceed the O/M ratio of 2.0. Multiple gas species can be incorporated into the same deposit.

L. G. Morgan and L. L. Burger attended the American Nuclear Society Topical Meeting on Tritium Technology, April 29 - May 1, 1980 in Dayton, Ohio.

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8. IODINE-129 FIXATION

L. L. Burger - Program Manager

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

SUMMARY

Long-term leaching studies will employ both the static test recommended by the PNL Materials Characterization Center and the modified IAEA (International Atomic Energy Agency) test used in our previous studies. The former have started for cement-encapsulated barium iodate, lead iodate, and mercuric iodate.

Thermogravimetric analysis (TGA) was used to study the varied behavior of iodine loaded silver sorbents. Qualitative differences in the iodine volatility at temperatures >550°C for the various sorbents suggest differences in iodine species.

Rockwell Hanford Operations (RHO) prepared and characterized iodine sodalites containing 18 to 20 wt% iodine. Little difference was seen in the density, porosity, and leaching whether the sodalites were prepared in helium or under vacuum.

LEACHING STUDIES - R. D. Scheele

Long-term leaching studies will employ both the static test recommended by the PNL Materials Characterization Center and the modified IAEA test used in our previous studies. The former have been started for barium iodate, mercuric iodate, and lead iodate in Type III portland cement. Some difficulty was encountered in preparing the lead iodate cement (10 wt% iodine). A long curing time was required to obtain sufficient sample strength for the tests. It was hoped that cuprous iodide and lead iodide could be tested in cement, but the cement offered little protection, and both compounds hydrolyzed rapidly, giving very high I^- concentrations in the leachate. No tests on iodides are currently under way or planned. The tests will also include iodine-loaded zeolites, the Bayer material, AC-6120, and an iodine-containing sodalite prepared by RHO. Selected tests will involve distilled water, Columbia River water, and sea water.

ZEOLITE CHARACTERIZATION - R. D. Scheele and L. L. Burger

Previous tests have shown a varied behavior of iodine-loaded silver zeolite with respect to iodine extractability, with CCl_4 and thermal behavior in the range to 200 to 900°C. A large fraction of the iodine even when loaded to only 50 to 70% of theoretical, is rather loosely bound, and is evolved on heating to 250 to 350°C. No consistent pattern has been found relating methods of iodine loading, e.g., rate, temperature, presence or absence of water, zeolite type, and previous history, or even the color of the product--which may vary from grey to yellow to green to violet. Preliminary extraction data using CCl_4 to determine free I_2, as reported in the previous quarter,(1) do not agree with iodine losses observed in TGA studies. The latter are being continued along with DSC scans. Also under way are surface analysis studies (ESCA) to determine the chemical species present.

In the last quarterly report,(1) we discussed the effect of iodine loading levels on iodine volatility from the different iodine-loaded silver sorbents. In the present report, we discuss volatility at temperatures >550°C as shown by thermogravimetric analysis (TGA).

Qualitative differences in the volatility of iodine at temperatures >550°C for the various iodine-loaded silver sorbents suggest the presence of different iodine species and a different trapping mechanism for each sorbent. In general, for AgZ, Ag°Z, AgX, and NaZ, water is lost between room temperature and 300°C, elemental iodine volatilizes between 260 and 550°C, and an unknown iodine species volatilizes above 550°C. For AC-6120 water is lost between room temperature and 150°C, NO_2 from $AgNO_3$ decomposition is lost between 400 and 500°C, and a light yellow iodine compound volatilizes above 600°C.

Figure 8.1 presents TGAs up to 1000°C for as-received silver mordenite AgZ, hydrogen-reduced silver mordenite Ag°Z, silver faujasite AgX, and 12 wt% silver AC-6120; each material is loaded with elemental iodine to 50% Ag use. AgZI and Ag°ZI lose iodine, 2.0 wt% of the sample, at a slow, steady rate from 600 to 940°C; the rate then increases, and 0.2 wt% of the sample is lost. AgXI loses 2.2 wt% between 700 and 860°C, with most occurring in two stages between 760 and 850°C. AC-6120-I loses 6.8 wt% between 600 and 940°C. In each case, we are ignoring the large iodine loss at lower temperatures and focusing on the high-temperature region.

Comparing Figure 8.2, TGAs of three different mixtures of NaZ and AgI, with the TGA for AC-6120 (Figure 8.1D), one sees an almost identical weight loss pattern for each. This indicates the presence of free silver iodide in or on AC-6120. The differential scanning calorimetry (DSC) studies presented in the last quarterly report(1) indicated the absence of AgI. AgI has a crystal change at 146, melts at 560, and boils at 1506°C. The lack of similarity of NaZ plus AgI to the other silver sorbents indicates the presence of chemical species of iodine on AgZ, Ag°Z, and AgX different from bulk silver iodide.

It is interesting to note that not all the AgI volatilizes from the AgI-NaZ mixture up to 1000°C and that the zeolite's final color is light yellow.

SODALITE STUDIES - W. I. Winters, G. A. Wolf (RHO)

The results of the characterization of products prepared under helium and vacuum using the same pressure, temperature, and time conditions as described by Strachan(2) are summarized in Table 8.1. The average weight percent of iodine loaded in the samples was 18.5%, or 85% of the theoretical value (22%). The samples were analyzed at PNL using x-ray fluorescence. These iodine-loading values are comparable to those of Strachan's work.

Densities and porosities were determined using techniques described by J. T. Jones and M. F. Bernard.(3) In these analyses a bulk sample of the product is weighed dry, saturated with a liquid of known density, and suspended in a liquid of known density.

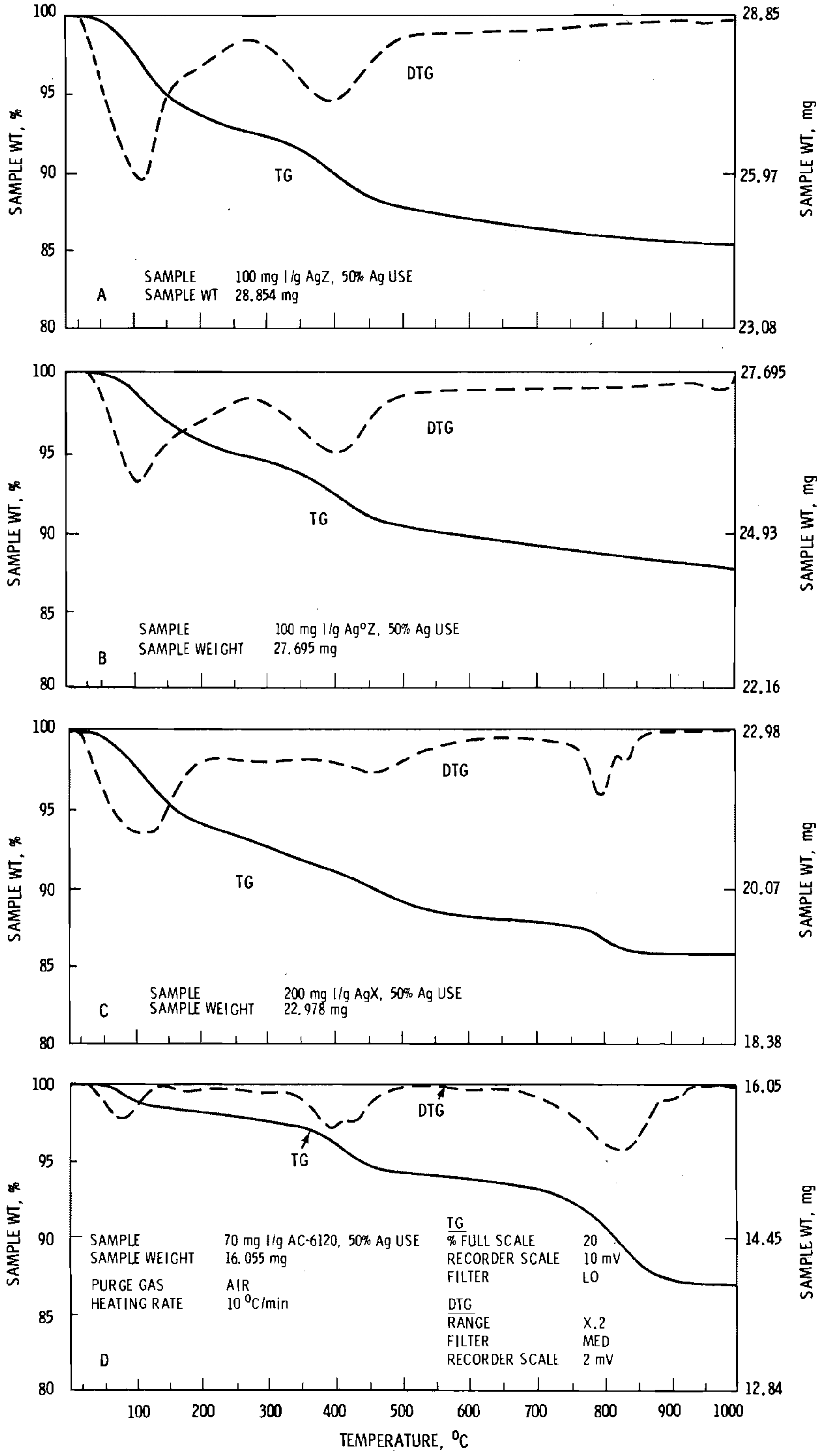

FIGURE 8.1. Thermogravimetric Analyses for A) AgZ, B) Ag°Z, C) AgX, and D) AC-6120

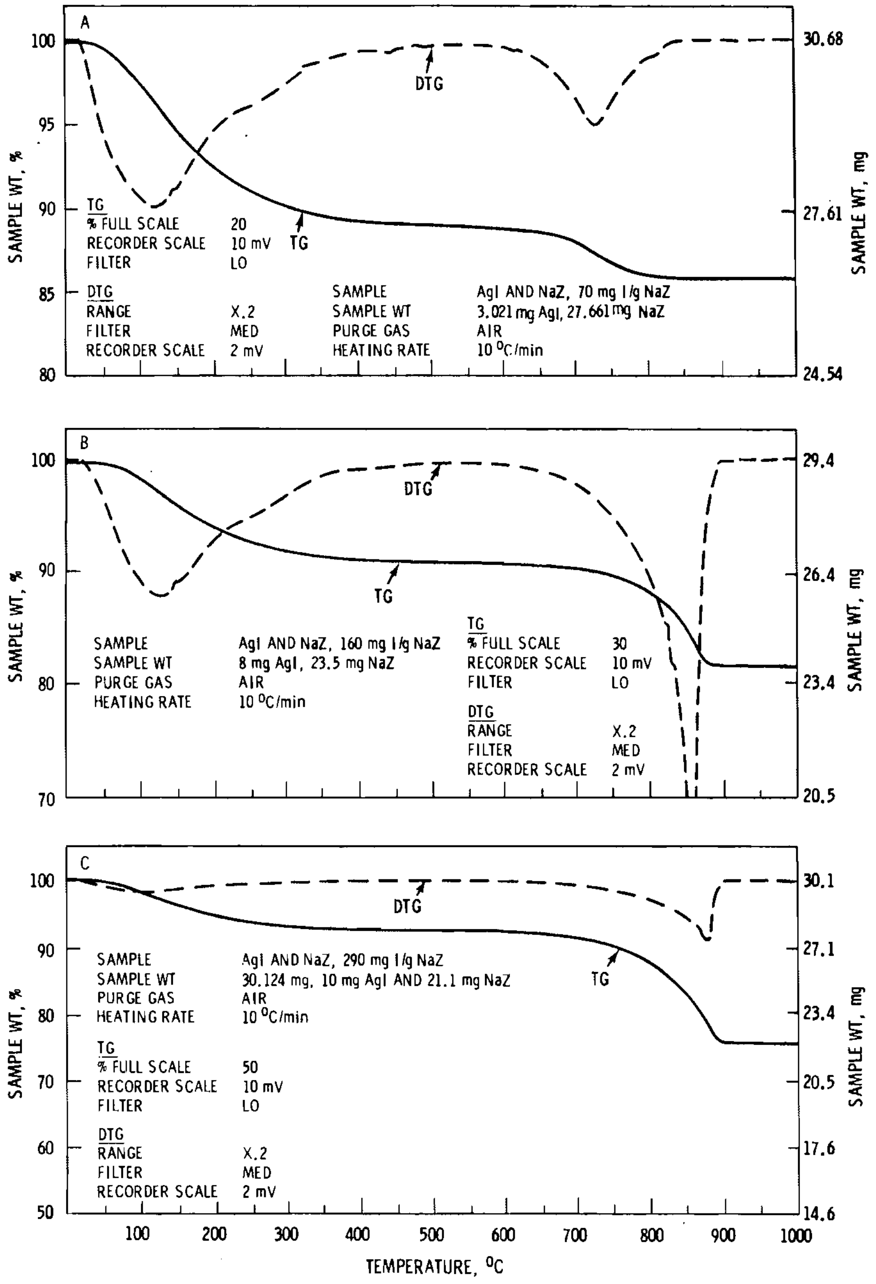

FIGURE 8.2. Thermogravimetric Analyses of Three Different Mixtures of NaZ and AgI

TABLE 8.1. Characteristics of Sodalite Products Prepared Under Helium and Vacuum

Physical Characterization					Soxlet Leach Test Results		
Sample No.	I^-, wt%	Density, g/cm	Porosity, %		1st 24 hr	2nd 24 hr	3rd 24 hr
VAC-1	18.93	1.4226	43.21	IND(a)-wt%	22.04	26.31	22.66
				CUM(b)-wt%	22.04	42.56	55.67
				IND-ppm-I^-	201	181	108
				CUM-g I^-	0.050	0.095	0.122
				IND-% I	26.5	30.6	24.7
				CUM-% I	26.5	50.3	64.5
				pH	10.5	10.0	9.8
He-3	18.62	1.5537	39.13	IND-wt%	13.13	7.74	4.09
				CUM-wt%	13.13	19.85	25.53
				IND-ppm I^-	184	59.3	54
				CUM-g I	0.046	0.061	0.074
				IND-% I	24.7	9.20	8.36
				CUM-% I	24.7	32.7	40.0
				pH	10.1	9.5	9.4
He-4	19.92	1.4866	29.55	IND-wt%	31.86	20.54	29.68
				CUM-wt%	31.86	45.85	61.92
				IND-ppm I^-	230	120.7	139.7
				CUM-g I	0.058	0.088	0.123
				IND-% I	32.1	24.7	28.5
				CUM-% I	32.1	48.9	68.3
				pH	10.8	9.8	9.8

(a) IND--Individual losses for 24-hr period.
(b) CUM--Cumulative losses for successive periods.

The densities recorded by this procedure for these samples were significantly lower (~60% of theoretical) than those reported by Strachan (~90% of theoretical). These differences cannot be explained at this time but could indicate incomplete consolidation.

The products' susceptibility to leaching was measured using the Soxhlet leach test. One gram of product with particle sizes between 40 and 60 mesh was placed in a 200-mesh basket; the material was leached for three 24-hr periods with deionized water at ~100°C and a basket dump rate of once every 3 min. Only the He-3 sample showed a leach rate comparable to the lowest leach rate reported by Strachan. Cumulative weight losses for the products range from 61.9% for He-4 to 25.5% for He-3. Iodine content of the leach solutions was determined by specific ion electrode. The cumulative iodine percent loss was high (40-70%) for all three samples. The He-3 sample showed the lowest iodine leach rate (24.7%), and this decreased to 9.2% and 8.4% on successive leaches.

Porosities for the samples prepared in a helium atmosphere appear lower than the one sample prepared under vacuum. These are, however, the first porosity values determined for the sodalite products, and no definite conclusions can be drawn from these limited data. There appears to be no correlation between the porosity values and the leach rates of the products. Even though the data are limited, there seems to be no real advantage of operating with vacuum over operating with helium. Because of continuing intermittent problems with the vacuum system on the hot press, it was decided to use helium to ensure that this work can be completed on time. These first tests provided valuable experience for establishing our procedures for the hot-press parameter studies. These parameters will be studied during the next period.

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9. MONITORING AND PHYSICAL CHARACTERIZATION OF UNSATURATED ZONE TRANSPORT

S. J. Phillips - Project Manager

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

SUMMARY

Field monitoring has continued with evaluating the migration of radionuclides and water. Data indicate an overall downward movement of liquid-phase tritium, with tritium being significantly transported via liquid- and vapor-phase mechanisms out of the caisson. Data for both the ambient and irrigated caissons appear to show a positive linear relationship.

PHYSICAL MODELING

With the experiment completed, the model was disassembled, and the data were sent to Dr. P. J. Wierenga, New Mexico State University, for analysis.

FIELD MONITORING - S. J. Phillips, K. O. Schwarzmiller and A. C. Campbell

Monitoring systems and methods for measuring radionuclide transport and water migration in the partially saturated zone are currently being tested at a buried waste test facility (BWTF). The third repetition of destructive sampling of sediments contaminated with tritium and cobalt has recently been completed. Laboratory analyses of tritium and cobalt samples taken from the ground surface to a depth of ~7 m have been completed. These samples consist of sediments collected horizontally through the walls of buried caissons. The caissons containing contaminated sediments are located in the BWTF and are subjected to ambient and increased precipitation conditions.

Figure 9.1 is a plot of tritium concentration versus depth in the ambient precipitation caisson of the BWTF. Tritium tritiated water plus soil at standard water count was initially placed at the depth of the 59.5 to 60.5 cm in this caisson. Tritium concentrations for the inclusive sampling dates show a marked change in the peak concentration over the geologic media profile. That is, the peak concentrations occur lower in the profile at ~45, 25 and 12 nCi g^{-1} at depths of ~0.5, 1.1, and 2.6 m (Table 9.1) respectively. This indicates an overall downward movement of liquid-phase tritium over an 8-month period. However, the concentration of tritium at the 6.25 m depth has not changed in this caisson during the same time period.

Table 9.2 shows the results of numerical integration values of the percent relative concentration of tritium for the tritium-contaminated BWTF caisson. It is interesting to note that the concentration delineated for 2/14/80 is significantly lower than that for 5/30/80. This appears inconsistent with the concentration shown for 5/30/80. Further

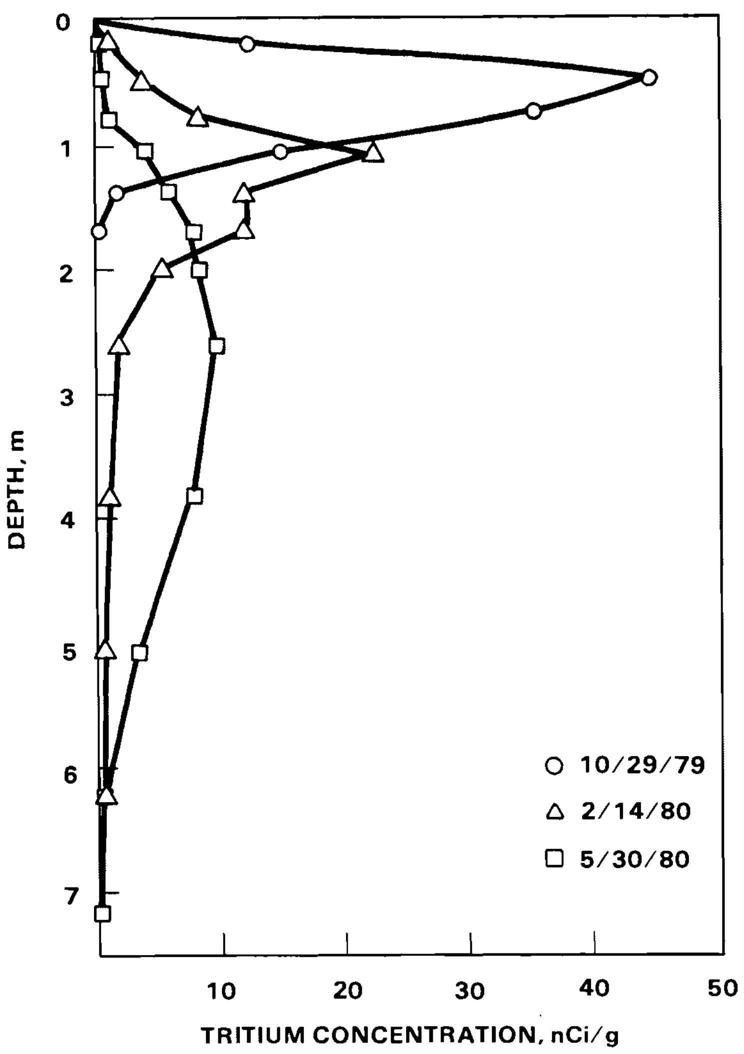

FIGURE 9.1. Tritium Concentration Versus Depth in Ambient Caisson

TABLE 9.1. Peak Concentration Depths, m

	Caisson	
Date Sampled	Ambient	Irrigated
10.29/79	0.5	0.6
2/14/80	1.1	1.75
5/30/80	2.6	5.0

TABLE 9.2. Percent of Initial Concentration of Tritium Remaining in Caisson

Date Sampled	Ambient	Irrigated
10/29/79	51.4	57.6
2/14/80	35.7	51.5
5/30/80	49.5	23.0

sampling and analysis of tritium concentrations planned for August are expected to suggest where the error occurred and may confirm the validity of the relative concentration value derived on 2/14/80. However, the data tend to confirm the observation that tritium is being significantly transported via liquid and vapor phase mechanisms out of the caisson.

Figure 9.2 is a plot of tritium concentration versus depth in the irrigated (precipitation plus two times ambient precipitation)

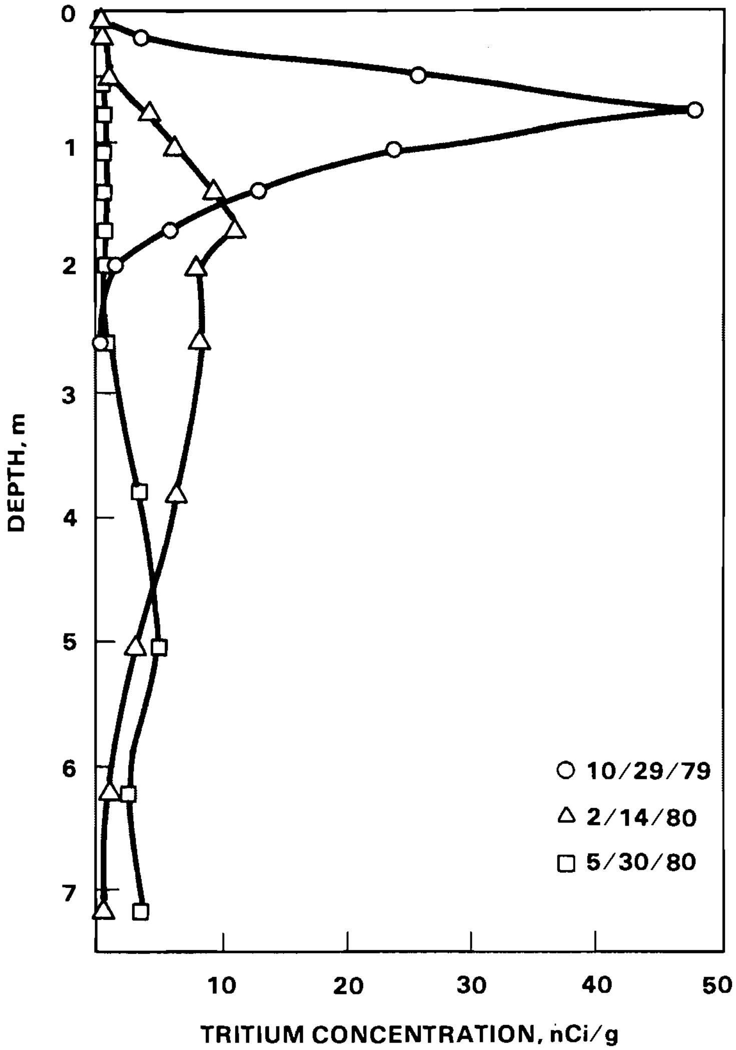

FIGURE 9.2. Tritium Concentration Versus Depth in Irrigated Caisson

caisson of the BWTF. Tritium was initially added to this caisson in the same concentration, depth, etc., as the ambient caisson. Peak concentrations for the three sampling dates show a similar downward trend as shown in Figure 9.1. Table 9.1 also shows the peak concentration depths for the sampling dates shown in Figure 9.2 for the irrigated caisson. In a general way the data for the ambient and irrigated caissons appear to correlate and to show a positive linear relationship between peak concentration depth and time. This indicates a general downward trend of tritium concentration to date. However, both upward and downward vertical transport is occurring.

Figure 9.3 is a plot of the quantity of water versus depth for two caissons at the BWTF (irrigated and ambient Northwest caissons). The difference between water content (centimeter per meter) between these caissons does not vary significantly throughout most of the caisson depth. Marked differences occur only near the interface between the geologic media and the atmosphere, and at 6.5 m near the bottom of the caisson. This suggests that ambient precipitation and applied artificial precipitation (irrigation) enters the geologic media and is transported chiefly by gravity potential in such a way that the water quantity does not greatly exceed 8 cm/m throughout the column.

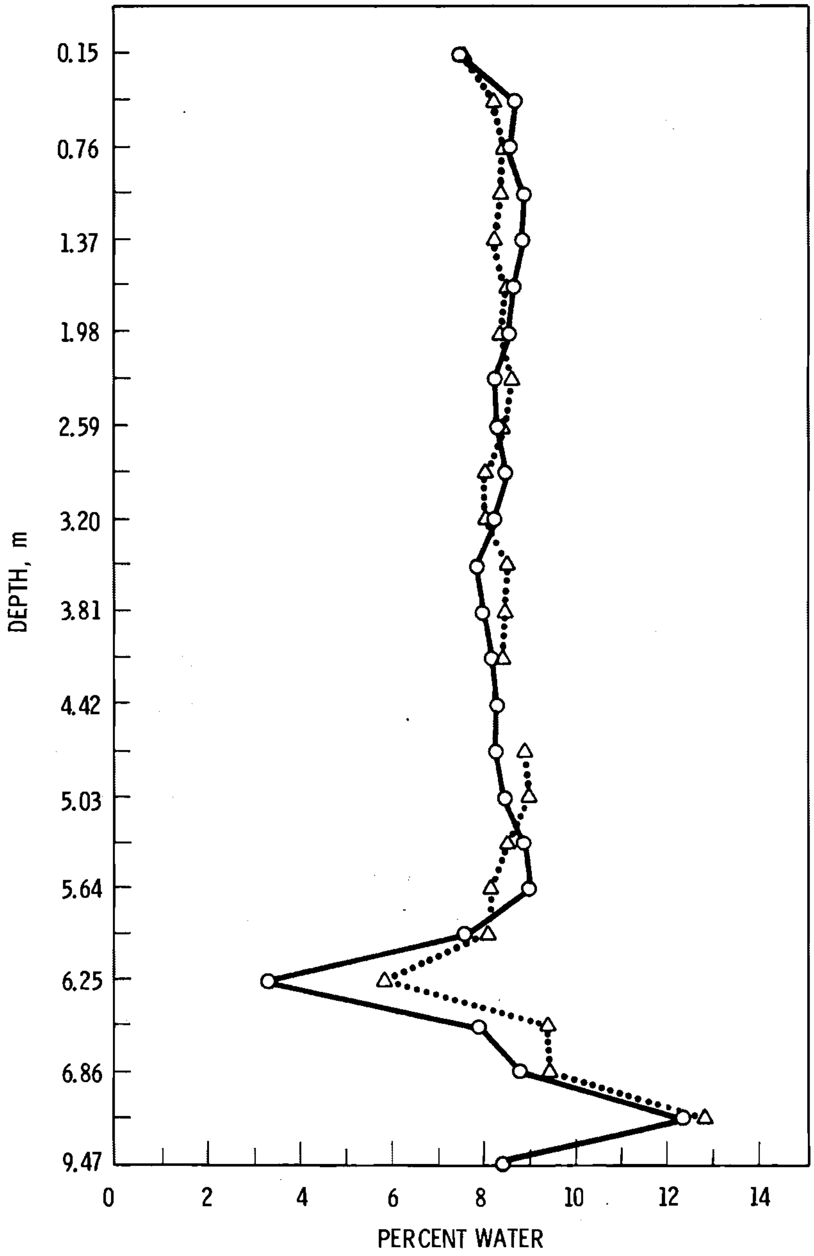

FIGURE 9.3. Moisture Content in Ambient and Irrigated Caissons as Measured by Neutron Probe 2/15/80

10. WELL-LOGGING INSTRUMENTATION DEVELOPMENT

R. L. Brodzinski - Project Manager

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

SUMMARY

The neutron activation analysis experiments on ^{90}Sr have demonstrated the thermal neutron capture cross section to be <17 mb, which is in sharp disagreement with the literature value of 800 mb.

Arrangements have been made with the U.S. Geological Survey at the Idaho National Engineering Laboratory to perform field tests of the ^{90}Sr bremsstrahlung detection logging equipment at the Idaho Falls site.

Discussions have been held with research and operations personnel at Oak Ridge National Laboratory regarding possible transfer of the ^{90}Sr bremsstrahlung measurement technology for application to their burial ground characterization and monitoring.

Assembly and testing of the tritium logging system is proceeding on schedule.

An operations manual, Monitoring Transuranics in Sediments by Neutron Activation of Metals, has been drafted for Rockwell Hanford Operations.

Field testing of the photon detection technique for determination of actinides by well-logging has been completed. The results of these tests are detailed. The technique can quantitatively measure plutonium concentrations of <10 nCi/g in only 4 min. The system is capable of collimation such that stratification of transuranics in sediments can be defined in situ with a resolution of 1 cm. The technique is capable of simultaneous determination of ^{239}Pu, ^{241}Am, and other transuranic isotope concentrations.

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

In situ determination of ^{90}Sr by neutron activation analysis was considered a viable option based on the reported 800 mb cross section(1) for the $^{90}Sr(n,\gamma)^{91}Sr$ reaction. The sensitivity of this technique will also be subject to the levels of interfering radioactivities generated in the matrix by the neutron source. Initial experiments have been conducted in the laboratory utilizing a ^{252}Cf-fueled subcritical neutron multiplier as the activation source. Comparison/calibration standards of ammonium bromide have been used due to the similarity of the nuclear parameters in the strontium capture reaction and the $^{81}Br(n,\gamma)^{82}Br$ reaction. These relevant parameters are listed in Table 10.1. Simultaneous irradiation and identical counting scenarios for samples of ^{90}Sr and ^{81}Br have clearly identified the ^{82}Br capture product at the anticipated activity levels but have failed to indicate any ^{91}Sr activity. Since ^{91}Sr is a fairly well characterized fission product, the decay

TABLE 10.1. Comparison of the Relevant Nuclear Parameters for the $^{90}Sr(n,\gamma)^{91}Sr$ and $^{81}Br(n,\gamma)^{82}Br$ Reactions and Products

Parameter	$^{90}Sr(n,\gamma)^{91}Sr$	$^{81}Br(n,\gamma)^{82}Br$
Capture cross section, mb	800(1,2)	2700(2)
Product half-life, hr	9.48(2)	35.344(2)
Gamma ray detected, keV	555.57(2)	554.322(2)
Branching fraction,%	60.7(2)	70.7(2)

scheme data are assumed to be well known. Therefore, the absence of measurable ^{91}Sr activity in the irradiated ^{90}Sr sample implies the reported 800 mb neutron capture cross section is erroneously high. In fact, comparison to the bromine capture reaction yields an upper limit of 17 mb for the $^{90}Sr(n,\gamma)^{91}Sr$ reaction. These experiments will be repeated in a higher flux Triga reactor to define precisely the ^{90}Sr thermal neutron capture cross section.

The above results indicate that the detection limit for in situ determination of ^{90}Sr by thermal neutron activation analysis will be at least a factor of 50 worse than originally expected. Consequently, the bremsstrahlung detection technique developed earlier in this program is more likely to provide higher sensitivity for the in situ detection of ^{90}Sr, and increased effort will be directed towards continuing its development. Arrangements have been made with the U.S. Geological Survey at the Idaho National Engineering Laboratory to perform field tests of the ^{90}Sr bremsstrahlung detection logging equipment at the Idaho Falls site. Similarly, discussions have been held with research and operations personnel at Oak Ridge National Laboratory regarding the possible transfer of the ^{90}Sr bremsstrahlung measurement technology for application to their burial ground characterization and monitoring.

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

Assembly and testing of the tritium logging system are proceeding on schedule. Most component parts have been received or fabricated, and some temporarily idle electronic equipment has been borrowed from other programs for use during the construction and testing phase. Remaining capital equipment requirements have been determined, and purchase requisitions have been placed.

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

An operations manual, Monitoring Transuranics in Sediments by Neutron Activation of Metals, has been drafted for Rockwell Hanford Operations. This detailed document constitutes transfer of technology developed in this instrumentation program to an operator in the field for use in characterizing transuranic-contaminated environments.

Field testing of the photon detection technique for determination of actinides by well-logging has been completed. This activity was not previously planned for this fiscal year, but following the surprisingly successful laboratory experiments reported last quarter, it was deemed worthwhile to accelerate the schedule in this area because of the large potential economic savings achievable with this technique. These field tests were performed in cooperation with Rockwell Hanford Operations, and the technology is currently being transferred to them for routine use.

These field tests were conducted in well W18-159 in the 216-Z-1A crib, an area that has been characterized by the passive neutron monitoring technique developed earlier in this program, by the IRT Neutron Activation Analysis system, by the Sandia Neutron Activation Analysis system, and by core sampling. The photon detector was calibrated in both sectors of the Rockwell Hanford Operations 4π plutonium calibration facility. Although this facility has been shown to be nonrepresentative of plutonium in Hanford sediments for neutron detection techniques,(3) the gamma-ray detection technique should be less affected by the unusual matrix material and should provide more realistic calibration information. However, this calibration facility is not likely to be either useful or accurate for use with the IRT and Sandia Neutron Activation Analysis systems. In fact, the calibration data obtained with the photon detection technique used here indicate that the facility is less than reliable even for photon measurements.

The calibration tank contains two sectors filled with homogeneously spiked Del Monte sand having plutonium concentrations of 135.5 nCi/cm^3 and 13.55 nCi/cm^3. The net count rates of the ^{239}Pu 414 keV photopeak in these two sectors were 0.905 and 0.133 counts/sec, respectively. This disparity indicates that the low-concentration sector value is influenced by the close proximity of the high-concentration sector. An obvious corollary of this conclusion is that the calibration factor for the high-concentration sector is also incorrect due to the small size of the tank, which does not represent an infinite source. These data and previous neutron measurement experiments in this facility indicate that the nonrepresentative matrix may also have photon attenuation properties substantially different from those of Hanford sediments.

Despite these shortcomings, the photon detection logging system was calibrated in both sectors of the 4π Rockwell plutonium facility. Calibration factors were also obtained in the 329 Building point source facility and by comparative inference to another detector that was calibrated in the Rockwell 4π gamma-ray calibration facility. Needless to say, four calibration methods yielded four widely different calibration factors, which reaffirms the need for constructing a reliable 4π plutonium calibration facility.

The results of photon well-logging in W18-159 are given in Table 10.2 for each of the four calibration factors along with the results available from the IRT and Sandia neutron activation probes, laboratory analysis of core samples, and monitoring with the metal activation technique. Each of these techniques interrogates a substantially different sample volume, and the plutonium in the 216-Z-1A crib is known to be deposited in very narrow stratified layers. For all the above reasons, close agreement between the results from the various techniques should not be expected. It is not possible at this time to determine which technique provides the most accurate value for the average plutonium concentration in a large volume of sediments. Arguments can be presented, however, for choosing the lower concentration limit based on the Rockwell 4π plutonium calibration facility low sector and the upper concentration limit based on the metal activation monitoring technique. Hence, the best estimates for the plutonium concentration limits around W18-159 are represented by the first and last columns in Table 10.2.

TABLE 10.2. Plutonium Concentrations Measured in Well W18-159 in the 216-Z-1A Crib by Various Techniques. Assumed that nCi ^{239}Pu/nCi Pu = 0.7868 and $\rho = 1.5$ g cm^{-3}.

	Total Plutonium Activity in nCi cm^{-3} Photon Detection Calibration							
Depth, ft	Rockwell 4π Low Sector	Rockwell 4π High Sector	329 Bldg. Facility	Rockwell 4π Gamma Facility	IRT 252 Cf Probe	Sandia (D,T) Probe	Core Samples	Passive Metal Activation
9.0	13,100	19,300	74,100	113,000		3,300		311,000
9.5						4,100		452,000
10.0						3,000		479,000
18.5	2,210	3,240	12,500	19,100		900	918	4,950
23.0	1,310	1,920	7,410	11,300		83	797	4,690
34.0	265	388	1,500	2,290		0	<3	609
41.5	602	882	3,400	5,190	720	23	443	3,550

Of much greater significance to this instrument development program is the fact that, provided a suitable calibration facility becomes available, the photon detection technique for in situ determination of actinides is capable of adequate sensitivity at very low costs. The field tests indicate that the detection limit is even lower than estimated from the earlier laboratory experiments. A plot of the detection limit at the 90% confidence level for ^{239}Pu in Hanford sediments relatively free of fission product activities is shown in Figure 10.1 as a function of count duration. The fiduciary 10 nCi/g limit is measurable in <4 min, implying that in situ analyses can be made at a unit cost of <\$5.00 with equipment costing <\$50,000.

The photon logging system can also be fit with a collimator so that precise definition of the stratification or layering of the plutonium can be obtained simultaneously with concentration measurements. Resolution of layers as thin as 1 cm can be obtained. No other in situ detection system is capable of providing this important information.

The photon detection technique for actinides has the additional advantage of being isotope specific. It is the only in situ technique available which can simultaneously measure the ^{239}Pu and ^{241}Am concentrations. The photon detection system was calibrated for ^{241}Am by the inference method and in the point source facility described earlier. The measured concentrations of ^{241}Am based on these two calibration methods are given in Table 10.3 for the 216-Z-1A field test. These concentrations are commensurate with the expected concentrations based on historical inventory data.

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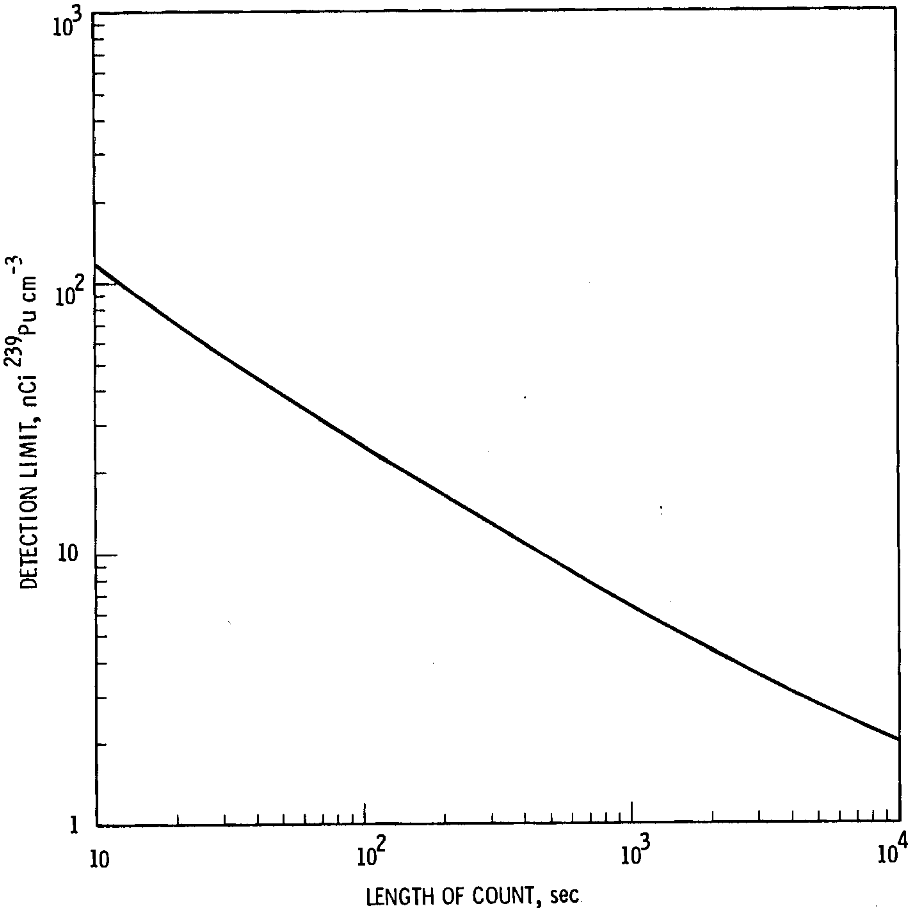

FIGURE 10.1. Detection Limit for In Situ Determination of ^{239}Pu in Fission Product-Free Sediments by Gamma-Ray Spectrometry

TABLE 10.3. ^{241}Am Concentrations Measured in Well W18-159 in the 216-Z-1A Crib by Photon Detection Calibrated by Different Methods and from Core Samples

	^{241}Am Concentration, nCi cm^{-3}		
Depth, ft	329 Bldg. Point Source Calibration Facility	Inferred from RHO 4π Gamma Calibration Facility	Core Samples
9.0	5520	4180	-
18.5	527	400	189
23.0	440	334	97
34.0	154	116	42
41.5	224	170	109

11. MOBILITY OF ORGANIC COMPLEXES OF FISSION PRODUCTS IN SOILS

J. A. Franz - Project Manager

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

SUMMARY

The extended desorption study (45 days) of reduced ^{99}Tc has been completed this quarter as well as the investigation of soil interactions of synthetic technetium complexes Tc(IV)EDTA and TC(V)DTPA . The synthetic technetium complexes were highly mobile on Hanford soil. The desorption studies (where both citrate and EDTA were used as the desorbing ligands) indicate that these organic ligands have a negligible effect on mobilizing technetium (via complex formation) that has been reduced and sorbed on soil in the absence of organic complexing agents, even at ligand/metal ratios of 10,000:1.

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

TABLE 11.1. Comparison of %^{99}Tc Sorbed from 10- and 45-Day Desorption Studies of Reduced ^{99}Tc by Na_3 Citrate on Hanford Soil

^{99}Tc Concentration, M	Cit/Tc Molar Ratio	% Tc Sorbed* 10 Day	45 Day
1×10^{-6}	1:1	96	94
	10:1	93	95
	100:1	95	95
	1,000:1	95	95
	10,000:1	85	88
1×10^{-7}	1:1	93	91
	10:1	94	91
	100:1	91	91
	1,000:1	89	90
	10,000:1	89	89
1×10^{-8}	1:1	93	94
	10:1	89	95
	100:1	86	95
	1,000:1	88	96
	10,000:1	87	91
5×10^{-9}	1:1	76	92
	10:1	77	89
	100:1	73	97
	1,000:1	61	67
	10,000:1	39	58

*Results represent average of duplicate runs.

The long-term (45-day) desorption study of technetium, with sodium citrate as the desorbing ligand, has been completed. The results are compared, in Table 11.1, with those of the 10-day study. The experimental conditions for the extended study were analogous to those of short-term (described in the previous quarterly report) except for the time factor. As can be seen in Table 11.1, the percent of technetium sorbed, overall, has increased in the extended study, particularly at the lower concentration levels (10^{-8} to 10^{-9}M). These results, coupled with the data from the study of desorption by use of EDTA, suggest that technetium tends not to migrate, even in the presence of a large excess of organic complexing agent, provided that the technetium is reduced, in the absence of chelating agents, prior to soil contact. Since the organic content is insignificant in the Hanford soil, the TcO_4^- was reduced by hydrazine to Tc(IV) or lower valence states in the presence of the soil.

The behavior of synthetic technetium-complexes [Tc(IV)EDTA and TC(IV)DTPA] was also examined using Hanford soil. The air stability of these complexes permitted the 10-day soil study to be conducted in air. Absorption spectra taken before and after the soil experiment were identical, verifying that the respective oxidation states had been maintained. Only the results for the 10^{-5} to 10^{-7}M concentration level are presented in Table 11.2; minor discrepancies appeared in the 10^{-8} to 10^{-9}M levels, necessitating that these experiments be repeated (counts for soil-reacted samples exceeded control). As can be seen from the data in Table 11.2, very little sorption occurs for either technetium complex (with only 1 to 6% being sorbed); i.e., these complexes would be expected to migrate readily in Hanford soil. Since only cationic species tend to sorb strongly on silica minerals, neutral and anionic complexes should display negligible sorption. Our characterizations of these complexes indicate that they are anionic.

A report summarizing our results on the effects of organic ligands on the soil behavior of technetium has been submitted to the American Nuclear Society. Acceptance will result in the presentation of a paper at the International Conference of the American and European Nuclear Societies being held at Washington, DC (November 16-21, 1980).

Studies on desorption of ^{154}Eu are to commence in July.

TABLE 11.2. ^{99}Tc(V)DTPA and ^{99}Tc(IV)EDTA Interaction with Hanford Soil*

^{99}Tc Complex Concentration, M		K_d	% ^{99}Tc Complex Sorbed
Tc(V)DTPA	10^{-5}	1.19	4
		1.63	5
		0.64	2
	10^{-6}	1.74	6
		1.34	4
		1.30	4
	10^{-7}	1.00	3
		1.04	3
		3.66?	11
Tc(IV)EDTA	10^{-5}	0.42	1
		0.85	4
		1.27	3
	10^{-6}	0.34	1
		0.19	1
		0.45	1
	10^{-7}	0.24	1
		0.09	0.3
		0.41	1

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*Shaken 7 days in air.

12. INTERNATIONAL PROGRAM SUPPORT

K. M. Harmon - Project Manager

The objectives of this program are to provide required assistance to DOE-Nuclear Energy Waste (NEW) in coordinating and promoting the exchange of waste management technical information with other countries and in evaluating the results of international cooperative activities; assist in disseminating information derived from the international program; and prepare special studies.

SUMMARY

Information on nuclear waste technology in other nations was compiled and was disseminated as appropriate. The program plan for informational exchanges and cooperative efforts was prepared.

TECHNICAL PROGRESS

The Report to the President by the Interagency Review Group on Nuclear Waste Management, March 1979, stressed the importance of international cooperation in the waste management field in order to profit from others' practical experience, to further U.S. nonproliferation objectives through shared expertise on the disposal of spent fuel, and to save time and money with cooperative laboratory and in situ testing. The effort to maintain and possibly increase international nuclear waste technology cooperation, outlined in the IRG report, is supported by PNL's International Program Support Office (IPSO).

Diversified information on nuclear waste technology in countries other than the United States was compiled in several ways. These include a calendar of future events; addresses and key personnel of foreign commercial concerns, research organizations, and international and governmental agencies involved in the nuclear fuel cycle; and a file of recent foreign publications. This information was maintained and disseminated as appropriate.

Assistance was provided to DOE in assembling the International Waste Management Information Exchange Program Plan (INFX) for exchanges of nuclear waste technology information and other cooperative efforts. During the past quarter there was considerable emphasis on Federal Republic of Germany/United States programs. The work focused on planning for cooperative in situ brine migration and waste/rock interaction tests at Asse and discussions of specific interactions in other areas of waste management technology.

K. M. Harmon participated in a visit by a U.S. team on high-level waste to the Federal Republic of Germany and the United Kingdom to review their waste management programs and discuss potential areas of cooperation. He worked also with the IAEA in preparing a history of the Technical Committee on High-Level Waste and Alpha Bearing Wastes.

13. WASTE MANAGEMENT SYSTEM STUDIES

J. V. Robinson - Project Manager

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

SUMMARY

Work continued toward issuing two reports based on work PNL did for the International Nuclear Fuel Cycle Evaluation. One report is on waste arisings and the other summarizes four release consequence analyses for geologic repositories.

The Human Affairs Research Center continued work on six of the seven FY-1980 tasks in this program. Activity was heaviest this quarter in assisting in the design of a public participation program toward developing a National Plan for Radioactive Waste Management.

The concept of dilution disposal of radioactive wastes is under investigation. Major concerns have been identified as 1) long-term safety and health impacts and 2) process applicability. Preliminary findings indicate that relatively large volumes can be diluted with earth to consequence levels comparable to those of a natural uranium ore body.

An effort is under way to provide standardized sections and methodologies for use in future Hanford EISs. In this project five areas for standardization have been identified, a set of computer programs chosen, and standardized sets of data and methods for quality control established.

Preliminary literature searches have begun as the initial step in preparing a report on nuclear waste management understandable to interested laymen.

An update of Commercial Nuclear Reactors and Waste: The Current Status is being prepared. It shows a sharp decline in the declared size of the commercial LWR nuclear industry.

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

Pre-contract agreements have been reached with The Analytical Sciences Corporation for a study defining and characterizing containment systems. This study is to provide a basis for strategy in the selection of technologies.

To support DOE Headquarters' development of a National Plan for Radioactive Waste Management, PNL was requested to perform a scoping analysis of the scenarios, questions, and issues that should be addressed by an integrated systems studies program. To begin this effort, a workshop is being planned for senior PNL staff experienced in waste management.

INTERNATIONAL NUCLEAR FUEL CYCLE EVALUATION (INFCE)

Work continued toward publishing two PNL reports based on the work we did on behalf of INFCE WG.7. Technical editing of the one on waste arisings was completed, and the report was scheduled for submission to RL for clearance early in July. The report is entitled Wastes From Selected Activities in Two Light-Water Reactor Fuel Cycles, PNL-3425. The second report describes the methodological approaches and results of four geologic repository release consequence analyses, two of which were done for INFCE WG.7. The other two were done for the Office of Nuclear Waste Isolation (ONWI). A draft report was completed in June and is planned to be published next quarter.

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

Battelle's Human Affairs Research Center (HARC) continued work on the seven tasks they are performing under the FY-1980 program. Task 1 is the development of a social science research plan for nuclear waste management. Technical program plans and waste management-related reports were collected and read during last quarter. The social science research areas to be covered were expanded slightly from the original proposal, and an outline of the report was formulated. The plan will be written next quarter.

Task 2 involves a survey of perceived comparative risks of various hazardous facilities, including waste management facilities. The sample was drawn second quarter, and the names and addresses of the potential respondents were entered into the word processing machines last quarter. The survey questionnaires were finalized and submitted for review in April. Final approval on the questionnaire and sampling plan was received in late June. The questionnaires are currently being worked up by a printer. Data collection and analysis will begin next quarter. This task is about six weeks behind schedule because of the unanticipated delay in the approval process.

Task 3 involves an analysis of factors contributing to the preservation of information over long time periods. Although the literature review has not been exceptionally fruitful, some information from library sciences, regarding the storing and retrieving of archival material, has been uncovered and is being analyzed. In addition, an analysis of information needs is complementing the literature review. A report will be prepared during next quarter.

Task 4 is an identification of remaining technical problems in nuclear waste management that may become future social issues. This small task has been held in abeyance pending inputs from Tasks 1 and 7.

Task 5 involves consulting with experts on the applicability of environmental mediation techniques in the siting of nuclear waste facilities. The principal investigator attended the second RESOLVE conference in April. In May several work meetings were held regarding this task. To make the task more meaningful, the focus of this task was changed slightly as a result of these meetings. At this time, issues that are relevant both to environmental mediation and to the consultation and concurrence process are being developed. These issues will be further refined and will serve as the basis for the consultants' meeting to be held during the fourth quarter of the year.

Task 6, the publication of topical reports based on FY-1979 work, has been completed. Task 7 involves providing assistance to MITRE Corporation in designing and executing a public participation program that will be carried out for the development of a National Plan for Radioactive Waste Management. Task 7 was a source of much activity during the quarter, resulting in the preparation of an expanded version of the public participation section of the National Plan.

This expanded version was sent to DOE Headquarters in June.

WASTE MANAGEMENT DATABOOK[a] - R. W. McKee

It was decided not to prepare a HTGR section for the PNL Waste Management Databook such as was done for the LWR.

J. V. Robinson attended the fourth meeting of the Steering Committee at DOE-HQ on June 3 for Oak Ridge National Laboratory's (ORNL) data base project entitled Spent Fuel and Waste Inventories and Projections, ORNL/TM-7320.

DILUTION DISPOSAL OF RADIOACTIVE WASTES - G. L. Benson

The basic premise of dilution disposal is to mix radioactive waste with a sufficient volume of earth such that the resulting soil concentrations are environmentally acceptable. The purpose of the FY-1980 effort is to qualitatively investigate the preliminary feasibility of this concept for several radioactive waste streams.

Initial work on the project involved identification of the basic evaluation criteria for the dilution concept. The principal concerns of importance for evaluating the dilution concept were identified as 1) the impact on long-term safety and public health, and as a subheading to this, the effects of any environmental consequences of the dilution concept, and 2) the process applicability. Based on these considerations, six central criteria were identified for evaluating the concept:

1. radiation dose commitments
    - population radiation dose
    - occupational radiation dose
2. thermal effects
3. criticality
4. economics
5. processing
6. recoverability.

The prime consideration for the present effort is the long-term safety of the dilution system as measured by possible dose commitments to man. Two alternative radioactive inventories are being analyzed and compared to a natural uranium ore body. To establish a bounding estimate of the system, a conservative (worst case) consequence analysis is being performed on all three radioactive source terms.

The basic release scenario used in this analysis assumes that following closure of the disposal site a well is drilled through the site. Water from this well is used to supply an individual's needs (drinking water, irrigation water, etc.) for a 70-yr lifetime. This analysis produces a radioactive dose commitment for the "maximum individual." It should be noted that this scenario differs drastically from the one used by A. D. Little in support of the EPA draft criteria, which uses only a single year of consumption. If the A. D. Little approach were used, it would reduce the calculated doses for our analyses by about a factor of 70.

A representative dilution site has been established that is similar to an existing uranium ore body. Conservative sorption coefficients and solubility limits for each isotope have been assumed for a host sandstone soil matrix. The site is conservatively assumed to be saturated with water; however, the present analysis does not

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[a] For background information see PNL-3000-5, the prior report in this series.

consider any ground-water migration. A decrease in dose commitments of two to three orders of magnitude could be realized by using more realistic site characterization values; however, in an effort to bound the possible consequences, only conservative values were used.

The "maximum individual" (70-yr lifetime) dose commitments were calculated based on the previously described information using the standard PNL dose codes.

The preliminary results indicate that relatively large volumes of radioactive material can be diluted to consequence levels comparable to those of a natural uranium ore body with about 1 billion cubic yards of material. Altering the soil characteristics would not alter the natural uranium ore body consequences because of the sorptive characteristics of ^{226}Ra. As expected, the initial consequences of the radioactive inventory dilution were very high because of the large amounts of ^{90}Sr and ^{137}Cs present within the system. Efforts are ongoing to determine the effect of removing ^{90}Sr or chemically increasing its retention characteristics so that more reasonable dose commitments would be obtainable.

Thus far, preliminary calculations indicate that dilution disposal may be a viable disposal alternative for a number of different radioactive inventories. These analyses also indicate that the final dose commitments would vary dramatically, depending on site-specific soil characteristics and the specific geochemical regime for any particular release scenario.

Among the problems encountered in this effort, the difficulty in obtaining a reference radioactive inventory was the most significant. Depending on the initial source and the assumptions used, projected inventories can differ dramatically. To counter this problem we have simply chosen two reference inventories documented within the literature.

Other problems have related primarily to the difficulty in evaluating a generic system. This is to be expected when dealing with this type of effort and is being resolved by documenting the conservative assumptions made in preparing the analysis.

Activities planned for the fourth quarter of FY-1980 include additional dose calculations both for different dilution ratios and more reasonable soil characteristics. In conjunction with these calculations, the other criteria that have been identified will be analyzed for the reference dilution case of 1 billion cubic yards.

ENVIRONMENTAL IMPACT STATEMENT (EIS) ANALYSES - M. A. Mueller

The objective of this project is to provide standardized sections and methodologies that are acceptable to the DOE Richland Operations Office and the Hanford contractors, and that will be used in environmental impact statements prepared for activities to be conducted at the Hanford Site. Five areas for standardization have been identified: routine operations dose methodology, accident dose methodology, Hanford Site description, health effects methodology, and socioeconomic environment for Hanford waste management activities. The proposed standardized section on methodology will be presented to DOE-RL and the Hanford contractor upon completion. Discussions will be held as necessary to reach agreement on the acceptability of the material presented and to get the appropriate commitments to use the material in future Hanford Site EISs. Two methodologies are to be completed in FY-1980.

Routine operations dose methodology involves standardizing the methods for calculating radiation doses to the public from routine releases of radionuclides to the environment. A set of computer programs has been chosen, and standardized sets of data and methods for quality control have been established. The ingestion dose programs ARRRG, FOOD, and PABLM are accessible for use, but not for unauthorized modification by Hanford Site users, on BCSR UNIVAC 1100. The inhalation dose program DACRIN is in the process of being modified to run on the standardized data libraries. Background literature has been compiled for use in the upgrading of the standardized data libraries. All programs are being written in ASCII FORTRAN suitable for easy adaptation to offsite computer systems.

A computer program to calculate radiation doses from accidental releases of radioactive materials at Hanford is being developed for the accident dose methodology. The new program, entitled HADOC, has been designed, programmed in FORTRAN on the UNIVAC 1100/44 computer, and is currently being tested. After final testing, a program document will be published describing both the mathematical models and the computer operation. The program is based on existing models and subroutines. Radiation doses are calculated for both the maximum individual and the population exposed to the plume of atmospheric contamination. The semi-infinite cloud model is used for air submersion doses, and inhalation doses are calculated using dose factors from the DACRIN computer code.

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

A contract was signed with North Carolina State University to prepare a report on the subject of nuclear waste management information understandable by interested, intelligent laymen (WBS element 0602). Preliminary literature investigations on nuclear wastes were begun, with special emphasis on the semipopular literature, e.g., *Science*, *Bulletin of the Atomic Scientists*, *Scientific American*, etc., to determine areas of concern about wastes. A representative set of questions raised by members of a local (Raleigh, North Carolina) community task force was collected. A plan was developed for collecting, filing, and processing information in order to arrive efficiently at the final product document.

Under the direction of Dr. Raymond Murray, North Carolina State University, draft material for potential use by the public was developed on about half of the waste management topics prepared at PNL in February. Attention was given first to basic background science.

Dr. Murray and J. V. Robinson conferred with representatives John M. Mountain, Reuben W. Peterson, and John T. Suchy on objectives, procedures, and audiences of the project. There is no conflict with ONWI's program and they encouraged PNL to proceed and offered to advise as appropriate.

Dr. Margaret N. Maxey, Assistant Director of the Energy Research Institute, has agreed to comment on the waste management topics and later comment on draft written material.

(a) For background information see PNL-3000-5.

Administrative arrangements for her participation in the project have been made. Battelle's HARC will also participate in an advisory capacity.

WASTE FROM THE COMMERCIAL NUCLEAR POWER INDUSTRY(a)

A report entitled Commercial Nuclear Reactors and Waste: The Current Status, April 1980 (PNL-3317-1) was published. It was developed as the first of a series to track implications to DOE's waste management program due to changes (decline) in the declared size of the commercial LWR nuclear power industry in the U.S. The report is based on the declared(b) status of the industry as of March 1, 1980, and shows that that status date relates to a projected peak installed generating capacity of 162 GWe in the year 1997.

New computer runs were made more recently in anticipation of issuing the second report in the series (PNL-3317-2) in the next quarter. Those runs are based upon the status of the industry as of June 1, 1980, which projects to a peak capacity of 154 GWe in the same year, i.e., 1997. In the period March 1 to June 1, 1980, the utilities withdrew seven reactors (five BWRs and two PWRs) from the declared inventory and put them in an indefinite category. During the same period 34 plants announced delayed dates for being on-line.

As observed in PNL-3317-2, since 1977, when the President announced the moratorium on reprocessing, 61 reactor power plants have been cancelled or put in the uncertain category. Assuming a 40-yr operating life and 60% capacity factor for the reactors and a 50% conversion efficiency for oil use (as, say, in cars), that corresponds to about 10 years' supply of crude oil to the U.S. at our current rate of import.

We plan to publish PNL-3317-2 in August.

DEFENSE WASTES AND COMMERCIAL REPOSITORIES - R. Burns, consultant, J. H. Jarrett and J. V. Robinson

On February 12, 1980, President Carter announced his nuclear waste management plans, including that defense wastes would be placed in the first commercial repositories. It was decided to analyze the types and amounts of defense wastes that would be involved and, using heat loading in the repository as a design limitation, calculate the repository area requirements those defense wastes represent. They were then compared to the wastes (spent fuel) and area requirements represented by two scenarios for nuclear power growth in the U.S., i.e., 3600 GWe-yr generated by 2040(1) and the other, more optimistic at 10,000 GWe-yr.(2)

A draft report by Ray Burns, a consultant, J. H. Jarrett and J. V. Robinson has been prepared. It will be circulated for internal and external PNL peer review and submitted for clearance to DOE-RL next quarter.

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

The objective of this study is to define and characterize containment systems for waste management operations in order to provide a basis for strategy for selecting technologies. During the quarter, negotiations have begun and a pre-contract cost agreement was signed by The Analytical

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(a) For background information see PNL-3000-5.

(b) Reactors operating, in construction, or announced to be built.

Sciences Corporation (TASC) to perform this study. Dr. John W. Bartlett, who will be TASC's project leader for the study, visited PNL on June 12 to discuss and reach agreement on the program plan, approach and schedule.

We expect a contract to be signed and work to begin in July.

SYSTEMS ANALYSIS SUPPORT TO DOE HEADQUARTERS

J. V. Robinson

DOE Headquarters is currently engaged in developing a National Plan for Radioactive Waste Management and they are also securing the services of a contractor to perform integrated management-oriented systems studies related to the implementation of the plan. ORNL has been assigned responsibility for developing and maintaining a centralized/master data base for use in such systems studies.

According to Nuclear Energy Waste's Planning and Analysis Branch of the Division of Management Support, which has been assigned these responsibilities, the above-mentioned systems studies contractor may not be under contract before the end of FY-1980 and perhaps even later than that. Consequently, in anticipation of the performance of the systems studies envisioned to be performed by the successful bidder, PNL has been requested to provide some special planning assistance to the Planning and Analysis Branch during FY-1980. Specifically, we were requested to perform a scoping analysis of what scenarios, questions, and issues should be addressed by an integrated systems studies program.

It was decided that the most effective manner in which to develop such information would be to conduct a workshop to be attended by senior, experienced PNL waste management staff members. Preliminary arrangements were made to conduct such a closed workshop at the BSSP facilities in Seattle, July 15 through 17. Detailed arrangements will be finalized in June. John Fabian, Staff and Organization Development Technology Department, will be the workshop facilitator, and John Mendel, of the Chemical Technology Department, has agreed to document the findings and results of the workshop in a report. That report will constitute the deliverable to DOE-RL for this task.

REFERENCES

1. Platt, A. M. and J. V. Robinson, April 1980. Commercial Nuclear Reactors and Waste: The Current Status. PNL-3317-1, Pacific Northwest Laboratory, Richland, WA.
2. U.S. Department of Energy, April 15, 1980. Proposed Rulemaking on the Storage and Disposal of Nuclear Waste (Waste Confidence Rulemaking). DOE/NE-0007.

14. WASTE MANAGEMENT SAFETY STUDIES

P. J. Pelto - Project Manager

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

SUMMARY

Work continued on a state-of-the-art survey of systems safety analysis methods. A list of ongoing DOE, NRC, and EPA safety-related waste management programs has been assembled. A computer literature search was completed and relevant articles are being reviewed. As outlined in the last quarterly,(1) this survey is expected to identify some additional needs for methodology development in waste management safety. An issue paper discussing and prioritizing methodology development needs was begun.

This survey is also expected to aid in the identifying of waste management areas that require additional or more detailed safety research and development. A series of issue papers on various waste management safety areas have been initiated to assist in this effort. Areas presently under study include use of risk assessment in waste management safety, use of cost/benefit analyses in waste management safety, use of safety indices to assist in setting waste management R&D priorities, and waste repository operational safety issues.

REFERENCE

1. Platt, A. M. and J. A. Powell, comps., June 1980. Nuclear Waste Management Quarterly Progress Report, January Through March 1980. PNL-3000-5, Pacific Northwest Laboratory, Richland, WA.

15. ASSESSMENT OF EFFECTIVENESS OF GEOLOGIC ISOLATION SYSTEMS

A. Brandstetter - Project Manager

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

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

SUMMARY

An AEGIS Integrated Methodology (AIM) report, A Short Description of the AEGIS Approach, was completed and sent to clearance. This report was written to describe the basic components of the AEGIS methodology to the general reader. A preliminary draft report evaluating the potential of human intrusion into bedded salt was completed, and a status report documenting the use of geochemical information on the AEGIS program was begun.

The repository release scenario model was improved, and a user's manual that will document the code as it now exists was started. Work continued on the development of geohydrologic response functions as a means of evaluating the overall performance of a repository. In uncertainty modeling, methods have been provided for obtaining the variance of pore velocity when the individual variance components for the hydraulic conductivity and hydraulic gradient have been obtained through kriging.

Peer review for the salt dome reference site initial assessment (RSIA) report (PNL-2955) has produced 22 written responses, including comments from the Nuclear Regulatory Commission (NRC). Four salt domes were compared for ground-water flow and radionuclide retardation capacity in the strata overlying the domes. Based on the limited data available, Vacherie Dome appeared to be the most favorable of the four.

Two working papers, Basalt Conceptual Model and Mathematical Modeling Plan and Basalt Repository Release Scenarios, were completed and transmitted to the Office of Nuclear Waste Isolation (ONWI) and Rockwell Hanford Operations for review and comment. Each is intended to become a significant portion of the basalt RSIA report. The regional hydrologic model is currently being calibrated, and a computer code for calculating the areal distributions of regional recharge for a major section of the Columbia Plateau has been completed and tested. A presentation of the basalt scenarios to technical personnel from the Basalt Waste

Isolation Program (BWIP) of Rockwell occurred May 23. Folding, faulting, glacier-induced and human-intrusion scenarios were discussed, and the technical interchange of ideas was useful and constructive.

METHODOLOGY DEVELOPMENT - D. J. Silviera

Issues Analysis - D. J. Silviera

The status report on the potential for organic compounds to influence the transport rate of radionuclides was completed. An AEGIS Integrated Methodology (AIM) report entitled A Short Description of the AEGIS Approach was sent to clearance on June 30. This report, written to describe the basic components of the AEGIS approach for the general reader, completes the major program milestone as scheduled for July.

The evaluation of long-term effectiveness involves several distinct steps. First, the characteristics of the engineered components in the repository and of the existing geologic and hydrologic systems surrounding the repository must be adequately understood. Because natural geologic processes and future human activities may alter these systems over long periods, it must be determined whether there are plausible scenarios for breaching the repository. If such a scenario is identified, then the transport of radionuclides from the repository to the environment must be estimated. A final step may be added to estimate the effects of the radionuclides upon the human population. Each step of this approach is identified in Figure 15.1 and discussed in the report.

Work began on a study to evaluate the potential of human intrusion into bedded salt. The reference site for this study is the Paradox Basin of Utah and Colorado. The investigation involves evaluating the mineral resources contained in the Paradox Basin and determining the relative potential of human intrusion based on the exploratory and extraction techniques that may be used to obtain these minerals. To date, this study has resulted in a preliminary draft report.

Literature searches were completed on computer chemical models and the kinetics of dissolution/mineralization reactions. A test case of the computer chemical model EQ 3/6 was evaluated using compositions of Hanford basalt and ground water. The reaction path model produced a reasonable assemblage of secondary products from the basalt dissolution and will be a useful tool in further modeling work. A status report to describe the role of geochemistry in the AEGIS program was begun.

Scenario Methodology Development - J. T. Zellmer

General Development of the release scenario model continued. The submodels involved with folding and faulting were modified to reflect new theories on the origin of Columbia Plateau structures. The statistics team constructed a description of operating parameters for the release scenario model in a Monte Carlo mode. This work included altering the number and size of the time steps, identifying the best set of control variables, and identifying several additional variables that might be included in the output files to allow a more comprehensive analysis of the simulation. Work also began on a user's manual for the revised repository release scenario model as applied to basalt. This manual will document the computer code as it now exists and will also discuss the assumptions used in its development.

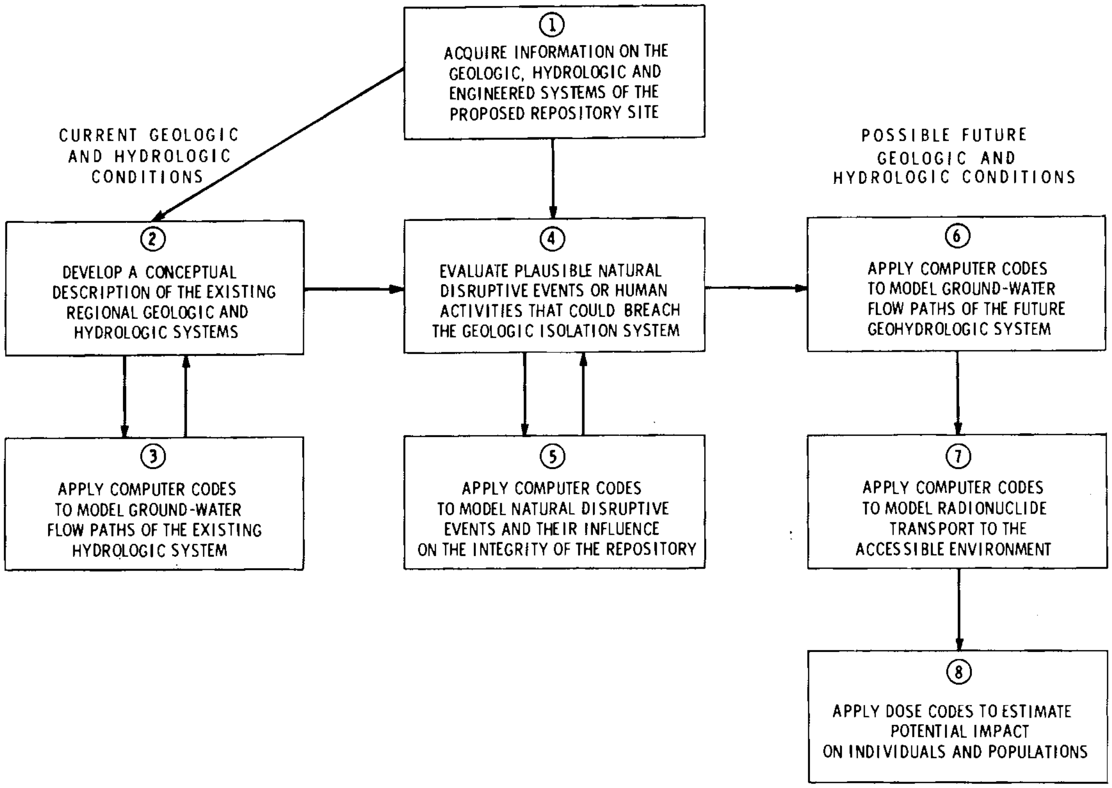

FIGURE 15.1. Assessment Flow Diagram

Transport Methodology Development - R. W. Nelson

Work continued on development of geohydrologic response functions as a means of evaluating the overall performance of a repository site. Initial work progressed on a distributed process control-type analysis to allow optimal placement of a repository in a known geohydrologic system.

In uncertainty modeling, methods were provided for obtaining the variance of the pore velocity when the individual variance components for the hydraulic conductivity and potential gradient have been obtained through kriging. The method for incorporating the variance of the velocity into the transport equations involves an extension of the Keller smoothing method. Initial programming was begun to incorporate this method for use in a two-dimensional test of containment transport with uncertainty.

Two results have been obtained that are of central importance in effectively testing and using the PNL extension of Keller's method in uncertainty analysis. The first result demonstrates that higher order statistical parameters or moments will be required in addition to more involved expansion terms when large variances occur. If required, such higher order moments may not be realistically determined from current field-measured data. The second result yields a precise measure for the size of certain matrices that must be small if the Keller approach is to have utility. It has been shown that the measure for the matrix is an appropriate norm. Specifically, the appropriate norm is the maximum, root-mean-square, absolute row sum. This sum is used to determine whether the Keller approach will apply in any given case.

Dose Methodology Development - J. K. Soldat

Documentations of computer codes ARRRG, FOOD, and PABLM have been cleared and published. The work on developing dose methodology has essentially been completed for this fiscal year.

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

Salt Dome RSIA

Peer review for the salt dome RSIA report (PNL-2955) was scheduled for completion on May 1; comments have continued to arrive, however, through the month of June. Written comments from 22 reviewers, including the NRC, have been received to date. The Environmental Protection Agency (EPA) provided oral comments. Comments were generally constructive and very positive, and the salt dome document triggered an internal debate within EPA on the meaning of institutional controls.

The ORIGEN code is currently being used to predict, over long time periods, the full suite of radioisotopes considering both spent fuel and high-level waste (HLW) inventories. Radiation doses from the solution-mining scenario for a repository containing spent fuel were calculated for mining operations commencing at 10,000; 30,000; 50,000; 100,000; 500,000; and 1,000,000 years. The calculated doses are significantly higher than natural background for all periods. New temperatures and leach rates were calculated for the solution-mining scenario for a repository containing reprocessed HLW in glass. Dose calculations are under way for the breach scenario occurring at 100 and 1000 years after closure.

Salt Dome Site Evaluation

A request came from ONWI to compare four salt domes for ground-water flow and radionuclide retardation capacity in the strata overlying the domes. Discussions were held with ONWI and Law Engineering Testing Company (LETCO) to define the work scope. The scenario analyzed assumes drilling from the side of the dome into the repository that allows ground water to flow through the hole, through the repository, and up through incompletely sealed shafts. Approximate travel times of the flow were computed, and the retardation capacity was evaluated qualitatively. Based upon the limited data available, Vacherie Dome appeared to be the most favorable of the four. A draft of the comparison was submitted to ONWI for review on June 12.

Basalt RSIA

Preparation of input for hydrologic models proceeded. Technical discussions with Rockwell Hanford Operations personnel have resulted in two additional studies to be performed at Battelle to provide better estimates of recharge in 1) the higher evaluations surrounding Pasco Basin and 2) regional agricultural acreage. These studies will not be complete until the end of FY-1980, but they will be used to refine input for hydrologic models on the basalt RSIA as appropriate.

A working paper entitled Basalt Conceptual Model and Mathematical Modeling Plan was completed in May and transmitted to ONWI and Rockwell for review and comment. This paper is preliminary and subject to substantial revision; it is expected, however, to contribute significantly to the RSIA draft report scheduled for December 1980.

A computer code for calculating the areal distribution of regional recharge for a major portion of the Columbia Plateau was completed and tested. The code includes a subroutine to access the U.S. Topographic Data Base and obtain a topographic data file of the Columbia Plateau. Input data describing the pumping distribution for the basalt RSIA within the Pasco Basin were prepared by a local consultant, and boundaries for the Pasco Basin hydrologic model were established.

Initial regional basalt recharge estimates were completed. The method for estimating recharge and the computer code that performs the estimation are currently being documented. Further sensitivity studies are being performed with the RECHARGE code in order to estimate the range in recharge available to the basalts.

The regional hydrologic model is currently being calibrated. Work on the local hydrologic model has been delayed while structure maps are being prepared for the Pasco Basin.

Analyses of the natural disruptive phenomena and other considerations for human intrusion have been drafted to be included in a working paper on release scenarios. The definition of a threshold value for groundwater flow that constitutes a "breach" received additional attention from AEGIS staff and consultants. The final value for ground-water flow will be incorporated into the scenario computer model for basalt.

A presentation of the basalt scenarios to technical personnel from the Basalt Waste Isolation Program (BWIP) of Rockwell occurred on May 23. Folding, faulting, glacier-induced and human-intrusion scenarios were discussed in a useful and constructive technical interchange. The presentation included estimates of base case, breach threshold, and bounding flow values for ground water.

A working paper entitled Basalt Repository Release Scenarios was completed in June and transmitted to ONWI and Rockwell for review and comment. The second of four working papers that are to be completed before the end of FY-1980, it is considered preliminary and subject to substantial revision.

TOPICAL REPORT PROGRESS

Final preparation of the following reports occurred:

To Clearance	
PNL-3398	A Short Description of the AEGIS Approach. D. J. Silviera et al.
Cleared	
PNL-2864	Identifying Suitable "Piercement" Salt Domes for Nuclear Waste Storage Sites. R. Kehle.
PNL-2928	Perspectives on the Geological and Hydrological Aspects of Long-Term Release Scenario Analysis. J. A. Stottlemyre.
Cleared and Printed	
PNL-2862	The Feasibility for Computer Interrogation of Experts for WISAP. L. H. Wight.
PNL-2882	Disruptive Event Analysis: Volcanism and Igneous Intrusion. B. M. Crowe.
PNL-3180	ARRRG and FOOD - Computer Programs for Calculating Radiation Dose to Man from Radionuclides in the Environment. B. A. Napier et al.
Printed	
PNL-2854	Geologic Factors in the Isolation of Nuclear Waste: Evaluation of Long-Term Geomorphic Processes and Catastrophic Events. S. J. Mara.

PNL-2857 *Structural Geology of the Columbia Plateau and Environs as Related to the Assessment of Effectiveness of Geologic Isolation Systems*. H. A. Coombs.

PNL-2858 *Hydrogeologic Effects of Natural Disruptive Events on Nuclear Waste Repositories*. S. N. Davis.

PNL-2859 *Preliminary Subsurface Hydrologic Considerations: Columbia River Plateau Physiographic Province*. M. D. Veatch.

PNL-2863 *Glaciological Parameters of Disruptive Event Analysis*. C. Bull.

PNL-2874 *WISAP 1978 Annual Report*. A. Brandstetter et al.

PNL-3162 *PATHS Groundwater Hydrologic Model*. R. W. Nelson and J. A. Schur.

PNL-3209 *PABLM - A Computer Dose from Radionuclides in the Environment*. B. A. Napier, W. E. Kennedy, Jr., and J. K. Soldat.

16. WASTE/ROCK INTERACTIONS TECHNOLOGY

R. J. Serne - Project Manager

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

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

PROGRAM MANAGEMENT - R. J. Serne

WRIT staff members were involved in several interactions with other DOE nuclear waste management programs. They contributed to the Materials Characterization Center's workshop on standardized leach procedure development. For ONWI, WRIT staff reviewed the technical merits of these proposals dealing with age dating and natural analogs. WRIT staff members are providing the AEGIS staff with technical data and conceptual models for source terms and site-specific retardation factors for AEGIS's basalt site analysis. WRIT staff set up a nationwide national laboratory tour for Nuclear Regulatory Commission (NRC) staff on a fact-finding trip dealing with nuclide retardation by geologic media.

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

Waste Form-Solution Interactions

Radioisotope leachate analysis is essentially complete for five leach time periods in the static tests at 25 and 75°C using actinide doped 76-68 glass. Results will be reported at the end of the next quarter. Elemental analysis by inductively coupled plasma spectroscopy (ICP) is also nearly complete and some important results are presented here. Table 16.1 compares the release of silicon under modified IAEA (International Atomic Energy Agency) and static leaching conditions for nearly equivalent times and temperatures. For deionized water roughly equivalent release occurs by these

TABLE 16.1. Release of Silicon at Long Times from 76-68 Glass Under Static and IAEA Conditions

Leachate	Release Fraction Static Test, 25°C, 341 days	 IAEA Test, 21°C, 331 days
Deionized water	6×10^{-4}	5.3×10^{-4}
Bicarbonate ground water	1.1×10^{-4}	2.5×10^{-3}

test methods; but for bicarbonate ground water a twofold increase in the IAEA test is found. The boron, sodium, and molybdenum release fractions are nearly the same, whereas silicon and calcium are removed to a lesser degree. The fractional release curves are approximated by a $t^{1/2}$ functionality. A comparison of silicon release from the three leachates used in this study show more silicon is released in the bicarbonate than in deionized water, and the least silicon release occurs in WIPP brine B. The deionized water and WIPP brine leachates appear to be equilibrating with the glass after 341 days, whereas the bicarbonate ground water continues to leach at this stage. Temperature has an inconsistent effect on release enhancement of glass constituents, as shown in Table 16.2.

The release of ^{99}Tc has been measured in a static leach test using spent fuel with a burnup of 28,000 MWd/tU. Table 16.3 shows the ^{99}Tc release in the five leach solutions after 8 days of static leach testing and also the available release data for nine other elements. The ^{99}Tc-based release of the fuel is higher than the matrix (uranium)-based number but lower than the cesium-based release data. Elements in spent fuel do not leach congruently with respect to the uranium.

The anoxic static leach test conducted at Argonne National Laboratory (ANL) results reported earlier lacked only some uranium analysis to complete the set of actinide leach data for the first 30 samples. Each datum includes the uranium recovered by scrubbing the polypropylene leach container with concentrated HF and O_3. In the 75° brine solutions much of the uranium (2-88%) was found on the container walls; the 23°C brine leachings retained the uranium in solution (except for the 2-day leaching). All of the 2-day leaching results showed relatively high wall adsorption. There appear to be two effects: an adsorption mechanism, accounting for about 0.03 μg uranium, and precipitation (over 3 μg uranium in the case of the 75°C brine, 106-day leaching).

The uranium analysis, completed to date, for the anoxic static leach tests of PNL 76-68 simulated waste-glass can be compared with the plutonium and neptunium results reported earlier. The leaching by bicarbonate solution at 75°C is more than a thousandfold greater for uranium than for plutonium. In 23°C water, the amount of uranium leached is comparable to the plutonium and less than the neptunium.

Waste Package Interactions

This quarter was devoted to characterization of the components from the first series of waste package tests conducted in 850-ml direct sampling autoclaves. Anion determinations will be incorporated in all future waste package tests.

Additional effort was spent examining the glass surfaces from the minicanisters by

TABLE 16.2. Increase in Leaching from 25°C to 75°C. Shown is the ratio of fraction released at 75°C to 25°C at 341 days.

Leachate	Element B	 Ca	 Na	 Si
Brine	3	(a)	--	4.5
Bicarbonate	25	3	--	15
Deionized water	34	4	25.5	18

(a) Not determined because of high background in initial leach solutions.

TABLE 16.3. Leach Solution Concentration (ppm) After Static Leach Testing Spent Fuel with a Burnup of 28,000 MWd/tu at 25°C for 8 Days

	Deionized Water	0.03M NaHCO$_3$	WIPP B Brine	0.03M NaCl	0.015M CaCl$_2$
^{137}Cs	8.8 E-02	1.3 E-1	7.1 E-2	9.8 E-2	5.7 E-2
Uranium	2.7	5.7	10	8.4	7.6
^{239,240}Pu	1.7 E-2	5.9 E-2	1.0 E-3	1.3 E-2	1.8 E-2
^{244}Cm	7.2 E-6	4.9 E-4	1.1 E-3	8.9 E-4	5.5 E-4
^{90}Sr + ^{90}Y	(a)	(a)	(a)	(a)	(a)
^{125}Sb	(a)	(a)	(a)	(a)	(a)
^{106}Ru	(a)	(a)	(a)	(a)	(a)
^{144}Ce	(a)	(a)	(a)	(a)	(a)
^{154}Eu	(a)	(a)	(a)	(a)	(a)
^{99}Tc	5.3 E-2	5.3 E-2	3.2 E-2	3.2 E-2	3.4 E-2

(a) Analytical data not available at time of publication.

scanning electron microscope (SEM). Problems of rock powder matrix material adhering to the glass surface and interfering with SEM analysis have led to a modified package configuration with an exposed surface that will be used in future tests.

Some of the solution analysis data from the first series of direct solution sampling tests are reported in Figures 16.1 and 16.2 for basalt and granite matrices. These tests were run for 30 days at 250°C/2000 psi. Solutions were sampled at the following intervals: 1) after reaching pressure and temperature, 2) after 1 week, 3) after 2 weeks, 4) after 3 weeks, and 5) after 4 weeks. In addition, samples were collected at 50°C intervals during cooldown, and the solution remaining in the autoclave after cooldown was also analyzed.

About 600 ml of solution was used in these first waste package tests and the components had the following masses, as shown below in grams.

Granite:

Minicanister + glass	50.1
Glass wafer	12.5
Granite wafer	6.5
Granite powder	122.5

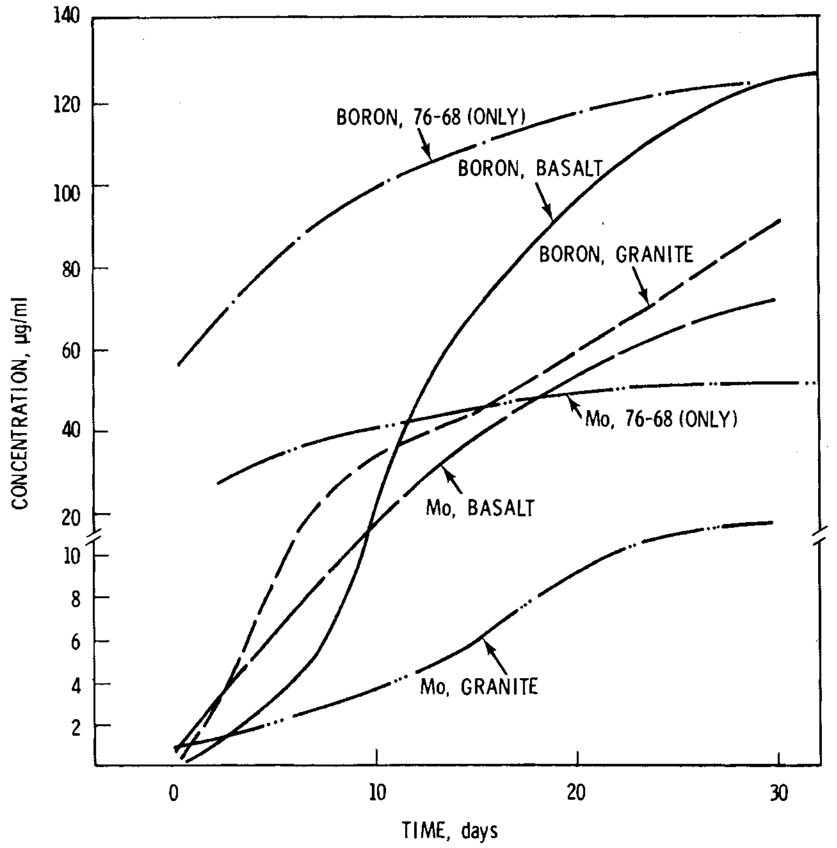

FIGURE 16.1. Solution Concentrations as a Function of Time for Boron and Molybdenum from Waste Package Tests Compared with 76-68 Glass Without Rock Media Present

Basalt:

Minicanister + glass	49.4
Glass wafer	12.9
Basalt wafer	6.7
Basalt powder	136.8

Figure 16.1 shows the solution concentrations as a function of time for boron and molybdenum. The initial solution was DI water, so this illustrates the buildup of some of the most mobile glass components in solution as the solution itself interacts with the rock matrix. Also shown on Figure 16.1 are solution concentrations of boron and molybdenum from some gold-capsule autoclave tests with glass and water only at the same P and T but differing solution volume-to-surface-area ratio, 20:1 cm (as opposed to 10:1 cm for the gold-capsule tests). Figure 16.1 suggests that solutions in a basalt matrix have less effect in preventing the leaching of boron and molybdenum than do granite solutions. This may be the result of a greater probability of forming molybdate alteration products in a granite environment than in a basaltic one, although such an interpretation is entirely speculative at this point.

Figures 16.2 and 16.3 show solution data for silicon, sodium, and cesium from both waste-package and gold-capsule experiments. As reported previously, the high silicon content in solutions from basalt experiments may be the result of partial dissolution of the glass component of basalt rather than

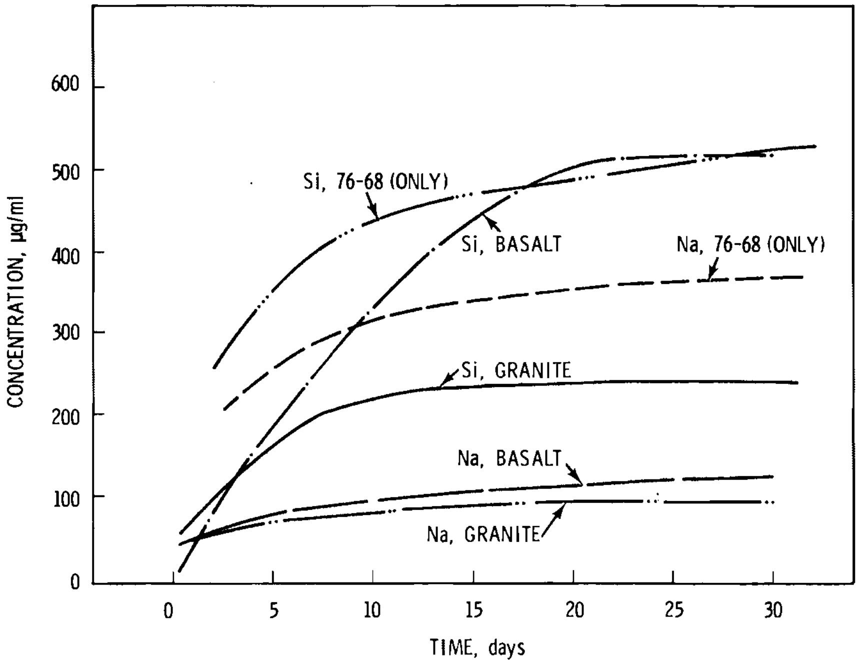

FIGURE 16.2. Sodium and Silicon Solution Concentrations as a Function of Time for Waste Package Tests Compared with 76-68 Glass Without Rock Media Present

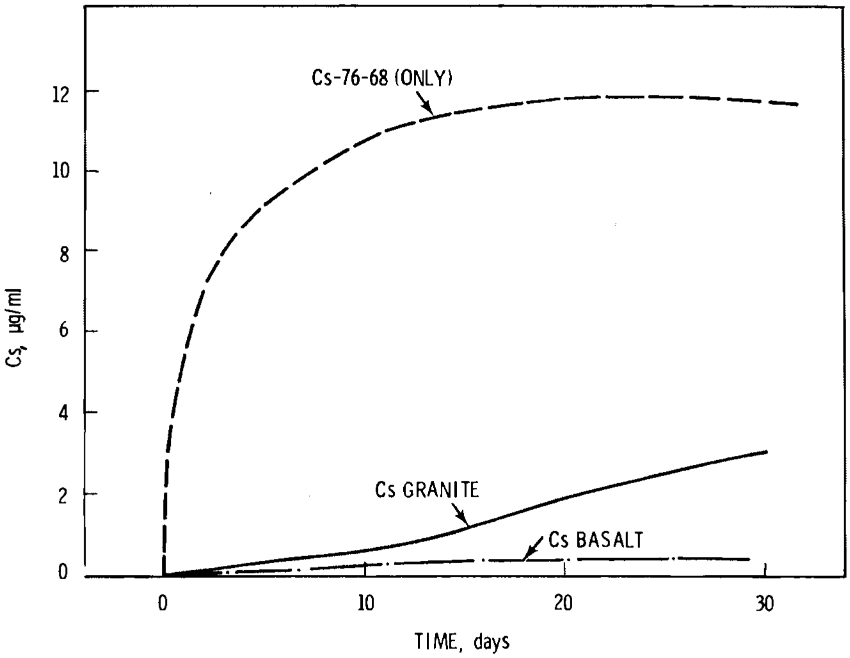

FIGURE 16.3. Cesium Solution Concentrations as a Function of Time for Waste Package Tests Compared with 76-68 Glass Without the Presence of Rock Media

the whole rock. A speculation on the different cesium concentrations in basalt and granite is that the granite originally has a higher cesium content than does basalt. Determining the source of elements common to several components can be achieved with spiked glasses or from experiments using fully loaded high-level waste (HLW) glass such as the one planned.

Table 16.4 shows concentrations of selected elements in solution from samples taken during autoclave cooling. It is interesting to note that the most mobile elements do not seem to change concentration significantly during cooling, although silicon is, as expected, considerably reduced. SEM study also showed a pervasive coating of silicon, probably as a gelatinous material, over all glass surfaces.

The test plan for the joint PNL-WIPP large-volume (5 gal) waste-package tests has been revised after receiving comments on the first draft. A large-volume (5 gal) autoclave has been identified for use in the first cold (UO_2)-doped 76-68 glasses test. A liner for this autoclave has been designed and is being fabricated. The liner will have a welded lid and will be pressurized by simultaneous internal and external pressurization to prevent soft corrosion of the autoclave. Appropriate fittings have been ordered, and instrumentation is being assembled.

The gold-capsule welder for the spent fuel tests has been tested outside the cell. After some minor cell maintenance is completed, it will be installed in the cell. Instrumentation has been checked out for the 50-ml autoclave currently in the cell. An accurate Heise bourdon tube gauge will be installed in time for use in pressure calibration.

Several informal discussions have been held with people working on the backfill-barrier program. As soon as it becomes available, a sample of engineered-barrrier material will be incorporated in the waste-package tests.

TABLE 16.4. Solution Concentrations During Autoclave Cooldown

	Basalt mg/ml						
	250°C	200°C	150°C	100°C	65°C	20°C	L[a]
Si	515	504	481	298	255	211	134
Ca	0.4	0.4	0.3	0.3	0.4	0.4	0.5
B	126	126	124	128	128	126	117
Cs	0.3	0.25	0.2	0.1	0.1	0.1	0.1
Mo	73	73	74	75	75	75	80

	Granite mg/ml					
	250°C	200°C	150°C	100°C	50°C	L[a]
Si	250	250	242	240	241	193
Ca	0.3	0.3	0.45	0.5	1.2	4.6
B	92	92	90	90	93	93
Cs	2.9	2.6	2.3	2.4	2.0	2.8
Mo	18	18	17.5	17.7	18.3	19.2

(a) Solution remaining in autoclave after cooldown and opening, analyzed 1 week after collection.

TRU Leaching Studies

A new set of portland cement specimens was prepared for modified IAEA testing at Brookhaven National Laboratory (BNL). This was done with the same series of leach solutions used at PNL to ensure uniformity in preparation and curing conditions. As such, the plutonium release data reported in the last quarter provides a degree of data replication. This specimen set also included one for static (25°C) testing in simplified bicarbonate-dominated ground water which, with specimens currently in leaching, completed that test's leachant matrix (demineralized water, WIPP brine B, and bicarbonate-dominated ground water) for plutonium release determination. Urea-formaldehyde and polyester-styrene specimens containing plutonium-contaminated incinerator ash were also prepared for modified IAEA leaching (in all five leachants) and for static (25°C) testing. Because of earlier data suggesting a relatively high rate of plutonium release from urea-formaldehyde (as compared to other waste forms), the static 25°C test for this waste form was conducted with only demineralized water as a leachant.

The following observation can be drawn from the data taken to date from the modified IAEA TRU leach tests:

- The leach rates decrease rapidly during the first week of leaching for all waste forms.
- Plutonium release from portland cement is highest in the $NaHCO_3$ leachate and lowest in WIPP B brine. The difference is about a factor of 30 at 53 days.
- Plutonium release from urea-formaldehyde samples is substantially more (up to a factor of about 400) rapid than from cement or polyester-styrene samples. The behavior is reversed with respect to cement; that is, in urea-formaldehyde samples, plutonium release is highest in DIW, NaCl and CaCl simulated ground waters, and lowest in $NaHCO_3$ and WIPP B brine.
- In polyester-styrene waste samples, plutonium release is affected much less by leach solution than the other waste forms; only a factor of about 3 difference is seen in cumulative release at 30 days. The plutonium release is very similar in value to that from cement.

Surface Science Studies

Waste glass 76-68 exposed to gamma radiation in deionized water showed strongly increased leaching rates when compared to unirradiated samples otherwise treated identically. These could be due to radiation damage to the glass structure or to the formation of reactive species by the radiolysis of water or of the air over the water. Water radiolysis can lead to the formation of H_2O_2 as well as reactive free radicals and ionic species.(1) HNO_3 is expected from air radiolysis in the presence of water.(2,3) A series of experiments were performed to evaluate contributions of the above possibilities to enhanced glass leaching with irradiation.

Leachate solutions were analyzed with ICP, and results are reported in Table 16.5. The leached glasses were examined with ESCA in combination with ion sputtering.

The highest dissolution rates at a given time and temperature were found for samples irradiated while leaching in the presence of air. Lowest rates were found for the unirradiated control, H_2O_2 leached, and irradiated prior to leaching samples. Intermediate rates were measured for samples leached in HNO_3 and for a sample irradiated while leaching in the absence of air.

TABLE 16.5. ICP Analysis of 76-68 Glass Leachates, ppm by Weight

Element	90°C 13 Days DIW GI[(a)]	90°C 13 Days DIW NI[(b)]	50°C 5 Days DIW GI	50°C 5 Days DIW NI	50°C 5 Days DIW IBL[(c)]	50°C 5 Days HNO_3, pH = 3.5 NI	50°C 5 Days 300 ppm H_2O_2 NI	50°C 5 Days DIW GI/AE[(d)]	50°C 5 Days HNO pH = 3.5 300 ppm H_2O_2
Na	130.0	18.5	5.0	1.8	1.0	2.4	0.88	4.7	2.2
Cs	-	2.2	-	0.13	-	0.18	0.045	1.8	0.16
Ca	7.8	1.0	0.80	0.18	0.13	0.37	0.099	0.41	0.39
Ba	0.8	0.1	0.19	0.03	0.03	0.09	0.014	0.07	0.08
Sr	1.4	0.2	0.14	0.03	0.03	0.07	0.014	0.07	0.06
Si	177.1	21.0	6.5	1.44	1.9	3.54	1.53	5.47	3.13
B	31.3	4.5	1.1	0.26	0.29	0.68	0.28	0.85	0.64
Mo	7.2	2.6	0.1	0.13	0.12	0.02	0.092	0.38	0.03
Zn	37.6	0.09	2.0	0.17	0.068	0.87	0.003	0.80	0.75
Nd	-	-	-	-	<0.02	0.72	0.00	0.13	0.62
Ce	-	-	-	-	<0.04	0.20	0.00	<0.003	0.17
Fe						0.30	0.00	0.015	0.36
Solution pH Before/After	5.7/4.6	5.7/8.5	5.7/3.3	5.7/7.2	5.7/7.2	3.5/3.9	5.3/7.0	5.3/6.5	5.3/4.0

(a) GI = Gamma irradiated
(b) NI = Not gamma irradiated
(c) IBL = Irradiated before leach
(d) AE = Air excluded

The pH of the leachate for irradiated specimens, except for the air-excluded sample, became acidic, as did the irradiated blank in DI water. Ion chromatographic analysis established a strong correlation between pH and the concentration of nitrate ions in solution. It can be concluded that HNO_3 is being formed under the experimental conditions where air (N_2) is present.

The effects of HNO_3 are particularly evident in the results of ESCA analysis. Figure 16.4 shows that the leached HNO_3 samples and the samples irradiated in the presence of air have neodymium removed from the near-surface region of the glass, while samples treated under all other conditions have neodymium enhanced at the surface. This enhancement is particularly strong in the case of the sample irradiated with air excluded. Similar results were obtained for zinc. Lanthanides and zinc may help to passivate the glass surface against further attack in slightly basic solutions. Thus removal of these elements in acidic solutions may explain some of the enhanced leach rate. However, the effect of radiation on the leach rate cannot be explained by HNO_3 attack only. In addition, the irradiated sample in the absence of air had a greater release rate than the control sample but less than the irradiated with air analog, again implicating reactive species in addition to HNO_3.

ESCA profiles of iron show increased near-surface concentrations under all conditions employed, with the strongest effects observed for the irradiated (with and without air present). Sodium depletion is greatest for the samples irradiated in air. It should be noted, however, that the depletion depth of sodium cannot account for all of the sodium detected in solution. Particularly in the case of the sample irradiated in air, extensive matrix dissolution

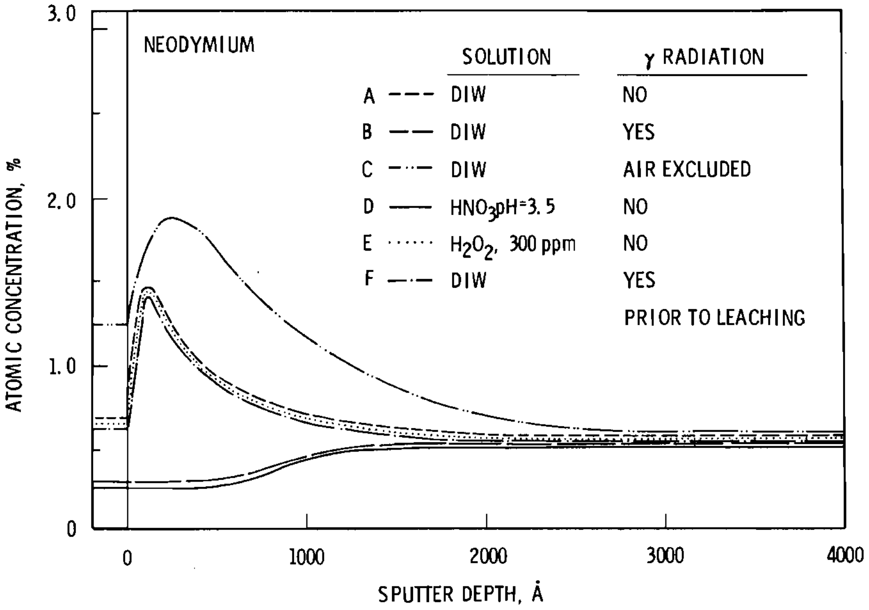

FIGURE 16.4. ESCA Profile for Neodymium Concentration in Glass Versus Solution and Radiation Treatment

must have occurred. The depletion depth of sodium represents less than one-tenth of the total sodium release, with the balance being due to the moving glass boundary (matrix dissolution).

ESCA shows silicon has been depleted to the greatest depth in the irradiated in the absence of air sample. However, ICP analysis reveals that silicon mass release is greater for the sample irradiated with air. The boundary of the glass may be retreating more quickly in that sample, reducing the apparent depletion depth of the silicon. The air-excluded sample showed a strong enhancement of zinc and lanthanides, slowing the rate of boundary retreat. It can be concluded that HNO_3 acid formation during irradiation in the presence of air can cause enhanced leaching due to the dissolution of the protective layer on the glass surface. This, however, can account only partially for the enhanced leaching observed in a gamma field. Some of the products of water radiolysis apparently also attack the matrix of the glass, causing enhanced reaction with the aqueous solution.

Spent Fuel Special Studies

These studies are to identify leaching mechanisms and determine leaching kinetics for the release of radionuclides from spent fuel during contact with aqueous solutions. Because the structure and microstructure of the spent fuel is complex, it is difficult to directly identify and understand the probable leaching mechanisms for spent fuel. Our research plan is to investigate the dissolution of the UO_2 matrix materials by studying single-crystal and polycrystalline pellets of UO_2. The knowledge thus obtained will be correlated to the leaching behavior of spent fuel.

During the previous quarter, we identified the effect of H_2O_2, which may be produced by radiolysis of water, to cause the formation of UO_3-hydrate scales. With time these porous scales increase in thickness and eventually crack, increasing dissolution. The work this quarter was concentrated on the effects of radiation, more specifically, to identify the radiation-induced surface activation.

Electrochemical measurement experiments made this quarter have confirmed the proposed mechanism for radiation-induced dissolution of UO_2. The radiation source used in the experiments was ultraviolet radiation (UV) of 40 mW/cm^2 intensity with a wavelength of <300 nm (>3eV). During an electrochemical dissolution experiment with single-crystal UO_2 in solutions of deionized water containing 300 ppm or 50 ppm H_2O_2, the application of this UV radiation increased the current density in the electrochemical cell twofold. This increased current density (indicating radiation-induced anodic dissolution) during electrochemical dissolution of an oxidized UO_2 surface was due to formation of UO_3-hydrate film, which is a semiconductor. Specifically, this film is an n-type semiconducting film with a bandgap near 4-5eV. Single-crystal UO_2 is a p-type semiconductor and was not susceptible to radiation-induced dissolution until an oxidized film of UO_3-hydrate was formed. Currently we are using hard x-rays as the radiation source. These results will be useful in planning future experiments demonstrating radiation-induced dissolution of UO_2 and spent fuel with gamma-radiation.

Work is in progress to design electrochemical cells and instrumentation for leaching spent fuel in a hot cell. A microprocessor-controlled potentiostat was purchased and received. Testing and calibration measurements are in progress. The leaching of spent fuel, in the hot cell, will be monitored continuously for identification of various leaching mechanisms and determination of the leaching kinetics.

Finely powdered UO_2 (fuel grade) was contacted (with continuous agitation) with deionized water, 0.015$\underline{M}$ $CaCl_2$ solution, 0.03$\underline{M}$ NaCl solution, 0.03$\underline{M}$ $NaHCO_3$ solution, and with WIPP B brine in order to determine equilibrium solubilities. Solution pH values were also determined at the beginning of contact and at each sampling time. Solutions have been set up with normal air, pure O_2, and argon as the gas phase. Solutions were thoroughly sparged with each gas to remove other dissolved gases. The solution in argon atmosphere contained iron powder or iron powder plus 0.0001$\underline{M}$ $EuCl_3$ as an electron carrier.

The solutions in contact with air have been sampled four times over a three-month period, and the equilibrium uranium solubilities appear to be ~10 ppm in deionized water, ~90 ppm in 0.015$\underline{M}$ $CaCl_2$, ~50 ppm in 0.03$\underline{M}$ NaCl, ~750 ppm in 0.03$\underline{M}$ $NaHCO_3$, and ~50 ppm in WIPP B brine at pH values of 5.7, 4.9, 5.0, 8.7, and 5.0 respectively. The deionized water has shown a twofold decrease in uranium concentration with time and may not yet be at equilibrium. The $CaCl_2$, NaCl, and brine solutions all showed a pH drop (from 6.7 - 7.2 to 4.8 - 5.0) as the uranium dissolved. These values seem too low for just CO_2 dissolution from air. The only apparent explanation for this pH drop during UO_2 dissolution is through formation of sodium or calcuim uranates or polyuranates as solid phases. A solution of 0.05$\underline{M}$ $(C_3H_7)_4NCl$ contacted with UO_2 for 15 days showed a pH drop from 7.7 to 7.3, and it is known that uranates of $(C_3H_7)_4N^+$ are quite soluble. All this points strongly to the formation of equilibirum solid phases of Na and Ca uranates in the Na^+ and Ca^{2+} containing solutions. Further sampling of all solutions is planned.

GEOLOGIC MEDIA-NUCLIDE INTERACTION STUDIES - J. F. Relyea

Evaluation of Experimental Methodology

Column experiments at PNL have shown a decrease in the effective porosity (as determined by tritium elution) of a column of crushed granite (12.7 cm long and 3.2 cm ID) as the flow rate increased from about 1×10^2 to 2×10^3 m/yr. The largest change in effective porosity occurred between flow rates of 530 and 1330 m/yr. The decrease in effective porosity from slowest to fastest flow rates was on the order of 10%, which would account for only a small part of the differences often observed between batch and column K_d values. However, in finer textured materials (with correspondingly smaller pores, porosity and water pathways) or intact low-porosity rocks, the decrease in effective porosity may be more pronounced with increases in flow rate. A decrease in the effective porosity of a column will result in a decrease in both the residence time for a radionuclide and the available surface area for radionuclide-rock interaction in a column experiment. Both of the above effects would confound the interpretation of the results. To generate useful data it is mandatory that flow rates in porous or fractured rock column experiments correspond to those expected in the geologic setting being investigated (on the order of 100 m/yr or less).

Batch and column methods were compared at Los Alamos Scientific Laboratory (LASL) using crushed argillite with ^{131}I and ^{95m}Tc as tracers. Flow rates in these experiments were 600 to 700 m/yr, which allowed a contact time of about 15 to 20 min between tracers and the rock. No retardation of iodine by the column was found (eluted with the tritium peak) in air or in a controlled atmosphere (<0.2 ppm O_2, <20 ppm CO_2). Technetium was retarded slightly (K_d of 0.3 to 0.4 ml/g) in both column experiments, but not nearly so much as predicted by the batch experiments (K_d = 31 ml/g in air and 175 ml/g in the controlled atmosphere). The batch K_d values were found to be strongly dependent on contact time; thus the low K_ds from column studies with short residence times are not surpising.

Argonne National Laboratory (ANL) has reported a comparison of 15- and 28-day batch adsorption experiments with column experiments using (Sentinel Gap) basalt and comparable cesium concentrations. The flow rate used in the initial column experiments was 5000 m/yr and yielded retardation factors that were an order of magnitude lower than retardation factors predicted by the batch experiments. Column experiments conducted recently at 430 m/yr yielded retardation factors that approached those found by the batch method. The maximum difference between batch and column retardation factor at the slower flow rate was only a factor of three.

A comparison of batch and column methods obviously must include residence time or contact time of the radionuclide with the rock. For sorption reactions that require hours or days to reach equilibrium, short contact times in short columns or at fast flow rates will preclude equilibrium conditions.

Mechanism Studies

Adsorption isotherms of strontium on argillite and basalt, neptunium on argillite, and plutonium and americium on basalt were investigated at Rockwell Hanford Operations (RHO). The desorption of strontium on all three rock types was also investigated as a function of time along with changes in the ground water chemical composition. Several interesting phenomena were observed.

The sorption isotherm for strontium on argillite was linear (constant K_d) over 5 orders of magnitude in strontium concentration from 10^{-10} to $10^{-6}\underline{M}$ strontium. This may indicate the presence of a natural strontium concentration of $\sim 10^{-6}\underline{M}$ maintained by the argillite. In the strontium-basalt experiment, natural or background strontium concentrations were low ($<10^{-7}\underline{M}$), and as the isotherm approached this level, the K_d increased drastically. This indicates a precipitation of strontium (probably $SrCO_3$, according to researchers at RHO).

The desorption studies of strontium from the three rocks indicated that strontium behavior closely follows that of calcium in argillite and granite. Over a 6-month period strontium and calcium concentrations were found to increase linearly with time in solutions contacting the argillite. Both elements were found to decrease with time in solutions contacting granite (however, magnesium increased for about 3 months and leveled off). In solutions contacting basalt, calcium concentrations increased slowly, but the scatter in strontium data was too great to say whether it really followed calcium or not. These results do show, however, that chemical analogs may be a useful tool in predicting behavior of some radionuclides (strontium-calcium and perhaps calcium-strontium-barium-radium).

The adsorption isotherms of neptunium on both basalt and argillite showed a decrease in K_d from $\sim 10^{-8}$ to $10^{-6}\underline{M}$. At concentrations above $10^{-6}\underline{M}$ the K_d increased, which (as in the strontium-basalt system) probably indicated the precipitation of some solid phase containing neptunium.

Sorption experiments with Hanford basalt yielded K_d values that decreased from about 4 to 2 ml/g with increasing plutonium concentration from $\sim 10^{-14}$ to $10^{-12}\underline{M}$ ^{237}Pu. Very little plutonium sorption work has been done at concentrations that preclude precipitation of plutonium as $Pu(OH)_4$. Plutonium K_d values this small are not usually expected or found, but the previous quarterly reported unusual behavior of plutonium on vesicular basalt at pH 4.0. The behavior of plutonium on basalt at RHO may be caused by complexation by CO_3 since the pH is ~ 9, but carbonate complexation of plutonium is not likely at pH values of 4.0 (the pH at which sorption of plutonium was low in previous work). The common element between the two studies at RHO and PNL is the basalt, which has a glassy phase that easily dissolves and releases silicon into solution. Several studies are yet needed to determine the behavior of plutonium in rock-water systems and the possible colloid or complex formation with silicon.

An attempt by RHO researchers to study the sorption of americium by basalt as a function of americium solution concentration showed that americium precipitates at concentrations above $10^{-11}\underline{M}$ if the pH is 8.5. At lower americium concentrations the K_d values were small on basalt, contrary to expectations. The behavior of plutonium and americium in solutions at high pH in contact with basalt should be investigated as it may have importance in the near-field environment if silica (rather than carbonate) complexation is the cause of low sorption. Silica solubility in the near field will be much higher than in far-field situations. If silica-actinide complexes are formed and transported to a lower temperature region, mineral precipitation may be the mechanism that controls the solubility of many transuranic elements in the repository.

Sorption isotherms of strontium and cesium on granite, argillite and tuff were conducted at LASL. The strontium results on all three rocks showed a constant K_d for tracer concentrations below the solution background levels of natural strontium from the rocks. At strontium tracer concentrations above the background level, K_d (strontium) was found to decrease with increasing concentration. Possible precipitation of $SrCO_3$ in the granite systems gave an apparent high K_d value for strontium at $\sim 10^{-3}\underline{M}$. Behavior of cesium on argillite and granite was similar to that of strontium except that there was no K_d increase at $10^{-3}\underline{M}$ cesium.

Site-Specific Data Generation

No work was performed in this area during the reporting period.

Methodology Evaluation Studies

No work was reported in this area during the reporting period.

Generation of Special Isotopes

A shipment of ^{95}Tc was sent to all interested WRIT subcontractors. ^{237}Pu and ^{235}Np irradiation and separations were performed. Shipment is expected in July.

NUCLIDE SOLUTION CHEMISTRY - D. Rai

Ground-Water Chemistry

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

Nuclide Solution Chemistry

The effect of $S^=$ and Fe(II) additions to tracer levels of $^{95m}TcO_4^-$ ($10^{-13}\underline{M}$) were studied in a WIPP brine solution containing vermiculite suspension. Separately or together, $S^=$ and Fe(II) reduced the Tc(VII). The sulfide added was observed to disappear within 4 hr of mixing; however, the reduction of TcO_4^- was slow and took about a day for a 50% decrease in concentration. An increase in pH during the equilibration time was also observed. After 10 days equilibration, the pH values of the samples were 0.3 to 1.5 pH units higher than those measured after 4 hr of equilibration. After 10 days a control sample [no $S^=$ or Fe(II)] addition showed 63% of the technetium in solution. Addition of Fe(II) dropped the soluble technetium concentration down to 10%; addition of $S^=$ dropped the soluble technetium concentration to 6 to 17%, depending on slurry pH. Addition of both $S^=$ and Fe(II) reduced the soluble technetium concentration to 4.8% after 10 days.

To study the leach rates of plutonium-containing wastes and determine plutonium migration potential, it is important to determine the solubility of plutonium compounds. Rai et al.(4) studied the solubility of ^{239}Pu(IV) oxide and hydroxide and observed a continuous decrease in sample pH with time. In response to this pH decrease, plutonium concentration increased proportionally. It was hypothesized that the decrease in pH was due to radiolysis effects of alpha radiation. The results discussed below show that the alpha radiation produced nitric acid, which was responsible for the observed pH behavior of air-equilibrated suspensions of plutonium compounds.

The hydrogen ion activity in PuO_2(c) and Pu(IV) hydroxide suspensions was plotted as a function of time. An increase of up to 5 orders of magnitude in H^+ activity occurred over a 3-year period for all types of plutonium suspensions. The increase in H^+ activity was accompanied also by a proportional increase in solution plutonium. The increase in H^+ ion concentration appears to be more rapid in the PuO_2(c) suspensions than in the Pu(IV) hydroxide suspensions. The rate of change, however, in the H^+ activity for both suspensions is proportional to the H^+ ion activity.

The plutonium solids remained near the bottom of the tube or attached to the stirring bar during the slow shaking periods. If the increase in acidity were due to radiolysis from only plutonium solution species, the plutonium hydroxide suspension should have about 100 times the rate of H^+ ion production at a given pH value. Within experimental uncertainty, both PuO_2 and $Pu(OH)_4$ suspensions have nearly the same rate of H^+ production for a given H^+ ion activity. This indicates that all plutonium in each tube (about the same for each suspension) is involved in the radiolytic increase in H^+.

Although the effect of alpha radiation on air/water systems to produce nitric acid has not been reported, Lind and Bardwell(5) published data showing NO_2 production from alpha radiolysis of N_2-O_2 gas mixtures.

To learn whether alpha radiation was oxidizing nitrogen into nitric acid, the nitrate concentrations in some of the Pu(IV) oxide and hydroxide suspension were determined after ~1000 days of contact time (Table 16.6). The pH and nitrate ion concentrations were also determined for $^{238}PuO_2$ suspension initially in triply distilled water. Because the original solutions did not contain NO_3^-, its presence should indicate the formation of nitric acid due to radiolysis. The results show that almost equivalent amounts of H^+ and NO_3^-, hence HNO_3, are produced in aged plutonium air-equilibrated suspensions (Table 16.6).

According to Wright et al.(2), the production of nitric acid is a result of the radiation energy deposited in the gas phase. The ^{239}Pu alpha particle has a range of about 35 μm in water, which is equivalent to a top surface volume of 1.8×10^{-5} cm^3. If one assumes that, at most, one-half of the alpha particles escape from the surface volume and deposit their energy in the air and that all the NO_2 (g) produced in the gas phase is converted to HNO_3 in solution, the highest rate of H^+ production observed (2×10^{-5} M/ℓ/day) would require over 7 g of ^{239}Pu in 20 ml of solution used in this experiment. This estimate greatly exceeds the solubility limit of $^{239}PuO_2$(c) in a solution of pH 2 and even exceeds the total plutonium compounds present in each tube. Therefore it is concluded that the nitric acid is produced from radiolysis of dissolved N_2 and O_2 (radiolysis of water can be an additional source of O_2).

TABLE 16.6. Effects of Alpha Radiation in Plutonium Solutions under Atmospheric Conditions

Sample	Contacting Solution	Contact Time, days	Log H+, Moles/ℓ	Log NO_3,(b) Moles/ℓ
$^{238}PuO_2$-1	Distilled water	<1	ND(a)	ND
		1266	-1.52	-1.38 ± 0.02
$^{239}PuO_2$-4	0.0015M $CaCl_2$	<1	8.5	ND
		1028	-2.65	-2.66 ± 0.04
$^{239}PuO_2$-15	0.0015M $CaCl_2$	<1	5.5	ND
		1021	-2.95	-3.14
$^{239}Pu(OH)_4$-10	0.0015M $CaCl_2$	<1	-7.0	ND
		1208	-2.15	-2.39 ± 0.03
$^{239}Pu(OH)_4$-22	0.0015M $CaCl_2$	<1	-4.0	ND
		1021	-2.10	-2.58 ± 0.13

(a) ND = not determined.

(b) Although nitrate concentrations were not determined at <1 day contact time, the NO_3^- at this time should be absent because the starting suspensions were made in distilled water. The reported concentration for each sample is an average along with the standard deviation from two or three measurements. Only one measurement was made for PuO_2-15 sample.

These results show that N_2 (gas) (the only source of nitrogen) was converted to HNO_3 due to alpha radiation of suspensions of plutonium compounds. The intermediate reactions for HNO_3 production were not identified. However, the final concentration of H^+, NO_3^-, and plutonyl ions were identified as the end products.

Solubilities of Compounds

Studies are being conducted to determine whether the plutonium and neptunium concentrations in solutions contacting doped glass beads are governed by a solid phase of the elements.

Pu/Np-doped glass beads were contacted with a dilute salt solution (0.0015M $CaCl_2$) containing quinhydrone (a redox buffer). The suspensions of crushed glass beads and the dilute solution were adjusted to pH values ranging from 3 to 8. The results on neptunium concentrations in 0.015 and 0.0018 mm filtrates were reported last quarter. It was also reported that quinhydrone effectively controlled the redox potential.

The concentrations of plutonium in the 0.015 and 0.0018 mm filtrates were similar, suggesting that the colloidal particles >0.0018 mm were not present in the solutions. When PuO_2(c) was added to the suspensions (Figure 16.5), the concentration of plutonium in solution did not change substantially, suggesting that the plutonium concentrations in solutions contacting glass beads may be controlled by PuO_2(c) or a solid similar in solubility to PuO_2(c).

To assess the potential environmental consequences of storage of plutonium-containing wastes in soils or geologic formations, plutonium migration rates must be estimated. These rates are affected not only by adsorption on the soils or geologic formations, but also by the plutonium solubility in the hydrologic environment. Further plutonium polymers are known to form, and their fate in the geosphere needs to be determined.

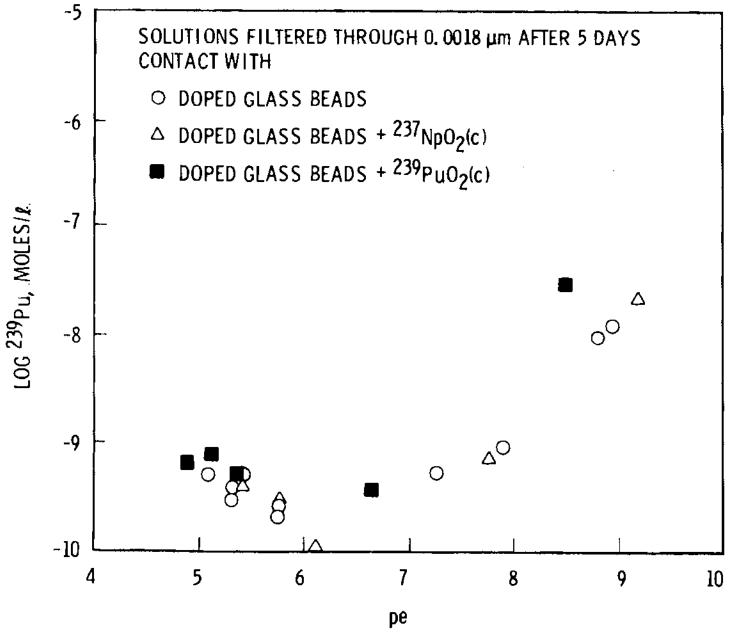

FIGURE 16.5. Plutonium Concentration in Solutions in Contact with Crushed Glass Beads

The following summary contains the results of six experiments in which preformed polymer solutions were adjusted to higher pH; five experiments in which precipitated (by hydroxide), preformed polymer was contacted with fresh solution; one experiment in which precipitated (by heating), preformed polymer was contacted with fresh solutions; one experiment in which a dilute Pu(IV) monomer solution was rapidly pH-adjusted; and two experiments in which rapidly precipitated Pu(IV) hydroxide was contacted with fresh solutions.

All the data from these different types of experiments fall in a general band that is intermediate between the solubilities reported earlier for amorphous Pu(IV) hydroxide and for crystalline PuO_2. While the data are generally comparable, there do appear to be some significant differences:

1. Preformed polymer exhibits higher solubility (by a factor of about 3) in nitrate solutions having ionic strengths of 0.02 to 0.04 than in dilute ($10^{-3}\underline{M}$) chloride solutions. The nitrate solution data include approaches to equilibrium from both directions; the close agreement indicates that an equilibrium condition was indeed achieved in these experiments.
2. Preformed polymer that has been heated exhibits lower solubility than that which has not been heated.
3. Rapidly precipitated Pu(IV) hydroxide has a higher solubility than does preformed polymer. The hydroxide solubility measured in this work is not as high as reported earlier by Rai et al.(4)

The plutonium in 2-nm filtrates from these experiments was essentially all Pu(V) and/or Pu(VI), as shown by the TTA extraction tests. The test results typically indicated that 1% or less was Pu(III) and/or Pu(IV) and that 85% or more was Pu(V) and/or Pu(VI). The close agreement between the sum of the ionic species and the total plutonium indicates that plutonium polymer was not passing through the filter in significant amounts. One preformed polymer solubility solution (pH 3.2) was tested by a spectrophotometric method and was found to contain Pu(V) rather than Pu(VI), Pu(IV) or Pu(III). Thus the oxidation state found for the soluble plutonium in equilibrium with plutonium polymer is in complete agreement with that found earlier for Pu(IV) hydroxide and $PuO_2(c)$.

PREDICTIVE MODEL DEVELOPMENT - W. L. Kuhn

Data Banks and Data Reduction

The sorption information retrieval system (SIRS) was demonstrated this past quarter, using a limited data set. Most of the debugging is finished and code validation has begun. SIRS has been divided into three packages: data generation (e.g., data entry), analysis, and auxiliary. By separating generation from analysis, the chances of inadvertently damaging the data base are minimized; the generation package must be called out separately. A debugging routine has proved useful in checking candidate data for errors prior to entry.

Leach Modeling

A key question pertaining to glass leaching is whether leach mechanisms are reversible in the sense of the mechanism slowing down as released constituents concentrate at the glass interface. For reversible mechanisms the behavior in the glass must be coupled with mass transfer behavior in a leachate in order to model the resulting release, and it implies that the release can be controlled by mass transfer in the leachate. A likely place to look for reversible release is in static leach experiments, where released constituents are allowed to accumulate in the leachate. Then reversibility implies that a limiting concentration in solution is approached asymptotically. The limit cannot be interpreted as a thermodynamic solubility since the mechanism is not the dissolution of a simple crystalline phase, but the concepts are similar.

In recent experiments crushed 76-68 borosilicate glass (simulated commercial high-level waste glass) was leached in (initially) deionized water in a static leach test at 35°C. The solution concentrations of both sodium and molybdenum seem to be approaching a limiting concentration after 500 hr. A plot of concentration versus square root of time shows a poor fit to pure diffusion behavior, and a semi-log plot shows a poor fit to exponential approach to a limiting concentration.

By assuming solid-state diffusion and a proportionality between the concentration in the solid at its surface and the concentration in solution rather than a zero surface concentration, a good fit to the data was obtained for both sodium and molydenum. This approach is similar to that of White and Claassen,(6) who considered the case of a Freundlich isotherm relating surface and solution concentration. Assuming a linear "isotherm" and that a negligible fraction of the constituent in the solid is lost during leaching (implying that a flat concentration profile recurs at equilibrium), we get for the solution concentration:

$$\frac{C}{C_\infty} = \frac{mC}{C_0} = 1 - \epsilon^{\phi} \operatorname{erfc} \sqrt{\phi}$$

where:

C = solution concentration, g/cm^3
C_∞ = limiting solution concentration, g/cm^3
C_0 = initial concentration in the solid, g/cm^2
m = C_0/C_∞ = proportionality constant
ϕ = $m^2 s^2 Dt$
s = solid surface area/liquid volume, cm^{-1}
D = diffusivity in the solid, cm^2/sec
t = time, sec

The results of fitting this functional form to the data are shown in Table 16.7 and Figure 16.6. The value of s was 49 cm^{-1}.

For release controlled by diffusion only, such as for the zero surface concentration condition, the release described by

$$\frac{mC}{C_0} = \frac{2}{\sqrt{\pi}} \sqrt{\phi}$$

or equivalently

$$\frac{C}{C_0} = \frac{2}{\sqrt{\pi}} s \sqrt{Dt}.$$

This is shown by the dashed line in Figure 16.6.

The fitted diffusivities are in the right ballpark for ions in glass, but they need more scrutiny before we can say they're accurate. It's encouraging that both sodium and molybendum data are fit well by this functional form. The similar values of m are perhaps not unexpected since we assume the molybdenum in the glass is in the Mo^{+6} state, which is rather soluble.

TABLE 16.7. Empirical Constants Derived from Glass Leaching Experiment

Parameter	Sodium Data	Molybdenum Data
C_∞	3.75×10^{-5} g/cm^3	4.5×10^{-6} g/cm^3
m	7500	9800
D	7×10^{-18} cm^2/sec	6×10^{-18} cm^2/sec

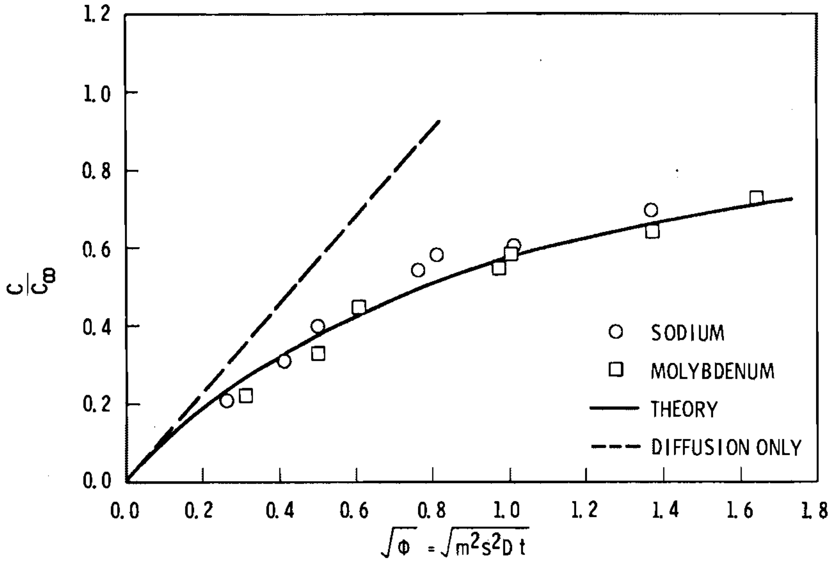

FIGURE 16.6. Plot of Reduced Concentration Data Versus Dimensionless Time. $s = 49$ cm^{-1}

Analysis of Sorption Kinetics

Laboratory column migration experiments discussed by M. G. Seitz et al. of Argonne National Laboratory rekindled interest in the analysis and especially extrapolation of laboratory data to distances and times typical of geotransport calculations. The sorption kinetics calculations discussed under this task in the October-December quarterly were reviewed, and a more revealing analysis was developed, based as before on classical ion-exchange chromatography theory.

If migration of radionuclides, say in a laboratory column experiment, is assumed to be controlled by linear sorption equilibrium and linear sorption/desorption kinetics, then, assuming dispersion is negligible, radionuclide migration is described by the classical equations of chromatography. From the equations it can be seen that a radionuclide peak at a column inlet will at first travel with the carrier velocity if sorption kinetics are not infinitely fast, and eventually reforms a retarded peak traveling at the expected velocity, reduced according to the linear sorption equilibrium coefficient. The transition from one behavior to the other depends on the number of theoretical mass transfer units, n, passed by the carrier fluid, where:

$$n = \frac{aK_a}{\varepsilon} \quad \frac{kx}{v}$$

a = surface area/volume in column, cm^{-1}
K_a = distribution coefficient based on area, cm
ε = void fraction in column
k = sorption kinetic constant, sec^{-1}
x = distance from inlet, cm
v = carrier velocity, cm/sec

Note that $K_a k$ is the desorption kinetic constant and aK_a is the same as the often-used K_d.

Values of $n = 10$ are required before the reformed, retarded peak begins to take its expected position according to the sorption coefficient. This then becomes the criterion for whether kinetics are important, given the above typical assumptions, since once $n > 10$ the peak assumes its "equilibrium" position. From the definition of n, it's the carrier travel time, $\frac{x}{v}$, which determines whether kinetics are important; the velocity alone should not be used as a measure. Furthermore, for $n < 10$, the peak location relative to the carrier "front" (e.g., the location of a peak of a nonsorbing tracer) is not determined by the sorption coefficient alone, and the peak location seems to correspond to a smaller than actual sorption coefficient. Thus laboratory column experiments utilizing small lengths (x) and faster than realistic water velocities (v) may force n to be smaller than 10, which would elevate kinetics to an important role. Again extrapolation to probable long-term safety assessment scenarios leads to the conclusion that reaction kinetics observable in short-term laboratory experiments are fast enough to be modeled by equilibrium concepts. That is, if kinetics are important to modeling real scenarios, the rates would be so slow that normal laboratory experiments could not detect the slow changes.

Geochemical Modeling

Through a subcontract with Lawrence Livermore Laboratories, the chemical thermodynamic code EQ3/EQ6 was applied to model basalt/water interactions to familiarize WRIT staff with the code. Table 16.8 shows the basalt and two water compositions that were used for the calculations.

The EQ3, or "speciation" code, was run separately to investigate the assumed initial water compositions. The deep Hanford groundwater compositions reported by Apps et al.(7) (Table 16.8) were found to be supersaturated with some clay minerals. The current disagreement between "theory" and field observations could be due to slow kinetics of clay precipitation, or uncertainties in the thermodynamic data base or field ground-water measurements; as yet we do not know if the apparent supersaturation is significant.

The EQ6, or "reaction path" code, was run to see if a reasonable assemblage of precipitated minerals is predicted, and that is the case. This gives us confidence in using EQ3/EQ6 to predict geochemical behavior in fresh fractures, to estimate changing deep ground-water composition with changing recharge rates, or to investigate other scenarios describing repository conditions.

PUBLICATIONS THIS REPORT PERIOD

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TABLE 16.8. Compositions Used for EQ3/EQ6 Calculations

Basalt		Initial Water Compositions				
Oxide	Mole Fraction	Distilled Water	Deep Hanford Ground Water			
SiO_2	0.55	pH = 7	Na^+	181 ppm	CO_3	27 ppm
Al_2O_3	0.09	Eh = 0	Cl^-	95 ppm	HCO_3	74 ppm
FeO	0.10	Temp = 37°C	K^+	2.0 ppm	SO_4	26 ppm
MgO	0.12		Ca^{+2}	0.26 ppm	F^-	21 ppm
CaO	0.11		SiO_2	153 ppm	pH = 9.8	
Na_2O	0.025				Eh = -46 mv	
K_2O	0.005				Temp = 36°C	

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17. SYSTEMS STUDY ON ENGINEERED BARRIERS

M. O. Cloninger - Project Manager

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

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

SUMMARY

The conclusions from the reference salt site analysis were modified based on the dispersion effects evaluation completed late last quarter. The reference shale site scoping calculations were completed. Redefinition of the reference basalt site was begun so as to utilize the latest Hanford basalt hydrologic and nuclide retardation data. The SAI Task 3.1 report was printed and issued. All modifications were completed on the BARIER code, and input files have been prepared for case runs during the next quarter. Documentation of the code was begun.

CONSEQUENCE ANALYSIS

Results from the evaluation of flow-field dispersion effects (as opposed to hydrodynamic dispersion effects) for a reference salt site indicated that the release rate of radionuclides from the waste package must be even lower than previously thought in order to provide any dose-reduction benefit. For a ground-water leach/transport scenario not involving any human intrusion into the repository or the contaminated aquifer, reducing the nuclide release rate generally resulted in no incremental benefit until the release rate was reduced to below about 10^{-6} yr^{-1} (fractional). This is because flow-field dispersion distributes the dissolved nuclides in time and space so that the overall result is equivalent to approximately a 10^{-6} yr^{-1} release rate. Order-of-magnitude accuracy is assumed, and the magnitude of the effect varies with ground-water transport distance.

Scoping calculations have been completed for reference granite and shale sites. They are now being analyzed to determine whether further detailed study is likely to yield any conclusions on engineered barriers incentives other than those of the detailed reference salt site study. Redefinition of the reference basalt site was begun to permit use of the most recent Hanford basalt hydrologic and nuclide retardation data. The scoping calculations for the basalt study will begin early next quarter.

BARRIERS PERFORMANCE ASSESSMENT

During the past quarter all necessary modifications were completed to the BARIER code and its subroutines. The new code has been debugged and checked for errors in sample test runs and is ready for analysis of a number of cases.

The new code improves essentially all subroutines. Heat transfer calculations now include heat transfer by radiation as well as conduction. Some sample calculations have been made to show that free convection terms are about equal to transfer rates by conduction. Two types of heat transfer calculations are made: maximum steady-state temperature if package remained intact (this is an initial check to screen packages having insufficient conductivity), and temperature of each barrier element as a function of time during the failure period.

A new data base has been developed to support the corrosion subroutine. Specific corrosion rates are chosen on the basis of existing conditions such as ground-water chemistry, oxygen availability, and temperature. For each material and set of conditions, the model uses the maximum corrosion rate from a group of values catalogued according to mechanisms (bulk corrosion, pitting, or crack propagation). The data base was developed from an extensive literature survey and discussions with a number of corrosion experts. Better data are still needed but will be available only from specially tailored tests in support of barrier performance analysis.

The nuclear radiation subroutine was completed during the quarter. A simple cylindrical geometry shielding model was developed from a buildup factor approach. Based on the assumption that 6.5-year-old, 33,000 MWD/T PWR fuel is charged to the repository, a time-dependent photon source was developed from ORIGEN runs. The subroutine calculates the exposure in R/hr of a barrier element as a function of time. The radiation level at the time of barrier element failure is reported.

Also completed is the release rate subroutine that assesses the rate of discharge after the barrier elements fail and fuel leaching begins. The resistance to transport of degraded barrier elements is accounted for as well as diffusion and sorption properties of a backfill, if present. The model is developed from an analytical solution to a differential equation describing diffusion and sorption in a slab with flux boundary conditions. The assumed slab geometry introduces some conservatism but allows for much simpler calculations.

Input files have been prepared for several pertinent design cases and for parametric studies and are ready for case runs through the revised code. The cases include all the types of designs studied in FY-1979 work plus some improved designs developed from earlier study results. Once some final check tests of the code are completed, the design cases will be run. The case studies will be completed during next quarter.

Near the end of this quarter the preparation of an Interim Report was begun. The Interim Report will stand alone as a BARIER code manual which documents the code methods and provides user information for use of the code. The Interim Report will be issued early next quarter.

18. CRITERIA FOR DEFINING WASTE ISOLATION

R. D. Widrig - Project Manager

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

SUMMARY

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

The criticality studies focused on the amount and concentration of plutonium required to sustain criticality when dispersed in dry rock. This assumes that criticality occurs in a water-moderated situation, that the water is heated and expelled, and that the reaction continues--in essence, a worst-case scenario. Rock composition and density, and ^{240}Pu and ^{238}U concentrations were all shown to be significant factors in determining the conditions required for this scenario to take place.

The uranium ore deposit studies concentrated on better defining existing ore deposit concentrations and other physical characteristics, associated ground-water velocities, and ore-body leach rates. This information indicates that a spent fuel repository in contact with flowing groundwater, equivalent to conditions assumed for waste repository consequence analyses, is generally comparable to existing uranium ore deposits in Wyoming and New Mexico.

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

Calculations have been performed to determine the critical mass (Mc) of homogeneous spheres of plutonium dispersed in and reflected by dry rock material. Should a criticality occur in a water-moderated situation, the energy released would heat up and expel water. The purpose of these calculations was to determine the conditions that would be required for such criticality to continue if all water were expelled.

The calculations were performed using the AMPX(1) computer code system. Cross sections were prepared from the Oak Ridge National Laboratory (ORNL) 218 group criticality library(2) by multigroup averaging using the XSDRNPM(1) code. The cross sections were averaged over an E^{-1} spectrum into a 27-group format routinely used for criticality safety analyses at ORNL and PNL.(3) Resonance self-shielding was then calculated for specific mixtures using the NITAWL(1) code, and the cross sections were collapsed by multigroup averaging, using the XSDRNPM code, into five energy group sets. The resulting cross-section sets had four epithermal groups and one thermal group having an upper energy boundary of 3.05 ev.

Low plutonium concentrations were studied, since the selective accumulation of plutonium in rock or sand would require a scenario of leaching, aqueous transport, and deposition. The concentration range of 1 to 100 g/ℓ (0.001 to 0.1 g/cm^3) was investigated. Calculations started with a highly optimized base case--pure ^{239}Pu (no higher Pu isotopes) in rock material of 80 wt% SiO_2 and 20 wt% Al_2O_3. This material approximates granite except that neutron absorbing materials are ignored. The density was assumed to be that of solid rock, about 2.9 g/cm^3.

For the base case, over the concentration range studied, Mc was calculated to have a minimum value slightly less than 18 kg. That occurred at a concentration near 7 g Pu/ℓ (0.007 g/cm^3) and corresponds to a sphere of radius about 85 cm. That result is unrealistically low due to the unrealistically optimized base case--e.g., the isotopic purity of the plutonium, the lack of parasitic neutron absorbers, and the assumption that the rock material is at full density (except for the small amount displaced by plutonium in the form of PuO_2).

The effects of replacing the overly conservative assumptions of the base case were explored parametrically. Replacing some of the Al_2O_3 by Fe_2O_3, so that the rock contained 4 wt% Fe_2O_3, increased the minimum Mc (over the range studied) to slightly less than 25 kg. That occurred at a concentration of about 8 g Pu/ℓ and corresponds to a sphere of radius about 91 cm. Reducing the density of the original rock by 30% void (conceivable for a sand deposit) increased the smallest Mc to slightly less than 36 kg at a concentration near 5 g/ℓ (a sphere about 120 cm in radius).

The plutonium in spent fuel contains the neutron-absorbing isotope ^{240}Pu in amounts which depend upon the duration of in-reactor exposure and the radioactive decay time after discharge. Calculations were performed assuming that different fractions of the plutonium were ^{240}Pu. The rock was assumed to be full density with no iron. For 3% ^{240}Pu the smallest Mc (over the range studied) was found to be slightly less than 31 kg at a concentration near 5 g Pu/ℓ. For 10% ^{240}Pu Mc was found to have a local minimum near 5 g Pu/ℓ (about 180 kg) but to be smaller at 100 g Pu/ℓ (about 110 kg) and to be decreasing with increasing concentration. (As neutron absorption is increased, a higher concentration of fissile material is required for criticality.) Further increasing the ^{240}Pu content to 25% yielded the result that criticality could not be achieved with even an infinite amount of material for Pu concentrations less than about 35 g Pu/ℓ. Above this concentration, however, Mc decreased rapidly from the infinite value to about 1350 kg at a concentration of 50 g Pu/ℓ, and down to about 260 kg at a concentration of 100 g Pu/ℓ. Large concentrations of ^{240}Pu are thus seen to be very effective in precluding criticality at low plutonium concentrations and in requiring large amounts of plutonium for criticality at higher plutonium concentrations.

Although the plutonium in spent fuel exposed to design burnup values contains roughly 25% ^{240}Pu, this fraction is not constant over time. The half-life of ^{240}Pu is 6.5 x 10^3 years, compared to 2.4 x 10^4 years for ^{239}Pu. Consequently, in the time frame around 10^4 years after discharge, the ^{240}Pu fraction of plutonium decreases. (Of course, the ^{239}Pu is decaying away also, but much more slowly.) Decay of ^{240}Pu yields ^{236}U, a less effective neutron absorber. To obtain an indication of the possible significance of this effect, the calculations for 25% ^{240}Pu were rerun with the ^{240} Pu replaced by ^{236}U. The results qualitatively resembled those of the calculation for 3% ^{240}Pu. Over the concentration range studied the smallest Mc was found to be slightly less than 29 kg of ^{236}U plus ^{239}Pu. This occurred at a concentration of about 8 g (U + Pu)/ℓ. Clearly, the effects of ^{240}Pu decay must be considered in more detailed evaluations of scenarios leading to separation of plutonium from other constituents of spent fuel.

The primary constituent of spent fuel is the nonfissile isotope ^{238}U. Any leaching, transport, deposition scenario resulting in selective plutonium accumulation will result in some uranium contamination of the plutonium. Consequently, calculations were performed assuming that ^{238}U was present along with ^{239}Pu in dry rock material. In fully burned spent fuel the ratio of ^{238}U to fissile atoms is about 45, and criticality is not possible in dry conditions. For an atom ratio ^{238}U/^{239}Pu = 9, criticality could not be achieved for any amount of material at concentrations below 100 g Pu/ℓ.

At lower ^{238}U/^{239}Pu ratios, however, criticality was found to be possible. Decreasing the ^{238}U/^{239}Pu ratio to 4 yielded the result that in the concentration range from 15 g Pu/ℓ down to somewhat less than 2 g Pu/ℓ criticality would be possible with a few hundred kg of plutonium. The minimum value of Mc was about 140 kg of pure ^{239}Pu, at a concentration of about 4 g Pu/ℓ in full-density rock. Further reducing the ^{238}U/^{239}Pu ratio to unity yielded a minimum Mc of about 29 kg at a concentration of about 5 g Pu/ℓ.

Contamination of plutonium by ^{238}U is thus a very significant factor in assessing the criticality potential of a leaching-transport-deposition scenario. Furthermore, the reader should note that these Mc values quoted would be increased by including in the calculation the effects of ^{240}Pu content, reduced density of the rock moderator (sand), and the presence of neutron-absorbing materials in the rock.

It is not possible to evaluate the accuracy of the calculational results because no benchmark critical experiments with plutonium moderated by materials such as aluminum and silicon have ever been performed. We have, however, used our calculational methods to analyze plutonium-rock systems previously studied at ORNL.(4) The ORNL calculations assumed a specific plutonium isotopic composition resulting from in-reactor fuel exposure. Primary constituents were ^{239}Pu, ~60 wt%; ^{240}Pu, ~25 wt%; ^{241}Pu, ~9 wt%. The rock composition assumed for the ORNL calculations was identical to that assumed for our calculations. Spherical geometry and full-density rock was assumed in both analyses.

Our calculations of the plutonium-rock system analyzed at ORNL yielded lower values of neutron multiplication over the range of concentrations that we studied. The ORNL calculations predicted Mc values of about 46 kg of plutonium for concentrations of 101 and 47 g Pu/ℓ and an Mc value of ~42 kg of plutonium for a concentration of ~22 g Pu/ℓ. In contrast, we found that for concentrations below ~28 g Pu/ℓ criticality could not be achieved with even an infinite amount of the plutonium-rock mixture. At higher concentrations Mc decreased rapidly, to ~640 kg of plutonium at 50 g Pu/ℓ and ~190 kg of plutonium at 100 g Pu/ℓ. The ORNL results are qualitatively similar to what we found for much lower ^{240}Pu concentrations. Approximations used in cross-section processing have been identified as the source of the discrepancy.

Considerable time and effort was spent in determining an unambiguous reason for the difference. Several different codes were exercised, and different cross-section sets and processing methods were used. Calculations using the KENO-IV Monte Carlo code(5) with Hansen Roach cross sections(6) supported the validity of our approach, with subcriticality predicted for plutonium concentrations below about 33 g Pu/ℓ.

The discussion of cross-section processing in the ORNL document(4) is extremely terse. A possible interpretation of the wording was determined to be that cross-section variations were incorporated only as a function of hydrogen content; for dry systems the effects of significant nonhydrogeneous moderation were not incorporated. Approximate calculations were performed which demonstrated that such cross-section treatment produced results indicating that criticality would be possible at concentrations well below 20 g Pu/ℓ. With this support for our conjecture, we telephoned the author of the ORNL document, who confirmed that we were correct. We conclude that our model more closely represents the actual physical situation.

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

Inventories of uranium in economic ore deposits of the Grants Mineral Belt, New Mexico (particularly the Ambrosia Lake District, the Gas Hills District, Wyoming, and the Shirley Basin District, Wyoming) approximate or greatly exceed the scheduled inventory of a waste repository. Concentrations of uranium range from 0.03% to 14% versus an average density of 0.16% for a repository. The uranium deposits occur in aquifers and are present at the surface and at depths exceeding 460 m compared to the nominal depth of a repository of 600 m. The median permeability of some ore-bearing strata is 230 m/year, and the gradient is 1.7%, resulting in a ground-water velocity of 3.9 m/year. The leach rate of a migrating ore body is about 0.15%/year. Equivalent values used in the consequences analysis of a waste repository are ground-water velocities of 0.1 to 10 m/year and a leach rate of 0.01%/year. The concentration of uranium in ground water from strata adjacent to an ore body is 60 ppb or less, and radium concentrations are commonly 5 pCi/ℓ or less. The concentrations of uranium from an assumed repository failure in contact with flowing ground water are calculated to be the same order of magnitude. The analogy between natural uranium deposits and waste repositories is quite close in many respects.

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19. SPENT FUEL AND FUEL POOL COMPONENT INTEGRITY PROGRAM

A. B. Johnson, Jr. - Project Manager

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

INTERNATIONAL ACTIVITIES

A. B. Johnson, Jr., attended a BEFAST(a) meeting in Paris, June 30-July 4, 1980. Delegates from the following countries attended: Austria, Belgium, France (four attendees), Federal Republic of Germany(b) (West Germany), Finland, Italy, Norway, Sweden, Switzerland, Spain, United Kingdom, and United States. The Nuclear Energy Agency (OECD)(c) and International Atomic Energy Agency (IAEA) also were represented. The delegates summarized spent fuel activities under way in each country. None of the countries has experienced problems with water storage of water reactor fuel.

The BEFAST committee was established as a forum to discuss issues and exchange information related to spent fuel and fuel pool component integrity and also to coordinate national programs to avoid duplication and to provide a mechanism for international cooperation in spent fuel research and development programs where joint programs are desirable.

ACQUISITION AND EXAMINATION OF SPENT FUEL - W. J. Bailey, E. R. Bradley and D. C. Langstaff

Prior quarterly reports(1,2) have indicated characteristics of spent fuel that is undergoing detailed examination to determine the status of cladding and assembly components after water pool storage. The fuel includes the following:

- one Shippingport fuel assembly (1512 GJ/kg U) with Zircaloy-clad fuel rods that has been stored in deionized water since 1964
- one partial Shippingport fuel assembly (336 GJ/kg U) with Zircaloy-clad fuel rods that has been stored in deionized water since 1959
- one Connecticut Yankee qualification fuel assembly (2701 GJ/kg U) with stainless steel-clad fuel rods that has been stored in boric acid pool chemistry since 1975.

The assemblies have been shipped to the Battelle Columbus Laboratories' hot cell at West Jefferson, Ohio. Visual examinations are under way on the assemblies. Both nondestructive and destructive examinations are planned for FY-1980.

These detailed examinations complement spent fuel examinations in Canada,(3) the

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(a) BEhavior of Fuel Assemblies in STorage.

(b) Two attendees: one from the Ministry for Science and Technology, and one from Kraftwerk Union.

(c) Organization for Economic Cooperation and Development, Paris, France.

Federal Republic of Germany,(4) and the United Kingdom,(5) directed specifically to define the condition of spent fuel after considerable water storage. This is the first stage of a DOE spent fuel surveillance program to acquire, characterize, and periodically examine spent fuel over the time needed to monitor the condition of spent fuel until its final disposition is decided upon and implemented.

Behavior of Fuel Pool Components

Stainless steel components from three PWR (boric acid) spent fuel pools have been examined. Results are summarized elsewhere.(6)

An additional stainless steel rack section from the Zion Reactor (PWR, boric acid) will arrive for examination within the next month. Sections of spent fuel pool components from two deionized water pools also have been requested:

- La Crosse (BWR) spent fuel pool, located at La Crosse, Wisconsin
- Receiving Basin for Off-site Fuel (RBOF) located at the Savannah River Plant, Aiken, South Carolina.

Specimens from these two pools are expected to arrive at PNL during late August.

Mechanism Studies - R. H. Jones

During 1979, seven through-wall cracks were identified in the 304 stainless steel pipes at the Three-Mile Island 1 (PWR) spent fuel pool. Similar cracks have occurred at several other PWR pools, although inspections of all U.S. PWR spent fuel piping systems suggest that only a small fraction of the systems have the cracking problem.

A section of cracked pipe from the Three-Mile Island (TMI) fuel pool was sent to PNL for analysis.(6) Metallographic examinations indicated that the cracks had occurred in the heat-affected zone adjacent to a circumferential pipe weld.

A program is under way to define the factors that caused the pipe failure. A series of constant extension rate tests (CERT) have been completed on furnace-sensitized sections of the TMI pipe to evaluate effects of O_2 and Cl^- concentrations on the IGSCC (intergranular stress corrosion cracking) of this material (see Table 19.1). Samples were cut from the pipe and were furnace sensitized at 620°C for 40 min. This thermal treatment was selected to provide the degree of sensitization approximating that in the welded pipe/elbow section.

Tests were conducted in air-saturated boric acid with 0 and 50 ppm Cl^- (tests 5 and 7) and with 1 ppm O_2 and no Cl^- (test 6). The corrosion potential was 180 ± 20 mV (saturated calomel electrode) in air-saturated boric acid, 150 mV in air-saturated boric acid + 50 ppm Cl^- and 100 mV in boric acid with 1 ppm O_2.

During CERT testing of the furnace-sensitized pipe samples, the mode of failure was ductile microvoid coalescence with about 100% elongation and 70 to 80% reduction of area. Clearly, there was no evidence of stress corrosion cracking in these tests. These results support earlier tests conducted on welded specimens where IGSCC was observed only when the original pipe inner diameter surface was intact. Removal of this surface, which makes the as-welded and furnace-sensitized samples similar, removed the IGSCC for the conditions of our test. Therefore, the latest results support the conclusion that crack initiation sites on the ID surface of the as-welded pipe are important to the susceptibility of 304 SS to low-temperature IGSCC in boric acid.

TABLE 19.1. Summary of CERT Test Parameters and Results

Test Number	Specimen Type	Test Solution	Temp., °F	Cross-Head Rate	Ultimate Stress, MPa	Fracture Strain, %	Reduction of Area, %	Time of Test, hr	Fracture Mode
1	Full thickness, Welded	Air saturated 13,000 ppm H_3BO_3	90	10^{-3} mm/min (7×10^{-7} in/s)	---	Test was not to failure 42% in HAZ	--	285	IG cracks on ID surface 1 to 9 mm from weld
2	Full thickness, Welded	Air saturated 13,000 ppm H_3BO_3 + 15 ppm Cl^-	90	10^{-3} mm/min	657	63 (52)	41	265	~75% IG to 0.2 mm from ID mixed IG and ductile remainder
3	Milled, Welded	Air saturated 13,000 ppm H_3BO_3 + 15 ppm Cl^-	90	10^{-3} mm/min	554	53 (100)	63	222	Ductile
4	Full thickness, Welded	Air saturated 13,000 ppm H_3BO_3	90	10^{-3} mm/min	614	67 (116)	69	285	Ductile
5	Furnace-sensitized pipe, 620 C/40 min	Air saturated 13,000 ppm H_3BO_3	90	10^{-3} mm/min	607	98	69	~417	Ductile Ec = +180 ± 20 mV
6		1 ppm O_2 13,000 ppm H_3BO_3	90	~3×10^{-3} mm/min	616	--	75	145	Ductile
7	Furnace-sensitized pipe, 620°C/40 min	Air saturated 13,000 ppm H_3BO_3 + 50 ppm Cl^-	90	3×10^{-3} mm/min	624	109	78	143	Ductile

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20. ANALYSIS OF SPENT FUEL POLICY IMPLEMENTATION

M. K. White - Project Manager

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

SUMMARY

No progress report was submitted for this period. The next quarterly report will cover results of the 6-month period.

21. ASPHALT EMULSION SEALING OF URANIUM TAILINGS

J. N. Hartley - Project Manager

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

SUMMARY

Progress during the third quarter of FY-1980 included carrying out laboratory and field studies. Uranium mill tailings samples were obtained from the Grand Junction tailings pile and chemically and physically characterized. Radon seals were formulated from a variety of asphalt emulsions and concrete sand. Radon diffusion measurements for admix seals were continued. The radon collection efficiency of activated carbon was determined at various temperatures and gas flow rates. The stability of asphalt as a long-term sealing material was reviewed, and initial weathering tests were started. Application technology for applying a radon-tight seal was reviewed. Several equipment screening tests were successfully carried out and included the use of a cold mix paver, slurry sealer, continuous portable pugmill and a concrete mixer truck. A field radon flux measurement system was designed, and fabrication was started. A field test was scheduled for August and September at the Grand Junction tailings site. Application of a radon-tight seal will be investigated using four application techniques.

LABORATORY STUDIES

Tailings Characterization - M. R. Elmore

Tailings samples were obtained from the Grand Junction, Colorado, tailings pile. A proposed test plot was divided into nine sections and samples taken from each. Characterization studies done or in progress for the samples include the following:

1. field moisture content
2. noting occurrence of sands and slimes
3. depth of overburden on the tailings
4. particle size distributions
5. deionized water leaching of the samples followed by cation and anion determination for the soluble materials
6. x-ray fluorescence analysis of the tailings
7. radionuclide counting
8. Eh and pH measurements
9. saturation-extract tests.

Screening tests were completed on the Grand Junction tailings as well as water leach tests on each of the samples. Results have just been received on the second half of the leach tests. Analyses were done using the induction-coupled plasma spectrometer (ICP). Results agree closely with the first half of the tests. Predominant cations are Ca^{++}, Mg^{++}, and Na^{+}.

Anion analyses showed the material to be mostly SO_4, followed by Cl^-, and then NO_3^-. XRF analyses are yet to be done because analysis of ash from the Mount St. Helens eruption took precedence.

Water-soluble salts were determined for Grand Junction tailings by deionized water leaches. Example results are given in Table 21.1.

TABLE 21.1. Major Water-Soluble Salts in Grand Junction Tailings, µg/g[a]

Ions	Sandy Tailings[b]	Slimes[b]
Ca^{2+}	3125	3475
Na^+	180	675
Mg^{2+}	120	310
SO_4^{2-}	7250	7450
Cl^-	382	1500
NO_3^-	118	1173

(a) Data is average of duplicate samples, 24-hr leaches at 20% solids and ambient temperature (20°C).

(b) Major difference between sand and slime tailings is the quantities of Cl^- and NO_3^- ions present.

Seal Formulation - P. L. Koehmstedt

The objective of this subtask is to develop asphalt emulsion seals to be used in the field tests. This includes optimizing asphalt emulsion seal mix designs, investigating the effect of impurities in the asphalt seal (e.g., herbicides), and determining the effect of different base asphalts.

Current mix design tests are being carried out using heated asphalt emulsions 100 to 130°F, the temperature at which asphalt emulsions are usually delivered to a field site.

Currently the most successful seals have been prepared using a cationic medium set (CMS) emulsion and concrete sand. A range of CMS emulsions with zeta potentials ranging from +54 mv to +90 mv have been tested. The best seal formation has been with the +56 mv and +78 mv cationic asphalt emulsions.

Performance standards are also being developed to ensure suitable asphalt emulsions for field application. Part of the standard will include a mix design test.

Several specimens of asphalt emulsions containing various concentrations of Treflan® herbicide were tested. The foaming occurring upon addition of large amounts of herbicide to the asphalt emulsion for the biobarrier tests has led to additional cores being tested before they are checked for root resistance. Although complete results are available only for herbicides of low concentrations, it initially appears the herbicide has no effect on radon sealing capability.

Asphalt emulsions produced from various grades of asphalt were tested to define the best mix design. This included some lower grade asphalts that had been chemically treated to improve their quality and thus their long-term stability. From the limited radon flux reduction data it appears the chemically treated asphalts could be used as an asphalt source for preparation of emulsions for fabrication of radon-tight seals. This would permit a wide selection of asphalt sources. These "improved" asphalts will be tested for their long-term stability properties.

Most asphalt emulsions from West Coast distributors that were tested failed to meet our criteria. Most of these distributors add hydrocarbon solvents to some of their

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emulsions, which apparently give, for our purposes, undesirable properties.

Radon Diffusion Measurement - H. D. Freeman

Several tests were run on the efficiency of activated charcoal as a radon collector. The parameters investigated were types of activated charcoal, bed configurations, temperature, and flow rate.

Several types of activated charcoal were investigated to determine if they are more efficient than the Pcb 8-12 mesh activated charcoal now being used. The activated charcoals differed in size distribution and chemical makeup. The results of the tests (Table 21.2) indicate that Pcb 8-12 mesh charcoal is the most efficient radon collector.

Three different bed configurations other than a No. 1 can were tried. These included a 1-5/16-in.-dia x 24-in.-long aluminum tube, a 1-5/16-in.-dia tube with O-rings spaced 1 in. apart, and a 1-7/8-in. x 24-in. convoluted steel tube. The results of these tests are shown in Table 21.3. The convoluted tube was the most efficient bed configuration and therefore was the bed configuration chosen for the rest of the tests.

The effects of temperature and flow rate on the efficiency of activated charcoal were studied using 400 g of activated charcoal in a 1-7/8-in.-dia convoluted tube. Flow rates of 2 ℓ/min and 4 ℓ/min were investigated at temperatures ranging from 0 to 60°C. Results of these tests are shown in Table 21.4.

Based on the results of these tests, a radon collection system using activated charcoal at ambient conditions at a flow rate of 2 ℓ/min was developed.

TABLE 21.2. Results of Radon Absorption Tests Using Various Types of Activated Charcoal

Tests	Radon Capture Efficiency, %
1-7/8-in. x 24-in. convoluted tube. Type-A activated charcoal	>99.9
T using Type-B activated charcoal	88.1
T using Type-C activated charcoal	99.5
T using Type-D activated charcoal	89.6
T using Type-E activated charcoal	58.8

T = 1-5/16-in.-dia x 24-in. aluminum tube.

TABLE 21.3. Results of Radon Absorption Tests Using Various Bed Configurations

Tests	Radon Capture Efficiency, %
1-5/16-in. x 24-in. tube (T)	96.0
T with 1/8-in. O-rings spaced 1 in. apart	96.4
1-7/8-in. x 24-in. convoluted tube	>99.9

TABLE 21.4. Summary of Radon Absorption Results Using 1-7/8-in. Convoluted Tubing

Temp., °C	Flow Rate, ℓ/min	Radon Capture Efficiency, %
0	2	>99.99
22	2	99.95
50	2	99.93
60	2	93.95
0	4	>99.99
22	4	>99.99
44	4	84.68
60	4	57.58

Seal Stability - R. L. Clark

Literature pertaining to asphalt degradation has been compiled and examined. These sources discuss several routes to asphalt degradation:

- oxidation (increased viscosity)
- photolytic (UV degradation, enhanced oxidation)
- evaporative (loss of maltene fraction)
- ozonolysis
- freeze/thaw cycling
- thermal (dehydrogenation and enhanced oxidation)
- microbial degradation
- chemical (aqueous).

Each of these routes will affect the durability of asphalt exposed to the atmosphere. Several of these routes are obviously related. An additional literature search has been performed regarding leaching and asphalt stability.

Most sources regard oxidation and evaporative processes as the rate-determining step to degradation. Oxidation is enhanced by photolytic (UV) and thermal exposures. Ozonolysis is difficult to separate from direct oxidation. Evaporative processes (the loss of low molecular weight materials) are enhanced by UV, thermal and aqueous exposures. The loss of the low-molecular weight fraction (maltenes) allows viscosity to increase, with potential embrittlement and loss of strength. The maltenes actually plasticize the asphalt layer.

The presence of a soil layer (overburden) will markedly decrease all degradation routes except microbial and chemical. Neglecting the "potential" reaction of inorganic salts and acids, the chemical route may continue to be active in asphalt degradation. This would be due to exposure to ground water or rain, which can be a mechanism for removal of maltenes.

All durability tests in the literature are directed at asphalt exposed to atmospheric conditions. Thus we are modifying two ASTM tests (D-1754 and D-2872) to reflect conditions expected at the Grand Juncton test site. The thin-film oven test (D-1754) and the rolling thin-film oven test (D-2872) are accelerated aging tests that determine the effect of heat and air on asphalt. The results can be related to atmospheric exposure. Initially we expect to decrease the oxygen content of the oven (nitrogen dilution) over a specific (low Po_2) range. We then plan to measure Po_2 under 1 to 4 ft (more, if necessary) of soil or sand. We hope to correlate the Po_2 to the durability.

We also are examining plastic and concrete weathering tests to determine whether any are applicable to this project. Analysis of weathered asphalt (Grand Junction site) will be helpful. Samples exposed to atmosphere and covered with overburden will be examined. Analyses will include IR, elemental analysis, and GPC or HPLC.

A sample of asphalt is being exposed to accelerated weathering and will be examined using the radon pressure-test apparatus. This should permit estimation of worst case (theoretical) radon diffusion.

Preliminary experiments to determine 1) the effect of accelerated weathering on asphalt emulsion seals and 2) the chemical stability of asphalt under severe conditions have been planned and the necessary materials obtained. The first experiment will measure changes in the radon flux through admix seals caused by exposure to salt brines and oxygen. The second experiment will test for changes in the chemical properties of asphalt after refluxing and/or autoclaving with different salt brines. The test cells for the accelerated weathering test were constructed. Several admix seals were prepared for weathering using five different base asphalts. Work was started in preparing dried emulsion samples for IR spectroscopy.

As part of the stability tests discussed above, portions of an admixture seal test specimen and Grand Junction tailings were leached at room temperatuture for 5 days in a variety of acid solutions at a pH of 2 to simulate a worst case at the Grand Junction tailings pile. The acids used in the tests were HNO_3, HCl, H_2SO_4, aqua regia, and HCl at 44°C. Weight loss data on each seal specimen, along with analysis of the leach solutions for 15 elements of interest, were obtained. Weight losses of the seals were all <0.43%, which can be attributed to the leaching of the exposed tailings and not to the asphalt itself. The major elements detected in the leach solutions were calcium, magnesium, aluminum, potassium, sodium, iron, and vanadium. Calcium, magnesium, and potassium, however, were about an order of magnitude lower in the seal leach solution than in the tailings leach solution. This suggests the asphalt effectively sealed the unexposed tailings from the acid solutions.

In the evaluation of existing seals and asphalt emulsions, the bitumen content of several admix seals was determined by centrifugally extracting the bitumen from the seal using trichloroethylene (ASTM D-2172). In all cases, the relative error of the nominal asphalt content from the true value was <11%. The water content of several asphalt emulsions was determined by refluxing the asphalt emulsion with xylene and collecting the water in a Dean-Stark trap (ASTM D-95). The water content ranged from 34 to 39 wt%.

FIELD STUDIES

Application Technology - D. J. Esterl and J. L. Buelt

The objective of this subtask is to evaluate the application technology for covering uranium mill tailings with reliable and durable asphaltic seals.

In April, two equipment screening tests were held near Sacramento, California, using the Mitchell Slurry Sealer and the Midland Cold-Mix Paver. Valley Slurry Seal of Sacramento and Thermobond, Inc., of San Francisco, respectively, were contracted to apply asphalt emulsion admixes containing up to 18 residual wt% asphalt.

In May, through review of the technical literature and conversations with industrial representatives, evaluations of four additional pieces of equipment continued: the portable pugmill, the concrete mixer truck, the hydrostatic soil stabilizer (Bomag MPH100), and the pneumatic gun.

During June, an equipment screening test was conducted in Eugene, Oregon, in preparation for larger scale field tests in August. A continuous portable pugmill and a concrete mixer truck were used to mix asphalt emulsion and concrete sand. An asphalt paver was then used to apply the mastic admix.

Cold Mix Paver

The objective of the cold mix paver test was to determine whether a Midland Cold Mix Paver can produce a mastic admix containing 20 wt% residual asphalt.

The Midland Cold-Mix Paver, admixtures were laid down using Union 76 cationic asphalt emulsions CSS-hl and CMS-2 with concrete sand used as the admix aggregate. Our activities encompassed laying several admixture strips 10 ft wide, totaling 600 ft in length. Several of these strips, 1-1/2 to 3 in. thick, were laid on a 1 in 10 slope, with only minor run-off of asphalt emulsion occurring. Several strips were laid down adjacent to each other to show how easily joints can be achieved.

Results of samples taken from the asphalt emulsion admixtures indicated that a seal could be obtained. Our initial observations, though, pinpoint the following problems with the Midland Cold-Mix Paver: 1) calibration and precision of the asphalt emulsion pump and aggregate feed mechanisms needs to be improved upon; 2) capacity of the asphalt emulsion pump should be doubled; 3) the admixture spreading mechanism needs to be either modified or replaced with one suitable for our purpose; and 4) a continuous feed system to the aggregate surge bin is needed. However, no insurmoutable problems were encountered.

Slurry Sealer

A Mitchell Slurry Sealer was tested with both Shell's CCS-1 and Chevron's cationic quick-set (CQS) asphalt emulsions. Several test strips, 8 ft wide, totaling 400 ft in length, were laid up to 1-1/2 in. in depth. One interesting feature of this testing was our attempt to form a thixotropic mixture, one that is very fluid when mixing but once laid down stiffens and has no run-off. This was accomplished by use of the additive aluminum sulfate. We will further investigate the potential of this additive in the laboratory, including its possible effect on long-term stability. We are awaiting results of lab analysis to evaluate the admixtures laid down by the slurry machines.

Our initial observation is that the Mitchell Slurry Sealer has severe control problems for our use. Areas needing many improvements for our application included: 1) doubling the capacity of the asphalt emulsion and additive pump, 2) calibration and improvement of the precision of the asphalt pump and the aggregate feed mechanism, and 3) a continuous feed system to the aggregate surge bin.

The slurry seal admixture spreader mechanism is good for applying mats up to 1-1/2 in. thick, using Chevron cationic quick-set emulsion.

Both of these machines seem to present no insurmountable problems to laying down a seal. Further equipment screening tests will now be directed toward finding systems exerting finer control over the seal application process.

Portable Pugmill

The objective of the pugmill test was to determine whether a portable pugmill can reliably produce a mastic mix containing 20 wt% residual asphalt. The pugmill was expected to give better mixing for a more complete coating of the aggregate by the asphalt, thus producing a more reliable radon seal.

The asphalt emulsion used in this test was a cationic, medium-set emulsion (CMS-2) produced by adding hydrocarbon solvents to a rapid-set emulsion. Normally, medium-set emulsions would not be considered for fine aggregates such as tailings and <1/4-in. concrete sand, but because of the seal's high asphalt content, medium-set emulsions are well suited to this application.

The equipment-screening field test in Eugene showed that a portable continuous pugmill can be used to mix concrete sand and asphalt emulsion, forming an admix with 20 wt% asphalt. Certain precautions, however, must be observed when applying such equipment to cover technology:

- Measures must be undertaken to ensure the high emulsion content in the admix. This could easily be achieved by larger emulsion pumps.
- Pugmill calibration is affected by numerous factors. At least two days of the summer field test must be allowed for initial calibration and frequent checks performed during operation.
- Automated pugmills are preferred for ease of control and calibration.

Concrete Mixer Truck

In conjunction with the pugmill field tests, a cement mixer truck was also tested as a portable batch mixer for asphalt emulsions and concrete sand. The objective of testing the cement mixer was to determine whether mixing is adequate for sufficient coating of the aggregate particles. The batch mixer offers greater convenience in handling, transportation, asphalt incremental addition rates, and calibration.

Paving and compacting data with high residual asphalt mixtures were also gathered. The asphalt layed out with a Barbur Green paver was compacted with a rubber-tired pneumatic roller. This compactor has an advantage over the vibratory, steel-wheeled compactor in that a kneading action helps remove the water, fill the voids, and compress the asphalt layer. The kneading action occurs from the different forces that result when the front and back tires, which are staggered, roll over the asphalt.

A data collection scheme was prepared for the field tests. Enough samples and data were collected to determine:

- temperature of the emulsion before mixing
- temperature of the aggregate before mixing
- moisture content of the aggregate before mixing
- mixing times and mixing rates
- paving rates and depth
- relative asphalt/aggregate contents
- moisture content before and after compacting
- final product characteristics.

Results were less encouraging because a very stiff mastic formed inside the mixer which was difficult to remove. With the portable mixer, a soupy, flowable product is desirable.

The batch mixer should be tested again with these considerations in mind:

- The emulsion should be added at high rates since long mixing times cause the admix to become too stiff.
- The mixer should not be revolving while adding the emulsion. This would limit the amount of mixing time so that a thick mastic solution does not form.
- The emulsion should contain no hydrocarbon solvent.

The third item tested in Eugene was a standard asphalt paver, and its performance was suitable for our purposes. The only problems were those previously encountered in use at the Midland Cold-Mix Paver. The screed must be supported, preferably hydraulically.

Hydrostatic Stabilizer

Improvements to the Bomag MPH100 hydrostatic stabilizer have been made by the manufacturer. Though one is not readily available on the market, efforts are under way by Koehring to have one ready for the field tests in August.

The main improvements include an automated asphalt feed control and a new machine design to minimize grade variations by at least 50%. Asphalt is automatically metered to the aggregate as a function of the engine speed. This will greatly help control the asphalt content to near the desired 20 wt% level.

Pneumatic Guns

The use of pneumatic guns normally used for gunite, shotcrete, etc., was reviewed as a method of supplying asphaltic seals on a technical and economic basis. Though technically the guns have some definite applications, they are not economical to operate at a large-scale operation such as at tailings sites where conventional pavers can be used.

The application rates that can be expected with a pneumatic gun with asphalt are between 5 and 10 yd^3/hr. This compares to 120 yd^3/hr attainable with the hydrostatic stabilizer. Since the guns require large capital investments because of the air compressor requirements, they would not serve as substitutes to pavers. There are technical advantages, however, in using pneumatic guns to apply asphalt seals to seams, sloped dike walls, and spot patching. Because the asphalt is applied at high velocities, no compacting is required. Many types of guns and nozzles are available. Technical evaluations are currently under way so that field testing can take place in August.

Radon Measurement Systems - H. D. Freeman

Based on the data obtained from the activated charcoal tests, a field radon measurement system has been designed and is being fabricated for use at the Grand Junction tailings pile. A radon measurement plan for the Grand Junction field test this August has been completed. Eighty radon measurements for the asphalt emulsion system and 32 measurements for the multilayer system will be made before and after seal application. The radon tents are to be calibrated in July.

Field Test - J. N. Hartley and D. J. Esterl

The objective of the FY-1980 field test is to investigate the effectiveness of asphalt emulsion sealing system consisting of: 1) site preparation, 2) seal application, 3) biobarrier application (herbicides and rock) and site reclamation (overburden, riprap, revegetation). The field test is scheduled to be held at the Grand Junction tailings site from July 28 to September 30, with the various seals being applied during August.

As discussed earlier under "Application Technology," the equipment to be tested for seal application includes a soil stabilizer, a cold-mix paver, a pugmill and paver, and a concrete truck/paver or a batch plant/paver. Also being considered is a batch plant/paver combination using a selected hot asphalt-sand mixture. Laboratory radon diffusion tests are being run on hot mix cores before a decision is made.

The test area selected for seal application is about 250 ft x 250 ft and is just east of the FY-1979 field test site. Contract negotiations are under way for a general contractor, application equipment, asphalt emulsion, and supplies. A field test outline and schedule was prepared. Site preparation will begin July 27, and seal application will begin August 13.

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

J. F. Cline - Project Manager

The objective of this project is to develop and evaluate the effectiveness of physical and chemical barriers designed to prevent the breaching of uranium tailings containment systems by plants and animals for approximately 100 years.

SUMMARY

Six polymeric carrier/delivery (PCD) systems were produced to test for their potential use as barriers to plant root intrusion of uranium tailings sealants. Treflan® release rates were determined for three of the above PCD systems. The rates varied between 6.6 and 91.7 μg of Treflan/cm^2 of polymer/day. Phytotoxic screening studies showed that ~0.2 μg of Treflan/g of dry soil was an effective concentration to inhibit root growth.

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

Organic polymeric materials that permit sustained and controlled release of phytotoxins at well regulated rates are being developed to prevent plant root intrusions of sealants placed over uranium mill tailings. Certain herbicides are available that prevent root growth in the treated zones but do not kill or harm other plant parts. Treflan, one of this type, was selected as the first herbicide.

Several polymers (listed here) were judged to have properties suitable for the preliminary screening studies:

- two types of silicone rubber
- polyethylene-vinyl acetate
- polyethylene
- polyetherpolyurethane
- polypropylene
- thermoplastic elastomeric polyester
- polyamide
- polyolefin copolymer elastomer.

Treflan is being studied with various organic matrices. These include not only homogeneous mixtures of Treflan with the polymer, but also polymer/chemical reservoirs surrounded by a polymer coating that controls the diffusion rate of the Treflan from the reservoir. Release rates were determined for three polymer matrix/herbicide systems. Six release systems from other polymer matrices have been prepared and are either in release-rate testing or waiting to be tested.

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

Analytical effort has involved the development of a new analytical method for Treflan, the purchase and construction of additional flow cells to determine release

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®Treflan is a registered trade name of Elanco Products, a division of Eli Lilly Co., Indianapolis, IN.

rates, and the estimation of the release rates for three polymers.

After difficulties with developing gas chromatographic methods, the possibility of a spectrophotometric method was pursued. In quantifying Treflan, a wavelength of 420 nm resulted in maximum absorption of Treflan with minimum absorption of Triton X-100.® To further reduce the interference of Triton X-100 in the absorption measurement, an extracted sample of the solution (Triton X-100/methanol/water) in the reservoir will be used as the blank. This procedure eliminates the need for an internal standard but increases the need for accurate determination of volume before determining the concentration in the spectrophotometer.

During May and June the three polymers listed in Table 22.1 were run in the flow system. Release rates were determined for six time periods ranging from 8 to 25 days after the flow testing began. There is some variability in the day-to-day release rates; one set of data from each polymer was excluded from the determination of release rates. All analyses were run in duplicate; the duplicate analyses generally agreed quite closely.

A spherical pellet 1 in. (2.54 cm) in diameter will weigh ~10 g and have a surface area of 20 cm^2. If this device were made of polyurethane and loaded with a 40% concentration of Treflan, at the above release rate of 6.6 $\mu g/cm^2/day$ the device would have sufficient Treflan to release for 83 years. (In fact, in the last years of its lifetime, the release rate of the device would slow down enough to extend release probably out to 100 years.) We therefore appear to have at least one good candidate for a polymer to be used as a release control barrier.

TABLE 22.1. Release Rates of Treflan from Three Polymers

Polymer Type	Release Rate, $\mu g/cm^2/day$
Polyurethane (sandwich)	6.6 ± 1.5 SD
Microthene 783 EVA	9.3 ± 3.3 SD
MDX4-54515 Silicone Rubber	91.7 ± 16.8 SD

PHYTOTOXICITY AND DEGRADATION STUDIES - D. A. Cataldo

This study is to define the short-term requirements for providing a minimal level of a phytotoxin effective in restricting longitudinal root development past the barrier. To be determined are 1) the effects of environmental variables on chemical and microbial decomposition of the PCD system and 2) the mobility of the phytotoxin in the soil following release from PCS system. These data are necessary for the development of PCD systems prior to laboratory and field testing.

Toxicity screening for Treflan to root growth is in progress using Russian Thistle and Ritzville silt loam soil. The first study used Treflan concentrations of 0, 0.1, 0.5, 2, 10 and 20 μg/g/dry soil. Longitudinal root growth was markedly inhibited at concentration >0.5 μg/g. Under the conditions of this study, 2.0 μg/g appears to be an effective concentration. This will set the minimal release rate for the PCD systems being developed and tested for laboratory and field tests. It should be noted that these minimal phytotoxic concentrations may need to be increased, depending on the rates of chemical and biological degradation. The latter will be investigated at some depth as soon as background data becomes available.

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ANIMAL INTRUSION STUDY - K. A. Gano

A list of burrowing small mammals likely to inhabit the various uranium milling tailings sites was compiled using range maps from Hall and Kelson, 1959.(1) The list was organized in Table 22.2 and matched with the sites where the species are likely to be found. The burrowing habits of potentially important species are also being investigated.

Construction of the animal intrusion test site as shown in Figure 22.1 was begun in June. Two enclosures have been completed using the multilayer earth sealant. The additional six enclosures (four using asphalt two control) are still under construction and are expected to be completed by mid-July. Ground squirrels will be placed within the completed enclosures.

REFERENCES

1. Hall, E. R. and K. R. Kelson, 1959. The Mammals of North America, Vol. I and II. The Ronald Press Co., New York, NY.
2. Department of Energy Environmental Control Technology Division, Office of Environmental Compliance and Overview Assistant Secretary of Environment, December 1979. Annual Status Report on the Inactive Uranium Mill Tailings Sites Remedial Action Program, DOE/EV-0060.

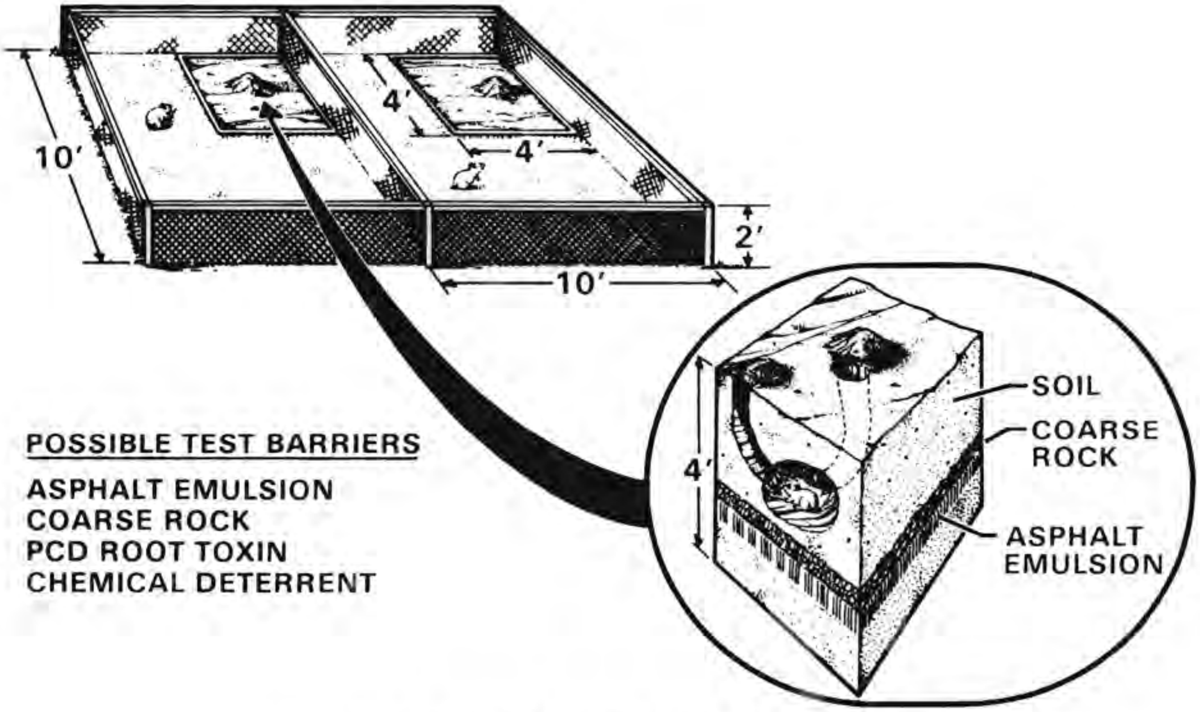

FIGURE 22.1. Design of Animal Barrier Test Facility

TABLE 22.2. Burrowing Rodent Species Possibly Associated with U-Tailings Sites

	Mill Tailing Sites$^{(2)}$																				
Order Rodentia - Rodents	High Priority								Medium Priority						Low Priority						
	Salt Lake City, UT	Durango, CO	Shiprock, NM	Grand Junction, CO	Riverton, WY	Gunnison, CO	Old Rifle, CO	New Rifle, CO	Mexican Hat, UT	Lakeview, OR	Falls City, TX	Tuba City, AZ	Naturita, CO	Ambrosia Lake, NM	Green River, UT	Slick Rock (NC), CO	Slick Rock (UCC), CO	Maybell, CO	Monument Valley, AZ	Lowman, ID	Converse County, WY
Family Sciuridae - Squirrels and Relatives																					
Eutamias minimus (Least chipmunk)	X	X	X	X	X	X	X	X	X	X		X	X	X	X	X	X	X	X		X
Eutamias amoenus (Yellow pine chipmunk)																				X	
Marmota flaviventris (Yellow-bellied marmot)	X	X		X	X	X	X	X		X			X		X	X	X	X		X	X
Ammospermophilus leucurus (White-tailed antelope squirrel)	X	X	X	X		X			X			X	X	X	X	X	X	X	X		
Spermophilus townsendii (Townsend's ground squirrel)	X									X										X	
Spermophilus richardsonii (Richardson's ground squirrel)				X	X	X	X	X					X		X	X	X	X			X
Spermophilus armatus (Uinta ground squirrel)	X																				
Spermophilus beldingi (Belding's ground squirrel)										X											
Spermophilus columbianus (Columbian ground squirrel)																				X	
Spermophilus tridecemlineatus (13-lined ground squirrel)				X	X	X	X	X		X											X
Spermophilus spilosoma (Spotted ground squirrel)			X						X		X			X					X		
Spermophilus variegatus (Rock squirrel)	X	X	X	X		X	X	X	X			X	X	X	X	X	X	X	X		
Spermophilus lateralis (Golden-mantled ground squirrel)	X	X		X	X	X	X	X	X	X					X					X	
Cynomys ludovicianus (Black-tailed prairie dog)																					X
Cynomys leucurus (White-tailed prairie dog)				X	X	X	X	X							X						X
Cynomys gunnisoni (Gunnison's prairie dog)		X	X			X			X			X	X			X	X	X	X		
Family Geomyidae - Pocket Gophers																					
Thomomys umbrinus (Southern pocket gopher)	X	X										X				X	X	X	X		
Thomomys talpeides (Northern pocket gopher)				X		X	X	X	X	X										X	
Geomys bursarius (Plains pocket gopher)											X										
Family Heteromyidae - Pocket Mice and Kangaroo Rats																					
Perognathus fasciatus (Olive-backed pocket mouse)					X																X
Perognathus merriami (Merriam's pocket mouse)											X										
Perognathus flavus (Silky pocket mouse)		X	X						X			X		X					X		
Perognathus apache (Apache pocket mouse)		X	X	X					X			X	X	X		X	X	X			
Perognathus parvus (Great Basin pocket mouse)	X									X										X	
Perognathus hispidus (Hispid pocket mouse)											X										
Perognathus intermedius (Rock pocket mouse)												X									
Dipodomys ordii (Ord's kangaroo rat)	X		X	X	X	X			X	X	X	X		X	X				X		X
Dipodomys spectabilis (Banner-tailed kangaroo rat)			X									X		X					X		
Dipodomys merriami (Merriam's kangaroo rat)			X																		

23. DEVELOPMENT OF BACKFILL MATERIAL (DBM)

E. J. Wheelwright - Project Manager

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

SUMMARY

This project was authorized in March 1980. Since then the five-member advisory committee has been selected, has met and has made recommendations; the detailed work plan has been completed and submitted; and the initial definition of backfill performance requirements has been completed. Major emphasis is on evaluation of expanding clays.

INTRODUCTION

Backfill materials are being investigated as barriers to supplement waste form and containers in reducing the possibility of radionuclide migration from spent nuclear fuel or separated high-level waste in geologic disposal. Increasing the redundancy of barriers via a properly placed multicomponent backfill could provide a high-integrity seal against ground-water penetration and could ensure selective sorption of specific radionuclides such as ^{129}I and ^{99}Tc if ground water were to penetrate and leach the waste. Backfill components can improve the chemical stability of the canister or overpack by controlling the Eh and pH of the immediate environment.

This project is to 1) define and prioritize the desired attributes (quantitative specifications, where possible) of the backfill material; 2) screen potential backfill materials (including multicomponent materials) and select a manageable number of candidates--i.e., 6 to 12--for laboratory evaluation; 3) evaluate, in the laboratory, candidate backfill materials, measuring their performance against the defined requirements and document the results to provide the basis for selection of the optimum material(s).

PROJECT ADVISORY COMMITTEE

Five consultants were selected and placed under contract to serve as an advisory committee to the DBM Project. The committee members and their areas of expertise are:

- R. A. Berner, Associate Professor of Geology and Geophysics at Yale University--specialty, geophysics
- A. Lerman, Professor of Geological Science at Northwestern University--specialty, geochemistry
- P. F. Low, Professor of Soil Chemistry at Purdue University--specialty, physical chemistry of soils and clays
- W. L. Lindsay, Professor of Agronomy at Colorado State University--specialty, ground water chemistry.
- R. Rollins, Professor of Civil Engineering at Brigham Young University--specialty, geotechnical engineering.

The project advisory committee met in Richland, Washington, on May 14 to review the project planning and to make recommendations. Following their return home, each consultant submitted a detailed written report. The committee's recommendations are summarized as follows:

1. The waste repository should be located in the driest possible location. A place like the Valley of the Kings in Egypt would be ideal. There is so little water that the soil is 30 to 40% calcium carbonate.
2. The backfill material should do the following:
   - minimize or eliminate the mass flow of water
   - minimize or eliminate diffusion of charged species
   - be thermally conductive
   - be resistant to radiation damage
   - be thermally and chemically stable throughout the life of the repository
   - maintain its integrity during seismic disturbances and other stresses
   - produce anoxic conditions around the canister.
3. The backfill will need to be a multi-component mixture or a multizone system of single-component materials.
4. Materials suggested for evaluation include:
   - compacted bentonite clay (Na-Volclay®)
   - compacted bentonite clay treated with dichloro-dimethyl silane vapor to render the surface of the particles hydrophobic
   - Bentone®--a montorillonite clay treated so as to make the surfaces oil wet
   - Cab-Oil-Sil®--very fine spheres (0.007 μm) of amorphous silica exposed to dichloro-dimethyl silane vapor to make it hydrophobic.
5. Emplacement of such backfill materials can be made using existing technology.

In his report, Dr. Low calculated that under typical subsurface hydraulic gradients, water flow velocity through compacted sodium-bentonite would be about 1 m in 1.5 million years. The diffusion of ions dissolved in the water would be a small fraction of this rate.

PRELIMINARY DEMONSTRATION OF A MULTIFUNCTIONAL BACKFILL MATERIAL

The objectives of this activity are to provide an early laboratory-scale demonstration of a multifunctional backfill material, and in doing so, to gain useful experience for use in designing the subsequent screening experiments.

Initial laboratory experiments include evaluation of pure bentonite clay plus clay mixed with other selected exchange materials. The tests will evaluate compaction properties, the permeability of the compacted forms in a dynamic-flow system, and the determination of the migration properties of selected ions of interest (e.g., ^{129}I, ^{137}Cs ^{90}Sr, and ^{99}Tc).

One-inch-diameter pellets of pure bentonite have been pressed to densities of 2 g/cm^3 at ~2 t/in.^{2}. The pressed pellets are mechanically stable and do not crack or crumble with reasonable handling. Additional pellets are being evaluated as a function of pressing conditions, water content, and clay-exchange material ratio.

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® Bentone is a registered trade name of NL Chemicals/NL Industries, Inc., Hightstown, NJ.

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

In initial experiments, a heavy-wall stainless steel cylinder with a fritted plate in the bottom was used to investigate the effects of pumping water through pressed bentonite clay. It quickly became evident that the clay must be constrained by a fritted plate also on top of the bed. The equipment is being redesigned to include this feature, and we hope it will provide a measure of the pressure exerted by the bentonite against the confining cylinder and end plates as water is forced through the pressed clay bed at high pressures.

Techniques have been developed to determine batch distribution (K_ds) for a number of candidate backfill exchange materials as a part of the screening process to select 6 to 12 materials for a more comprehensive evaluation.

DEFINITION AND PRIORITIZING OF BACKFILL REQUIREMENTS

The objectives of this activity are to define the "reasonable purposes" of a backfill (its functions) and then convert the "reasonable purposes" to a prioritized and quantified list of backfill performance attributes. Backfill material could be used simply to fill in the space between the waste canister and the host geologic media. A more meaningful purpose, however, would be to provide a redundant barrier(s) to the migration of radioactive species from the waste to the biosphere. Any emplaced backfill material will be subjected to five influences:

1. mechanical pressure and stress
2. a high radiation field
3. above-ambient temperature
4. hydraulic flow of ground water
5. materials dissolved in the ground water.

The backfill material must continue to fulfill its function(s) while subjected to these five influences for time periods ranging up to 10^6 years.

Two backfill functions being examined that do provide redundant barriers are 1) minimizing the penetration of ground water to the encapsulated waste, and 2) controlling the chemical environment surrounding the encapsulated waste.

If ground water cannot reach the canister or if the rate of migration is so slow that the amount of water that can contact the waste canister even in 10^6 yr is small, canister corrosion will be significantly reduced and the chief mechanism for transporting radioactive species to the biosphere will be eliminated. The previous calculation implies that compacted bentonite clay can provide such a barrier.

The chemical environment surrounding the encapsulated waste can be controlled by placement of carefully selected materials in the backfill that will buffer the pH to a desired range and reduce the oxygen fugacity to near zero. Such careful control will minimize corrosion of the canister system and greatly reduce the migration rate of most cationic radioactive species. Additional chemical control is achieved by using backfill materials such as bentonite clay with high-cation ion-exchange capacity or by adding specialized absorbing material for selected nuclides such as ^{129}I.

A preliminary list of backfill attributes, given in Table 23.1, has been issued and distributed to the project review committee and to PNL staff for comment. Following receipt of comments, the list will be revised and reissued.

TABLE 23.1. Unordered List of Possible Backfill Materials Attributes

Attribute	Relative Importance									Experimentally Measurable Property	References	General Comments
	High			Medium			Low					
	1	2	3	1	2	3	1	2	3			
1. Water exclusion										Porosity (θ) Permeability (ε) Diffusivity (D) Low hydraulic conductivity Capillary pressure		Hydrophobic surfaces Very small pores
2. Radionuclide retention										Distribution coefficient (K_d) Dispersion coefficient (K_f) Radionuclides - specific loading capacity		Channeling (seams, cracks) Thickness (boundary effects)
3. Mechanical stability										Modulus of elasticity in shear (G) • in tension (E) • in compression (E)		
										Bulk modulus of elasticity (K) Modulus of resilience (U_p) Modulus of rupture (S_R) • in bending • in torsion		
										Atterberg limits		Atterberg limits are the plasticity index, liquid limit, plastic limit
										Activity		Activity = ratio of Atterberg plastic limit to fraction of clay in the substance
4. Thermal stability										Retention of chemical and physical properties during and after thermal stress Coefficient of thermal expansion (β)		Cracking Diagenesis
5. Radiation stability										Retention of chemical and physical properties during and after irradiation		Diagenesis
6. Satisfactory heat-transfer capability										Thermal conductivity (k) Emissivity (ε) Overall heat-transfer coefficient (U)		
7. Mitigation of long-term intrusion												Possible colored material Don't utilize materials currently or projected to be valuable or in short supply
8. Availability										Resource assessment Supply capabilities Resource utilization/conservation		

TABLE 23.1 (contd)

	Relative Importance											
	High			Medium			Low					
Attribute	1	2	3	1	2	3	1	2	3	Experimentally Measurable Property	References	General Comments
9. Cost/Cost-benefit												Resource available in adequate quantity
10. Homogeneity/ Reproducibility												Can the selected backfill be adequately reproduced with the same attributes?
11. Resistance to biological degradation										Retention of physical and chemical properties during and after exposure to biological attack		
12. Self-sealing ability/Ductility										See Item 3		
13. Ease of emplacement/Formability										See Item 3		
14. Compactibility										See Item 3		
15. Faulting characteristics										See Item 3		
16. Shear resistance										See Item 3		
17. Long-lived physical and chemical properties										Retention of physical and chemical properties with time periods up to and beyond 1000 h		
18. Radiation attenuator										Shielding properties		
19. Unconfined compressive strength										See Item 3		
20. Hydrophobic										See Item 1		
21. Swelling capability										See Item 1		
22. Large and permanent molecular and cationic (anionic) sorption capacity										See Item 2		
23. High consolidation rate												Rate of compression
24. Low sensitivity										Strength in undisturbed state divided by strength in remolded state		

TABLE 23.1 (contd)

Attribute	Relative Importance									Experimentally Measurable Property	References	General Comments
	High			Medium			Low					
	1	2	3	1	2	3	1	2	3			
25. Compatibility a. with geology b. with package c. with media solutions d. with other backfill components prior to and following any "reaction" (i.e., sorption)										Change in physical and chemical property following exposure to or reaction with (a), (b), (c), or (d)		
26. "Permanent" retention of radionuclides										See Items 2 and 17		
27. Enhances package retrievability												
28. Barrier to corrosion products/High ion-exchange capacity										Sorption capacity for possible corrosion products, H^+, OH^-, radionuclides, etc.		
29. Available in adequate purity										Low organic impurities		
30. Corrosion resistance												
31. High oxidation resistance												
32. General items										a. Diagenesis b. Thixotropy c. Precipitation in reaction d. Transport phenomena e. Filtration capability f. Radionuclide convection g. Particle shape (ψ), (η) h. Particle size (Do) i. Void ratio j. Swelling versus sorption/cross effects k. Density (ρ) l. Cushion effect m. Fluids content at time of emplacement n. Are any properties directional; Isotropy and Anisotropy o. What is the effect of density on mechanical stability?		

TABLE 23.1 (contd)

Attribute	Relative Importance									Experimentally Measurable Property	References	General Comments
	High			Medium			Low					
	1	2	3	1	2	3	1	2	3			
33. High Redox potential												
34. Enhances pH and Eh of environment										See Items 29 and 34		
35. Gettering properties for O_2, etc., are high										See Items 2, 29, 34		

SCREENING OF POTENTIAL BACKFILL MATERIALS

Potential backfill materials and combinations of materials will be screened to select a small number for exhaustive laboratory testing. Those showing the greatest promise of meeting the performance attributes defined will be chosen. Although expanding clays have been given major emphasis, other materials have not been excluded from consideration. Activities to date include an extensive literature search and documentation of materials properties to provide a basis for the ultimate selection.

LABORATORY EVALUATION OF SELECTED BACKFILL MATERIAL

The objective in this task is to experimentally measure the performance characteristics of the selected backfill materials and to evaluate the experimental results in terms of the defined attributes. Work has been started to define the number and kind of experimental tests that will be done and the specific procedures that will be used. The next phase will be to schedule facilities and equipment for those tests that will be performed in-house and to make contractual arrangements for any tests to be performed elsewhere. Testing of some of the materials for the effects of radiation damage will be started in August.

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