Nuclear Waste Management Quarterly Progress Report January Through March 1980

A. M. Platt
J. A. Powell

June 1980

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NUCLEAR WASTE MANAGEMENT
QUARTERLY PROGRESS REPORT
JANUARY THROUGH MARCH 1980

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

June 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 October Through December 1979, PNL-3000-4.

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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 (HIWIP) 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 a 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

The 11-component generic waste glass study document was cleared for publication. Statistical methods used to develop empirical models to predict leach rates, crystallinity, volatility and viscosity of glasses studied will be used in an expanded study of all likely nuclear waste glasses.

Studies of fatigue crack growth rate and corrosion in candidate metallic container materials, leach tests of ceramic overpack materials, and tests of polymeric materials exposed to radiation at elevated temperatures proceeded.

A high-temperature borosilicate glass composition, designed to vitrify radionuclides recovered from the Hanford residual waste, was processed in the high-temperature ceramic melter. This glass simulates the vitrified radionuclide removal product from the residual liquid treatment flow-sheet that Rockwell Hanford Operations is currently investigating.

Vitrification of a defense waste composition that included several added sludge-

processing chemicals expected to be in the waste stream was demonstrated in the spray calciner/in-can melter.

The calcine-fed ceramic melter was disassembled and examined to assess the extent of refractory corrosion/erosion. An improved redesign is in progress.

WASTE FORM DEVELOPMENT AND CHARACTERIZATION

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

The 11-component generic glass study document was cleared for publication. The statistical methods employed yielded empirical models that predict leach rates, crystallinity, volatility, and viscosity of the waste glasses in the broad compositional region studied.

Crystallinity in the 11-component system was found to have no adverse effects on leaching or volatility. All glasses studied were liquid-liquid phase separated. The

effects of this phase separation are under further study.

The 11-component study leaching results greatly advanced knowledge of composition effects on leach behavior. Highly durable glasses similar to ultraglass cause the leachate to become acidic for static tests at 90°C while glasses with poor durability cause the leachate to become basic. Aluminum and iron tend to protect the glasses from matrix dissolution. Alkaline earth elements decrease glass durability. In static tests on glasses with moderate to good durability, sodium levels in solution were found to fluctuate with time. The sodium is thought to alternately dissolve by ion exchange with hydrogen and readsorb onto the glass surface. This effect is under intensive further study.

Volatility tests at 1300°C showed that sodium and boron vaporize together in a compound of the form $(\text{NaBO}_2)_x$ regardless of their mole ratios in the glass. Volatility and leaching correlated strongly. Highly volatile glasses have high leach rates, and those with low volatilities have low leach rates.

There were no significant differences in the leach rates of radioactive borosilicate waste glass samples taken over a wide time span from a canister filled in the Waste Solidification Engineering Prototypes program. Samples were cored and leach-tested 6 months, 2.8 years and 8.5 years after the waste glass was made. The leach rate of another sample from the 8.5-year-old core was unchanged after remelting, indicating that radiation during this period has not affected durability. Leach rates of the 8.5-year-old glass determined by three different procedures were compared. Paige and ISO leach test methods using glass monoliths yielded comparable results. Leach rates ob-

tained from powdered samples were at least one order of magnitude lower than those from monoliths, which is consistent with similar tests of other glasses.

The studies of fatigue crack growth rate in titanium Grade 2 and Grade 12 under ambient conditions show that crack growth rate of Grade 12 is significantly higher than that of Grade 2, and the difference is more pronounced in sheet than in plate. These results form the data base for determining the effects of corrosive repository environments on crack propagation in titanium alloys.

Leach tests of 17 ceramic materials considered for overpacks indicate that graphite exhibits the best resistance to attack, with alumina next best. Titania and zirconia are promising alternatives.

Interim evaluation of 250°C Hanford groundwater corrosion specimens shows no cracking of any U-bend samples. Titanium alloys continue to show outstanding resistance to general corrosion; however, copper-nickel and cast iron specimens exposed to 250°C brine were severely attacked and were removed from the test.

Of the polymer containment materials tested, ethylene propylene rubbers and polyphenylene sulfide materials continue to appear most promising after autoclave exposure to 250°C and $5 \times 10^8 \text{ R } ^{60}\text{Co}$ radiation exposure.

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, incan melter and calcine-fed ceramic melter. Verification tests to confirm that waste processing technology is ready for plant application are part of the effort.

An advanced method for immobilizing existing commercial high-level radioactive waste in storage at the Western New York Nuclear Services Center was successfully demonstrated when 96 % of a simulated Nuclear Fuel Services waste plus glass formers were processed by direct liquid feeding in an electrically heated ceramic melter. The test was accomplished in a laboratory-scale melter at an average feed rate of 6.2 %/hr over 15-1/2 hr and produced about 30 kg of simulated waste glass.

Further crucible melt tests made in the investigation of glass foaming control indicate: 1) the amount of foaming is inversely related to the waste loading, 2) adding 1 or 2% water to the glass-forming batch increases foam height, and 3) improving the mixing, by grinding the frit and calcine blend to a -100 mesh, does not reduce the foaming.

A high-temperature borosilicate glass composition, designed to vitrify radionuclides recovered from the Hanford residual waste, was processed in the high-temperature ceramic melter. During a 5-hr test, 60 kg of glass were produced with an average melter feed rate of 13.7 kg/hr. A total of 0.44 wt% of the cesium volatilized at a rate of 115 mg/cm²-hr. The glass was subjected to 72-hr Soxhlet and 19-hr pH 4 and pH 9 leaching tests. Leach rates were 2.98×10^{-5} , 7.48×10^{-6} , and 1.04×10^{-5} g/cm²-day, respectively, indicating generally increased durability over other standard waste glasses.

Glass-making frit was added directly to the waste slurry feeding the pilot-scale

spray calciner to demonstrate that a more homogeneous mixture of calcine and frit can be produced. The test showed that 100% of the frit needed for glass production can be added in this way. The homogeneous calcine/frit mixture should produce a better glass and eliminates a frit feeder and air lock to the calciner.

A defense waste composition, which included several added sludge-processing chemicals expected to be in the waste stream, was vitrified in the spray calciner/in-can melter. The reducing nature of the organic additions tended to lessen foaming of the glass melt, but it also reduced some metal oxides to the metallic state. The average processing rate was 75 kg/hr of glass in a 24-in.-dia canister.

The calcine-fed ceramic melter has been disassembled and examined to assess the extent of refractory corrosion/erosion. Some damage to the melter lid, tank side walls, and particularly the underflow discharge throat and riser was observed. Molten glass migrated to some extent along the noncemented joints of the primary and back-up refractories but did not reach the Inconel 601 containment vessel. An approved redesign is in progress.

In-cell installation of the remote lab-scale waste treatment facility is complete, and cold shakedown tests are under way. The internal operational readiness review has been completed, and DOE approval of the operation safety requirements is pending.

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

Leach testing was conducted on five basalt-based waste forms at 90 and 150°C for 9 days in deionized water. The waste forms included as-received basalt, basalt glass, basalt glass plus 20 wt% PW-9 calcine, and two recrystallized samples of basalt glass with calcine. Recrystallization of the basalt glass plus calcine increases the leach resistance. Scanning electron microscope (SEM) observation of the recrystallized samples before and after leaching shows what appears to be selective leaching of a glass phase, leaving plate-shaped crystals behind.

Leach tests on supercalcine pellets coated with pyrolytic carbon (PyC) and/or Al_2O_3 have been completed for 14 and 28 days at 50 and 90°C in deionized water and 0.5M NaCl. Examination of the results suggests that the best coating is the duplex PyC/ Al_2O_3 coating. Work is continuing on measurement of carbon reaction rates with water/air mixtures.

A literature review has been completed on the use of catalysts to deposit low-tempera-

ture PyC coatings. It revealed that little attention has been given to maximizing the density of the deposits. Low-temperature PyC coatings have been deposited by Battelle-Columbus (BCL) on quartz sand at 425°C in a fluidized bed reactor using acetylene, hydrocarbon, and nickel tetracarbonyl. Orders have been placed for the major components of the laboratory-scale chemical vapor deposition (CVD) coating system to be constructed at Pacific Northwest Laboratory (PNL).

Pellets pressed from SPC-4 supercalcine powder were sintered in a thermogravimetric analysis (TGA) furnace using air, vacuum, and Ar-8% H_2 atmospheres to assess the effects of sintering atmosphere and time-temperature parameters on waste element volatility losses during fabrication. Preslugged SPC-4 powder was hot pressed in graphite and nickel-lined graphite dies using two different temperature-time programs and 4500 psi maximum pressure. Hot pressing densification and TGA data suggest that 1100°C is probably an optimum hot pressing temperature for SPC-4. Pellet densities ranged from 4.50 to 4.57 g/cc.

The 325A-B cell is being readied for fabrication of supercalcine containing

high-level waste. A stainless steel tray has been designed and will be fabricated to provide a working floor over several chemical process tanks occupying considerable space in the cell. A hydraulic press and motorized power unit for installation in B-cell has been procured. A modified sintering furnace for in-cell use has been ordered.

The second round of post-irradiation examination of the transmutation samples irradiated in the high-flux isotope reactor (HFIR) 1 year ago have been started. Only the two high cesium (~37 wt% Cs_2O)-containing glass samples showed significant density change with time. Although these samples demonstrated a 1% increase in density, subsequent measurements must be made before any trends can be established. No changes were observed for any of the samples by optical microscopy.

Cement samples containing 10 wt% PW-9 calcine and 3 wt% ^{244}Cm have not shown any changes after a total dose of 1.6×10^{17} α/g . Measurements on $\text{Gd}_2\text{Ti}_2\text{O}_7$ (pyrochlore) materials after a dose of 7×10^{17} α/g have indicated a change in the lattice of about +0.6% and a corresponding decrease in the density of about -1.8%. No significant changes have been noted for $\text{CaZrTi}_2\text{O}_7$ (zirconolite) materials after a dose of 3×10^{17} α/g . Methods are being developed for preparing sintered pellets of huttonite (ThSiO_4 , high-temperature form) and thorite (ThSiO_4). Samples will be doped with ^{238}Pu to study metamictization behavior.

The dust containment building for pellet fabrication process has been installed. The pin mixer, disc pelletizer and vibratory feeder have been mounted on their support frames.

Formulations have been completed to produce precise mixtures of 70 kg of SPC-4

supercalcine and 40 kg of SPC-5. Rockwell Hanford Operations (RHO) will receive 30 kg of the SPC-4 supercalcine for use in their waste/rock interaction program. Samples of PW-4b-7 calcine have been sent to Lawrence Livermore Laboratory (LLL) and North Carolina State University for use in their SYNROC programs.

The disc-pelletized supercalcine pellets produced by Ferro-Tech have been sintered using the in-can-melter furnace. Samples of the pellets had poor strength integrity. Resintering studies indicated that canister temperature profiles and atmospheric conditions required further investigation. Small batches of supercalcine pellets have been successfully sintered in the PNL vertical sintering furnace.

The advanced glass forms melter (AGFM) has been started up to produce glass marbles for the integrated marble/metal matrix demonstration. The marble machine has been improved by providing a wider range of speeds and by adding forced-air cooling. The in-can encapsulation technique using lead shot was demonstrated by encapsulation of ~35 kg of marbles in 230 kg of lead in an 8-in.-dia canister.

The document entitled Preliminary Evaluation of Alternative Waste Form Solidification Processes: Volume 1, Identification of the Processes, PNL-3244, was transmitted to the DOE-Richland Operations Office. A subcontractor has been selected to perform an independent technical assessment of the waste-form processes.

A presentation was made at the Waste Management '80 conference in Tucson, Arizona, on the basic equipment requirements for nine high-level waste solidification processes.

WASTE DEVELOPMENT AND CHARACTERIZATION

Product Development - R. O. Lokken (PNL) and M. F. Browning (BCL)

To assess the durability of basalt-based waste forms, six samples were evaluated. The samples consisted of as-received basalt, basalt glass, basalt glass containing 20 wt% PW-9 calcine, and three recrystallized samples of basalt glass with 20% calcine. The basalt glass and basalt glass with calcine were melted at 1500 and 1400°C, respectively, and annealed at ~550°C. Crystallization was produced by heating the basalt glass plus calcine to 670°C for 1, 2, or 4 hr for nucleation and to 920°C for 8 hr for crystal growth.

X-ray diffraction analysis of these materials clearly showed that the glass samples were essentially vitreous, with <2% crystallinity in the sample containing 20 wt% PW-9 calcine. During recrystallization, three main phases formed: augite/diopside, spinel, and a feldspar.

A literature review has been completed on the catalysis of carbon deposition from hydrocarbons by iron, nickel, and cobalt. Twenty-nine references have been collected. The literature suggests that the hydrocarbon feed gas must have access to the nickel for the mechanism to operate. Most of the interest in nickel-catalyst technology refers to porous or fibrous structures, and little attention has been given to maximizing the density of the deposits.

At BCL, low-temperature PyC coatings have been deposited on 30 x 50-mesh quartz sand. The samples were prepared in a 25-mm-ID quartz fluidized bed reactor at ~425°C using acetylene, hydrogen, and nickel tetracarbonyl. Maximum coating efficiency was found between

450 and 500°C. Coating adhesion and quality appear to increase with increased reaction temperature.

Weight loss during sintering of SPC-4 supercalcine was determined as a function of temperature and sintering atmosphere by thermogravimetric analysis (TGA). Cold-pressed pellets were heated at 6°C/min to 1100, 1200, and 1300°C in flowing air, flowing Ar-8%H₂ and vacuum. Heating was followed by sintering for 2 hr at constant temperature. Typical TGA results for the three sintering atmospheres are shown in Figure 2.1. Initial weight losses of 2 to 4% at temperatures below 200°C are mainly attributed to absorbed (and chemical) water. Above 400°C, greater weight loss in Ar-8%H₂ during heating is attributed to reduction (loss of oxygen). TGA weight loss is similar in air and vacuum up to ~1100°C. Above 1100°C, greater volatility in vacuum becomes significant, as illustrated by the weight loss after 2 hr at 1200°C. This effect, possibly caused by kinetics, is being investigated. Characterization of TGA-sintered pellets to determine waste element losses and phase structure is planned.

SPC-4 powders have been hot pressed in graphite and nickel-lined graphite dies. A temperature of 1100°C appears to be optimum in processing. At temperatures below 1100°C densification is incomplete, and above 1100°C die reaction and volatility problems increase. At 4500 psi densification begins at ~800°C and is completed at ~1100°C. Hot-pressed SPC-4 pellets are undergoing leach testing, microstructural, x-ray diffraction and waste element loss characterization studies. Bulk densities were (3 pellet average) 4.50 g/cm³ for pellets hot pressed in graphite dies and 4.57 g/cm³ for pellets hot pressed in nickel-lined graphite dies.

FIGURE 2.1. TGA Sintering Data for SPC-4

Weight loss during hot pressing has been in the 6 to 7% range for all pellets.

Leaching - J. W. Shade and W. J. Gray

Static leach tests were conducted on the basalt-based water forms at 90 and 150°C for 9 days in deionized water (DIW). The leachate was analyzed for dissolved species for ICP (inductively coupled plasma spectroscopy). Table 2.1 gives the results of the 90°C, 9-day leach expressed as the weight percent of available species leached per square centimeter of sample surface area. In general, recrystallized samples tend to retain all species better than does their glass counterpart. The variation in nucleation time for the glass-ceramic samples did

not prove to be a factor in leach resistance. SEM observations of the recrystallized samples before and after leaching show what appears to be selective leaching of a glass phase, leaving plate-shaped crystals behind.

Leaching studies at 50 and 90°C have been conducted on a disc-pelletized supercalcine-coated spheres in DIW and 0.5M NaCl solutions for 14 and 28 days. Five types of spheres were examined. Two were uncoated SPC-2 and SPC-4, one was SPC-2 coated with PyC, one was SPC-4 coated with Al₂O₃, and the last was SPC-2 with an inner coating of PyC overlain by an Al₂O₃ coating. Sphere diameters ranged from ~1 to 2 mm, leading to geometric surface areas of 0.08 to 0.16 cm².

TABLE 2.1. Leaching Results for Basalt-Based Forms

	Wt% Leached (a) / cm ²							
	Al	Ca	Mg	Si	Na	Mo	Sr	Cs
Basalt	--(b)	0.072	0.065	0.099	--	N.P.(c)	--	N.P.
Basalt Glass	--	0.008	0.005	0.006	--	N.P.	--	N.P.
Basalt Glass + PW-9	0.008	0.052	0.040	0.040	--	0.069	0.044	0.060
Recrystallized-1 ^(d)	--	0.013	0.004	0.018	--	0.032	0.033	0.034
Recrystallized-2 ^(d)	--	0.012	0.006	0.016	--	0.027	0.030	0.029
Recrystallized-4 ^(d)	--	0.009	0.003	0.016	--	0.027	0.003	0.029

a. Leached at 90°C for 9 days in deionized water.

b. Solution concentration below detection limit.

c. N.P.--Mo and Cs not present in basalt.

d. Numbers denote nucleation time at 670°C. Growth was at 920°C for 8 hr.

The results of the leaching studies at 90°C for 28 days are shown in Table 2.2 in terms of total micrograms of element in solution per unit geometric surface area. Examination of results suggests that the best coating is the duplex PyC-Al₂O₃ coating. This conclusion may be somewhat misleading, however, because the duplex coating is thicker than the single coatings. Comparison of the PyC with the Al₂O₃ coatings suggests that the Al₂O₃ coating is generally more effective, particularly in containing the more mobile elements such as cesium and sodium. This relationship seems to hold in both DIW and 0.5M NaCl solutions. Either 10 or 20 spheres, randomly selected from samples supplied, were used in each leach test. Consequently, the probability of using a poorly coated sphere as a given leach test was about equal for all tests.

Previous measurements of graphite reaction rates with water/air mixtures revealed that oxygen rather than water was the primary reactant. Measurements of graphite reaction rates with oxygen-free water are planned, as

are measurements in the presence of a gamma-radiation field both with and without oxygen present. Equipment is being assembled that will allow the water to be distilled from the reaction vessel and the graphite to be heated to 600°C. This should provide for better quantitative determination of the reaction products. Meanwhile, work on other types of carbons is proceeding, using the same procedure as in the earlier work.

Radiation Effects - J. W. Wald, D. W. Brite, W. J. Gray and R. S. Haaker

A crystalline waste form will be fabricated from high-level waste in FY-1980 in B-cell 325A Building, using a cold pressing and sintering technique. A stainless steel tray is being fabricated to provide a working floor over several chemical process tanks occupying considerable space in the cell. A hydraulic press and motorized power unit have been procured for installation in B cell. In selecting the press, its suitability for both cold and hot pressing of waste pellets

TABLE 2.2. Leach Resistance of Coated Supercalcine^(a)

Core	Coating	Element Leached, $\mu\text{g}/\text{cm}^2$											
		Si		Ba		Ca		Mo		Sr		Cs	
		DIW	NaCl (b)	DIW	NaCl	DIW	NaCl	DIW	NaCl	DIW	NaCl	DIW	NaCl
SPC-2	None	59	60	44	62	8.3	15	78	90	22	27	11.2	3.2
SPC-2	PyC	0.4	1.4	0.6	0.7	1.1	6.4	0	0.8	1.0	1.1	13.6	6.8
SPC-4	None	46	42	14	36	2.3	8	45	73	12	20	19.0	4.5
SPC-4	Al_2O_3	0.7	1.4	0.1	0.1	1	5	0.1	0.6	0.01	0.1	1.1	1.2
SPC-4	PyC/ Al_2O_3	0.7	1.3	0.03	0.1	1	6	0	1.0	0.02	0.3	<0.5	1.1

a. 90°C-28 days, SA/V = 1:10

b. 0.5M NaCl

was considered heavily. A commercial furnace with modified design capable of insertion into the cell through the 13-in.-dia entry port has been ordered. Delivery is scheduled for early May. A pellet-pressing die has been designed that simplifies the remote handling necessary during die filling, pellet pressing, and removal of pressed pellets from the die.

Pure phase titanate-base materials are being evaluated to assess their crystalline stability when subjected to the effects of α -recoil type damage. This is being studied on a pyrochlore structure, $\text{Gd}_2\text{Ti}_2\text{O}_7$, and on a distorted pyrochlore-type structure zirconolite, $\text{CaZrTi}_2\text{O}_7$. The active material used as the dopant in both cases is ^{244}Cm . To date, the $\text{Gd}_2\text{Ti}_2\text{O}_7$ material has experienced a cumulative α -dose of $\sim 7 \times 10^{17}$ α -decay/g, and the $\text{CaZrTi}_2\text{O}_7$ $\sim 3 \times 10^{17}$ α -decay/g.

Preliminary stability data plotted against dose is given in Figure 2.2 for $\text{Gd}_2\text{Ti}_2\text{O}_7$, listing both the immersion density and the measured x-ray lattice constant. Density measurements are made using standard techniques; the lattice constant is readily calculated from x-ray diffraction line positions because the pyrochlore structure is cubic. Figure 2.2 illustrates that this structure is susceptible to radiation effects, with a

1.8% decrease in density and a corresponding 0.6% increase in the lattice constants after 140 days exposure. These measurements are consistent within a first order approximation, which indicates that for cubic materials $\Delta V/V_0 = 3(\Delta a/a_0)$.

No large changes have yet been observed in the zirconolite samples; however, the total dose is still rather low. At this same dose level, the $\text{Gd}_2\text{Ti}_2\text{O}_7$ material had changed lattice constant by +0.3% and density by -0.8%.

In the same area of radiation effects studies, a Portland Type II cement product has been prepared with a loading of 10 wt% PW-9 calcine doped with 3 wt% ^{244}Cm . The cement samples have been monitored for 311 days and a total cumulative α -dose of 1.6×10^{17} α /g. No major changes have been observed in either the crystalline phases that make up this waste form $[\text{Ca}(\text{OH})_2 + \text{Ca}_3\text{SiO}_5]$ or in the overall product. At this dose level, though, based upon studies of other waste forms, we might expect to see a change of only 0.1 to 0.2% in x-ray measurements.

Methods for preparing sintered pellets of huttonite (ThSiO_4 , high-temperature form) and thorite (ThSiO_4) are being developed. Pellets of huttonite doped with 6.77 wt%

FIGURE 2.2. Percent Change in Initial Value of Density and Lattice Constant for $Gd_2Ti_2O_7$ Doped with ^{244}Cm

cerium have been prepared by firing at $1500^{\circ}C$. The product is estimated to contain 10 wt% $(Th,Ce)O_2$ and amorphous silica. After cerium-doped huttonite is examined by SEM and electron microprobe analysis, huttonite will be doped with 11.0 wt% ^{238}Pu . Thorite pellets and cerium-doped thorite pellets have been prepared by firing at $1100^{\circ}C$. Unless a fluxing agent (2 wt% Na_2CO_3 or tungsten carbide from ball milling) is present, $(Th,Ce)O_2 \cdot SiO_2$ powders are unreactive in the temperature range of 1000 to $1200^{\circ}C$. A sintering study is in progress on $(Th,Ce)O_2 \cdot SiO_2$ powders containing 0.0, 2.25, 3.39, 4.51, and 6.77 wt% cerium at 1000 and $1100^{\circ}C$. This study should indicate the proper

experimental parameters and doping level for polycrystalline thorite.

The second round of post-irradiation examinations of cesium transmutation samples irradiated in HFIR 1 yr ago have been started. Only samples H-2 and H-3 changed with time; the statistical T test showed this change to be significant at the 95% and 90% confidence levels for H-2 and H-3, respectively. These two samples are the glass samples with very high cesium concentrations (~ 37 wt% Cs_2O). H-2 also contains $^{244}Cm_2O_3$, but H-3 does not. The pollucite and supercalcine samples have shown no change in density. Despite the apparent density increase of H-2 and H-3,

subsequent measurements must be made before any trends can be established.

Optical microscopy of the transmutation samples left at Oak Ridge National Laboratory (ORNL) was completed in March. The same areas examined in May 1979 were also examined this time (i.e., no repolishing was required). No changes were apparent in any of the samples. Additional shielding added to the SEM at ORNL will permit its use in examining these samples. That work is scheduled for April; the results will be compared with backscattered electron images obtained by microprobe in May 1979. As the shielded x-ray diffraction equipment at ORNL is still undergoing modification, PNL's x-ray analysis work will not be completed until April or May. Examination of old ^{137}Cs and ^{90}Sr sources will also be delayed until the x-ray unit is back in working order. Leach tests are also scheduled to be performed at PNL in April.

PROCESS AND EQUIPMENT DEVELOPMENT

Ceramics - C. L. Timmerman and J. F. Nesbitt

The pin mixer, disc pelletizer, and vibratory feeder have been mounted on their support frames and positioned in their approximate locations in the 324 Building high bay second floor work area. A dust containment building housing the disc pelletizer and pin mixer was erected for the containment of dust encountered in the pelletizing operations. Water, power, lighting, exhaust ventilation, and emergency safety (fire sprinkler) systems are currently being scheduled and installed in the building.

Formulations of precise mixtures of SPC-4 and SPC-5 supercalcines have been completed for 40-kg batches of each. The majority of the necessary chemicals have been ordered. An additional run will be made for RHO to

produce 30 kg of a precise SPC-4 supercalcine mix. This is the same formulation as the above SPC-4 and will be combined with the above. Discussions are under way with the Rockwell Energy Systems group and North Carolina State University to produce simulated sludge, SYNROC, and tailored ceramic calcined powders. The calcines will be used primarily for PNL pellet fabrication and coating studies but will also be available for distribution to other sites. Calcine of the PW-4b-7 composition has been sent to LLL and North Carolina State University in their studies. In this total effort a problem encountered is the rising cost of palladium.

The SPC-4 supercalcine pellets produced by Ferro-Tech of Wyandotte, Michigan, were shipped back to PNL in January. These pellets contain ~5% cornstarch used as a binder. Various sized pellets (1 mm to 20 mm dia) were produced using the disc pelletizer while the pin mixer produced smaller (0.1 mm to 0.5 mm dia) agglomerated granules.

The pellets were sintered using the in-can melter furnace to heat a canister filled with disc-pelletized pellets and an alumina filler. During the canister and pellet heat-up, air was bubbled into the pellet/alumina media for oxidation and off-gas flow purposes until a temperature of 600°C was reached. A total of 41 hr of operation was needed to achieve a sintering temperature of 1200°C. When the canister was removed from the furnace, a 30% volume reduction was observed, as measured by the level change in the can. The sintered pellets were removed from the canister, tumbled to remove any residual alumina from the pellets, and then screened to separate alumina and pellets.

Pellet samples tested indicated normal sintering reduction but had weak integrity. Some pellets were resintered in a crucible to 1200°C to learn whether they would become

denser and stronger. After resintering, the pellets were more durable. Based on the information from the resintering, it appears that three areas in the full-scale sintering process need to be examined:

1. canister temperature profile
2. canister atmosphere (possible incomplete oxidation)
3. holding time and temperature.

Small batches of simulated supercalcine waste pellets were sintered successfully in PNL's vertical sintering furnace.

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

Preparations are under way to demonstrate an integrated process for converting simulated nuclear waste to glass marbles for encapsulation in a lead matrix. This demonstration will be full-scale and will be designed to show the practical feasibility of this process. The test will convert simulated Savannah River TDS calcine and 211 frit to glass marbles 1.25 cm in diameter. About 270 kg of marbles will be placed in a canister 40 cm in diameter and 2 m tall. About 1500 kg of lead, containing 3% antimony, will then be cast around the marbles, using lead shot and the in-can encapsulation technique. A schematic of the marble-in-lead encapsulation process is shown in Figure 2.3.

The advanced glass forms melter (AGFM) has been modified to supply glass for marble production. The melter was raised and re-insulated, and new services were installed. The melter was started using a conventional plasma torch as the source of heat. The torch was operated about 40 hr before glass became conductive and self-sustaining. This melter will use an air lift to regulate the pouring rate of the glass. The glass will pour directly into the marble machine or into a glass quencher. This quencher uses a water

spray to shatter the glass and cool it rapidly for easy handling. The marble machine used in past marble production tests has been improved by providing a wider range of speeds and by adding forced air cooling. The forced air cooling should facilitate higher production rates.

The in-can encapsulation technique eliminates the need for a molten metal reservoir and transfer points. Using lead shot, the technique was demonstrated in two pilot-scale tests this quarter. In a test about 35 kg of marbles were encapsulated in 250 kg of lead in a 20-cm-dia canister. Cross-section cuts of the canister showed that the lead encapsulated the marbles very well. Permeability tests of the matrix are currently under way.

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

Efforts begun this quarter to improve PyC capability at PNL have resulted in establishment and approval of a lab-scale system design. Orders have been placed for the major components. Visits have been made to BCL to consult with these coating experts and to facilitate transfer of PyC technology.

PAPERS AND REPORTS

A document entitled Preliminary Evaluation of Alternative Waste Form Solidification Processes: Volume 1, Identification of the Processes, PNL-3244, by R. L. Treat et al., was completed and transmitted to DOE Richland Operations Office on schedule. This 500-page document includes design information and criteria for 11 processes that could possibly be used to solidify high-level liquid wastes on a production basis. A subcontractor has

FIGURE 2.3. Schematic Drawing of the Marble-in-Lead Encapsulation Process

been selected to perform an independent technical assessment on the waste form processes identified in PNL-3244.

A presentation was made by R. L. Treat at the Waste Management '80 conference in Tucson, Arizona, on the basic equipment requirements for nine high-level waste solidification processes. Three equipment areas were compared: 1) processing components, 2) motorized parts, and 3) mechanical steps required to produce a canister of solidified

waste. The numbers of processing steps are compared in Figure 2.4. In general, it was concluded that the processes with the fewest processing components also require the fewest motorized parts and mechanical steps. Requirements for in-can glass melting, joule-heated glass melting and glass-ceramic processes are lower in all categories. The paper is to be published in the conference proceedings.

FIGURE 2.4. A Comparison of the Number of Processing Components in Each of the Solidification Processes

3. NUCLEAR WASTE MATERIALS CHARACTERIZATION CENTER

R. D. Nelson - Project Manager

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

SUMMARY

The MCC program plan was issued and, in addition, three proposed standard test methods were developed for submission to the MRB. These were static leaching test, a high-temperature vaporization test, and a test for alpha-recoil effects. A workshop was held in which 46 national experts reviewed the proposed MCC leach test program.

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

The MCC program plan was issued after it was modified to reflect internal and external comments obtained on the initial draft. The program plan describes the MCC work breakdown structure and MCC interfaces with other organizations and programs that are developing, characterizing, or using nuclear waste materials. The procedural steps are also outlined for developing and obtaining MRB approval of test methods and waste materials data for both the MCC and external groups. The program plan describes in detail the next 18 months, when the first edition of the Nuclear Waste Materials Handbook will be issued; beyond that time the plan is less detailed. It is expected that the plan will be updated annually to

ensure that the MCC continues to meet the current materials properties data needs of the nuclear waste community.

In addition to publication of the program plan, recognition of the MCC and its functions has been promoted by discussions with lead sites and some laboratories and by MCC participation in planning activities for the American Nuclear Society meeting in June. The MCC is also represented on the program committee for the 1980 "International Symposium on the Scientific Basis for Nuclear Waste Management."

WASTE FORM MATERIALS CHARACTERIZATION -

R. P. Turcotte and J. E. Mendel

Three test methods were prepared for submission to the Materials Review Board. They are 1) a static leaching test, 2) a high-temperature vaporization test, and 3) a test for alpha-recoil effects. The tests use techniques proven satisfactory for some waste forms and, except for the high-temperature vaporization tests, should apply to all candidate waste forms. The vaporization test needs to be modified somewhat for waste forms that lose or gain weight because of reactions other than the vaporization reactions of interest.

In developing the test method for static-solution leaching, a workshop was held in February to obtain peer review from 46 national experts on the MCC leach rate test development program. Five different tests are being proposed by the MCC to define leach behavior under static and dynamic conditions over a wide temperature range, including temperatures that require use of autoclaves. Minor modifications of the proposed test procedures were made as a result of discussions at the workshop and subsequent comments received on the draft of the summary report. Perhaps the most significant modification concerned three of the tests that originally included the use of rocks to simulate natural systems. It was concluded that omitting the rocks and using leachants of defined compositions would yield more easily interpreted data; systems tests that include rocks will be added later to the MCC test program. A summary report of the workshop, including comments of the participants, is now in publication. A follow-up meeting will be held in April to focus on the test requirements for research to establish mechanisms and to model leach behavior.

A workshop on radiation damage effects is being planned for July 19 and 30, 1980. The workshop will review the proposed alpha effects test method and provide a review of MCC plans for evaluation of all radiation effects.

A test method for determining the compressive strength of waste forms was selected and is being developed to apply to a range of waste forms. Personnel at ANL were visited in regard to impact testing of waste forms and their method of fines analysis. Potential test methods have been considered for evaluating the stability of waste forms at

various temperatures, and a method has been selected for further evaluation.

An outline of the Compilation Report was prepared, assignments were made, and initial drafting of some sections was started. The first volume of the Compilation Report will survey available waste form data, briefly describe waste form test procedures in use, and assess shortcomings in the data or the procedures when they have been identified.

The design and construction of a shielded x-ray diffraction system for testing high-level waste materials has begun. A stand-alone instrument is being designed, and a transfer cask will be used in the handling of the waste material.

ENGINEERED BARRIER MATERIALS CHARACTERIZATION - M. D. Merz

The major activity of engineering barrier materials characterization was to define relevant areas of performance and to begin review of currently used test methods appropriate to the performance of barrier materials. Selected areas of performance were corrosion (including general corrosion, non-uniform corrosion, stress corrosion, and radiation enhanced corrosion), mechanical properties (including impact testing, tensile strength, and creep rupture), and stability of materials under heat and radiation. Literature review of test procedures and data was started in the following areas: stress corrosion, materials properties, concrete properties for structural application, and delayed failure of alloys. Construction of an autoclave test apparatus for corrosion testing in a gamma-radiation field was started.

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 computer code for the multi-attribute decision analysis model was loaded and was then tested on a hypothetical set of immobilization alternatives and evaluation criteria. While the results of the test case demonstrated the applicability of the approach, they also illustrated the need for better definition of the attributes and performance measures.

Chemical analyses were received for three of the six process sludge samples from the aqueous waste treatment facility at Rocky Flats. These data correspond rather closely to earlier samples and to our analysis of the process flowsheets for the facility at Rocky Flats. The operating bases for the new facility and for the incineration processes have been clarified, resulting in a different sludge/ash blend.

Waste form development concentrated on cold-pressed and sintered ceramic pellets, and on pressed hydraulic cement waste forms. Fabrication parameters are currently being studied. Subsequently, performance testing will be started using test procedures recommended by the Materials Characterization Center.

DATA ANALYSIS - A. D. Chockie

Two major objectives of the comparison model development were achieved during the

quarter. The first was the loading and testing of the multi-attribute decision analysis computer model on the Battelle Columbus CYBER. A test case was developed in which three TRU waste immobilization systems (cast hydraulic cement, in-can melted glass, and cold-pressed/sintered silicate ceramic) were assigned performance-level estimates on four immobilization objectives (cost, process risk, bulk leach rate and insensitivity to compositional variation). The test was designed to gain familiarity with the model and to identify where additional work or information is required in the assessment process. The major result from this test case was the indication that the evaluation attributes must be more carefully defined. The performance measure must be quantitative and dimensioned; or if it is dimensionless, at a minimum it must include sufficient familiar examples of performance along the scale to make the relative scale semiquantitative.

The second accomplishment was the development of an approach to acquire the needed information regarding group utility function and weighting factors for the evaluation criteria. Comprehensive but concise attribute descriptions were prepared, and preliminary performance scales for the various attributes were developed. These actions will aid in producing as simple and efficient a method as possible for obtaining information. To illustrate the needs for further refinements,

several attempts will be made to gather the required information from a small group during the coming quarter. This will lead to final establishment of the weights and utility functions by October.

WASTE CHARACTERIZATION - G. H. Bryan

Characterization of the chemical and physical properties of process sludges and incinerator residues continued during the quarter. The Rocky Flats Plant (RFP) and the Los Alamos Scientific Laboratory (LASL) are currently performing analyses on process sludge produced at their respective sites. RFP has completed chemical analyses on three of six samples, with the preliminary results and a 1970 analysis shown in Table 4.1. Except for calcium, the results thus far do not differ greatly from those previously obtained. The reason for the higher calcium level has not been determined. LASL process sludge analyses are not yet available because of delays in placing the subcontract.

The residues of several common combustible materials are in the process of being analyzed in an effort to improve the data used by the algorithm ASHCMP. Improved techniques are being used for producing and analyzing the resultant ash. Preliminary results indicate that the ash recovery is about the same as during the first runs. Elemental analysis, however, has not yet been completed.

A revised chemical composition for a typical sludge-ash waste blend has been determined for an interim period and is shown in Table 4.2. This waste is based on the premise that the typical production rate of sludge will be about 144,000 kg/yr and that of ash will be about 46,000 kg/yr (typical of the Rocky Flats Plant). Because the ash composition is about 24 wt% of the total, the compositional variations in the ash could have significant effects on some im-

mobilization forms and must be considered in developing the waste form.

The plutonium-contaminated sludge and incinerator ash requested from RFP have not been received yet because of contractual difficulties and shipping container requirements. The contractual difficulties have been resolved, but a shipping date must still be established. The equipment necessary for the production of several alternative waste forms using plutonium-bearing waste produced at RFP is now in place and ready to operate.

WASTE FORM DEVELOPMENT - R. O. Lokken

Evaluation of two candidate immobilization systems for transuranic waste was initiated based upon waste characterization data. The waste represented a mixture of process sludge and incinerator ash at a 9:1 weight ratio (the apparent generation-rate ratio reported earlier; as mentioned above, this ratio is now being revised to 3:1). The TRU blended waste (referred to here as TBW) was prepared by dry ball milling a chemical simulant of the sludge and nonradioactive ash from a controlled-air incinerator together for 16 hr. The material appeared very homogeneous and was light grey.

One waste form studied consisted of 67 wt% reagent-grade bentonite and 33 wt% TBW. The mixture was ball-milled for 4 hr and pressed into pellets for sintering. Pellets were pressed at pressures from 4600 to 230,000 psi. Table 4.3 lists the green and sintered densities of the pellets. The pellets were then sintered at 1000°C for 8 hr in stagnant air. The sintered densities decreased with increasing compaction pressure. The samples pressed above 18,000 psi also showed evidence of cracking. All additional samples will be pressed at ~9000 psi and sintered for 8 hr at 1000°C.

TABLE 4.1. Chemical Composition of Process Sludge Samples from Rocky Flats Plant

	Composition, wt%			
	Current Sludge		1970 Average	
Al ₂ O ₃	4.4	3.3	3.8	6.0
B ₂ O ₃	0.0	0.0	0.0	0.0
CaO	21.0	36.0	25.7	11.2
Cr ₂ O ₃	0.0	0.0	0.0	0.0
CuO	0.1	0.0	0.0	0.4
Fe ₂ O ₃	15.3	9.1	10.6	6.4
Ga ₂ O ₃				4.7
K ₂ O	1.3	1.0	1.1	3.6
MgO	3.7	1.9	4.3	6.7
Na ₂ O	15.3	18.8	20.4	17.4
NiO	0.0	0.0	0.0	0.1
PbO	0.0	0.0	0.0	0.5
Pb ₂ O ₅	0.0	0.0	0.0	--
SiO ₂	37.1	28.3	32.3	44.2
TiO ₂	0.0	0.0	0.0	0.1
ZnO	0.0	0.0	0.0	0.0
SrO	2.0	1.6	1.8	--

TABLE 4.2. Assumed Chemical Compositions for Typical Sludge and Ash

Compound	Composition, wt%		
	Process Sludge	Incinerator Ash(a)	Waste Blend(c)
Al ₂ O ₃	3	20 ^(b)	7
CaO	24	8	20
Cr ₂ O ₃	--	2	0.5
Fe ₂ O ₃	10	8	9
K ₂ O	1	1	1
MgO	3	4	3
Na ₂ O	16	2	13
NiO	--	1	0.3
SiO ₂	29 ^(b)	35 ^(b)	31
TiO ₂	--	10 ^(b)	3
ZnO	--	2	0.5
C	--	3	0.8
Cl	0.5	0.5	0.5
H ₂ O	14	3	11
	100	100	100

a. Unleached.

b. Highly variable.

c. Based upon a sludge:ash generation-rate ratio of 3.

TABLE 4.3. Green and Sintered Density of TBW/Bentonite Pellets as a Function of Pressure

Pressure, psi	Green Density, g/cm ³	Sintered(a) Density, g/cm ³
4,600	1.68	2.50
9,200	1.88	2.50
13,800	1.96	2.48
18,400	2.04	2.46
23,000	2.07	2.37
230,000	2.10	2.36

a. Pellets were sintered at 1000°C for 8 hr in air.

Another waste form under development is a pressed hydraulic cement. The concept of pressed concrete waste forms has been studied extensively at the Mound Facility.⁽¹⁾ A paste of cement, waste, and water is pressed in a conventional punch-and-die apparatus. Excess water, that which does not fill the interstices of the solid matrix, is extruded from the die. The water remaining in the pellet is used for hydration of the cement particles. To determine the amount of water remaining after pressing, a known amount of cement paste (water-to-cement weight ratio = 0.5) was pressed at 23,000 psi. The pellet, weighed after pressing, was found to contain ~10 wt% water. This value is independent of initial (before pressing) water-to-cement ratio at a given pressure. As higher pressures are used, more water is extracted and higher pellet densities result; 13,800 psi yields a pellet density of 2.17 g/cm³ while 92,000 psi produces a pellet with a density of 2.47 g/cm³. Higher densities also mean that because less water is available for hydration, inferior physical properties may result.

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

Analysis of unit operations applicable to solid transuranic wastes continued during the quarter. Information has been obtained from 25 manufacturers of specialized solids-handling and treatment equipment. Operations examined thus far include solids classification, conveying, solids and slurry blending, drying, calcination, grinding, milling and pressing.

Process flowsheets are currently being prepared based on the available waste characterization data, the unit operations

analyses, and the process and product design criteria established last quarter. These flowsheets, to be completed in April, will provide the basis for detailed conceptual design analysis of each alternative.

REFERENCE

1. Lewis, E. L. and R. F. Herbert, Jr., December 1979. Pelletized Waste Form Demonstration Program: April-September 1979. MLM-2680, Mound Facility, Miamisburg, OH.

5.0 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

Operation of the disassembly, sectioning, and decontamination systems continued. A plutonium-contaminated Plexiglas® glove box with 65 ft² of contaminated surface area was disassembled, sectioned using circular and reciprocating saws, and decontaminated to non-TRU levels using vibratory finishing. Contamination-fixing films were used extensively during the disassembly and sectioning to minimize the spread of contamination. A radiation measurement system has been designed that will perform inventory control and criticality safety monitoring functions throughout the decontamination facility using polyethylene-moderated ³He neutron detector banks. A HpGe detector system was installed for use in glove box counting studies. A criticality safety study of the annular vibratory finisher was completed. This study shows the annular vibratory finisher to be critically safe with up to 4.5 kg of plutonium present, even under the worst possible combination of conditions. Three plutonium-contaminated glove boxes and a connecting conveyor system were disassembled and removed. Use of newly developed

fixatives eliminated the need for conventional containment enclosures, substantially reduced removal time, and permitted completion of the entire operation with no spread of contamination. Plutonium-contaminated stainless steel was successfully sectioned using a manipulator-held plasma arc torch. Operation of the torch in this manner was effective for flat surfaces. However, it was difficult to follow irregular surfaces using the manipulator without extinguishing the arc. More than 1380 kg of uranium-contaminated molybdenum were decontaminated to unconditional release levels using a combination of vibratory finishing and chemical treatment. Sixty stainless steel animal cages contaminated with ²¹⁰Pb were decontaminated by electropolishing to nondetectable levels.

PROCESS DEMONSTRATION

Routine integrated operation of the disassembly, sectioning, and decontamination systems continued. A plutonium-contaminated Plexiglas glove box with 65 ft² of contaminated surface area was disassembled, sectioned using circular and reciprocating saws, and decontaminated to non-TRU levels. The decontaminated material and components included Plexiglas from the glove box panels,

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the plastic glove ports, the Hypalon® gloves and the plastic bag-out bags. The only component not decontaminated was the high-efficiency particulate air (HEPA) filter. The glove box was about 43 in. long, 30 in. wide and 36 in. high. It was constructed entirely of Plexiglas: the top and sides were 1/2-in. Plexiglas; the bottom was 1 in. Plexiglas. A porous rubber mat was in the bottom of the glove box. The contents of the glove box included a balance, a weighing platform, and miscellaneous small hand tools. Before decontamination, the radiation level of the glove box was 10 mrem/hr and the contamination level $>4 \times 10^6$ dis/min·100 cm² (the maximum instrument range).

The accessible contaminated surfaces of the glove box were sprayed with a strippable contamination-fixing coating. However, the presence of the equipment and mat inside the box made it difficult to completely coat all contaminated surfaces of the glove box and enclosed equipment.

The glove box was placed in the sectioning/pretreatment facility (Figure 5.1) through the large equipment door, illustrating the ability to control contamination levels within the sectioning/pretreatment facility. This allows large items to be introduced without elaborate containment procedures. The contaminated external piping was removed from the glove box. The Plexiglas panels were then sectioned using a reciprocating saw and a circular saw with a special blade for sectioning plastic. During the sectioning operation, excessive contamination spread resulted in high levels of airborne contamination.

The source of the contamination was traced to the porous rubber mat in the bottom of

the glove box. Because of equipment on the mat not all of the mat nor the Plexiglas bottom of the glove box under the mat had been coated with the contamination-fixing film. Removal of the equipment and rubber mat from the glove box and the application of additional contamination-fixing compound permitted sectioning of the Plexiglas to be completed without further spread of contamination.

The Plexiglas was sectioned into approximately 6-in. squares, the plastic glove ports into 6-in. sections, and the Hypalon gloves and plastic bags into 3-in. squares. All the material was processed in the 4-ft³ vibratory finisher located in the sectioning/pretreatment facility. In addition, the small hand tools that had been in the glove box were also decontaminated in the vibratory finisher. A steel ballcone medium and NaOH compound were used for the decontamination. Processing time was 1 hr/batch of material. The different materials were processed simultaneously in the vibratory finisher. Not only was sorting of the material not required, but very flexible material such as the Hypalon and the plastic from the bags decontaminated better in the vibratory finisher when solid material was included in the batch to promote better movement of the flexible material in the medium. All the processed material was <10 nCi/g after decontamination.

The rubber mat was not decontaminated because the porous material does not decontaminate in the vibratory finisher. In addition, the balance was not decontaminated because of the time-consuming disassembly that would be needed for proper decontamination of the components. Both the mat and the balance were discarded as TRU waste.

The problem of contamination spread as encountered during the sectioning of this

® Hyplon is a registered trade name of E.I. Du Pont de Nemours Co., Inc., 1007 Market St., Delaware, MD.

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FIGURE 5.1. Plutonium-Contaminated Glove Box Prior to Sectioning and Decontamination by Vibratory Finishing. The capability for decontaminating the sectioning/pretreatment facility allowed the introduction of this glove box without the need for elaborate containment procedures.

glove box can be eliminated by the removal of all loose material from glove boxes. If removal is not possible, at a minimum, the internal items should be moved during application of the contamination-fixing films to ensure that all contaminated surfaces receive the contamination-fixing compound.

CONTAMINATION MEASUREMENT STUDIES

A radiation measurement system that will perform inventory control and criticality monitoring functions throughout the decon-

tamination facility has been designed under subcontract by the Health Physics Instrumentation group at Los Alamos Scientific Laboratory (LASL). This inventory control and criticality monitoring system will use polyethylene-moderated ^3He neutron detector banks located near tanks, valves and pumps where radionuclide hold-up is most likely. These detectors will have dedicated electronics compatible with a central data processing system that will monitor the amount and location of special nuclear material within the decontamination facility.

The information acquired by the inventory control and criticality monitoring system will be supplemented by systems that identify and quantify the special nuclear material as it enters the decontamination facility as feed material and when it leaves the facility as waste. Feed material entering the decontamination system will be surveyed using a HpGe (hyper-pure germanium) detector to identify nuclides and a sodium iodide detector to quantify the nuclides (Figure 5.2).

7912918-5

FIGURE 5.2. Sodium Iodide Radiation Detection System Used to Survey Glove Boxes Prior to Decontamination

A MEGAS system designed by the Health Physics Instrumentation group at LASL, capable of accurately detecting $<1 \text{ nCi/g}$ of plutonium, will be used to screen all low-density combustible waste. The system uses a rotating sample holder to thoroughly scan the waste package. Counting time is typically 200 sec. As many as fifteen 2-ft^3 boxes/hr can be processed on this equipment.

The most promising detector for surveying large volumes of decontaminated material is the proportional counter. These detectors can be built in large-area configuration yet remain very sensitive to alpha radiation. A proportional counter currently under evaluation has an effective area of 1050 cm^2 and is capable of detecting 15 counts/min over this entire area. Detectors with even larger areas and similar sensitivity can be built.

Contaminated liquids generated by the decontamination processes are monitored using a special shielded sodium iodide detector. The instrument is capable of quantifying plutonium in solution from maximum permissible concentration (MPC) levels up to the mg/liter range. This means that this one instrument may be used to determine the amount of plutonium in solution for liquid both before and after processing.

CRITICALITY SAFETY STUDIES

A detailed criticality safety analysis was conducted on the 12-ft^3 annular vibratory finisher (Figure 5.3). The approximate dimensions of the process tub are slightly less than 5 ft in outside diameter, with a 13-in.-wide annular region. The normal depth of media is about 7 in. although this varies because of the inclined bottom of the process tub. The finishing media are steel. The calculations which have been completed

8000578-23

FIGURE 5.3. Large, High-Production 12-ft³ Annular Vibratory Finisher Used for Fissile Material Decontamination. Studies show this vibratory finisher will remain subcritical with up to 200 kg of plutonium present under normal operating conditions.

look at the critical mass of plutonium required for several different conditions.

The worst case from the standpoint of criticality would be the removal of the steel media while retaining fissile material in the solution. The most conservative solution form would be ²³⁹Pu-water mixtures with no acids or other neutron poisons present. For this case, families of curves were prepared showing the effect of material height, plutonium concentration, and neutron reflectors (water) on the effective neutron multiplication factor (K_{eff}). These curves are shown in Figures 5.4 through 5.6. In these curves, the K_{eff} is given for different plutonium concentrations in the range of 10 to 1000 g Pu/liter for heights in the annulus varying from 1 to 22 in. The 22-in. depth considers the entire annulus being at the maximum depth at the lowest portion of the tub bottom, a conservative assumption. The three reflector conditions are bare, 1 in.

of water equivalent, and full water reflection. The normal situation is somewhere between bare and 1 in. of water equivalent, while full water reflection would approximate a flooded condition for a situation in which personnel surround the unit (as during repairs).

The data in Figures 5.4, 5.5, and 5.6 were further reduced to determine the minimum critical mass in the system. The critical height for a given concentration was determined and the total volume of solution calculated. The resulting critical mass values were plotted in Figure 5.7. These indicate that the minimum critical mass for the worst combination of reflection, concentration, material form, and geometry is about 4.5 kg of plutonium.

A final set of calculations was made taking into account the presence of the steel polishing medium. For this condition, 30% of the volume was assumed to contain plutonium oxide-water mixtures with the remaining 70% volume being steel. For these conditions, even with full water reflection and a 22-in. depth of material, the unit remained subcritical with plutonium concentrations up to 1000 g of Pu/liter. The total plutonium mass for the 22-in. depth was greater than 600 kg of plutonium and for the normal 7-in. depth was greater than 200 kg of plutonium. This means normal operation of the vibratory finisher with plutonium present in the kilogram range is very subcritical.

SECTIONING STUDIES

Contamination Stabilizing Coatings

A plutonium-contaminated glove box line and conveyor system which have comprised part of the pretreatment facility (Figure 5.8)

FIGURE 5.4. k_{eff} Versus Material Height for a 12-ft³ Annular Vibratory Finisher with Bare Reflector Conditions

FIGURE 5.5. k_{eff} Versus Material Height for a 12-ft³ Annular Vibratory Finisher with 1-in. Water Equivalent Reflection

FIGURE 5.6. k_{eff} Versus Material Height for a 12-ft³ Annular Vibratory Finisher with Full Water Reflection

FIGURE 5.7. Critical Mass Versus Plutonium Concentration for a 12-ft³ Annular Vibratory Finisher for Bare, 1-in. Water Equivalent and Full Water Reflection

7803286-3

FIGURE 5.8. Plutonium-Contaminated Glove Box Line That Was Removed Using Contamination-Fixing Films as the Primary Contamination Control Technique

were removed to make room for the new high-production annular vibratory finisher system. Contamination-fixing coatings were used extensively during the removal to facilitate work while providing excellent contamination control.

The glove box line consisted of three glove boxes. One contained a bead blaster, another a vapor degreaser, and the third was a general-purpose glove box with no permanently installed equipment. The conveyor system stretched the length of the three glove boxes and connected them with the unpacking glove box in the 400-gal electro-

polishing facility. A chain driven cart traversed the length of the conveyor. The general purpose glove box was slated for reuse in the high-production annular vibratory finisher system. The other glove boxes and conveyor will be used as feed material for the disassembly, sectioning and decontamination process demonstration studies.

All loose material and debris were removed from the glove boxes and conveyor system. The internal contaminated surfaces of the general-purpose glove box were sprayed with a strippable contamination-fixing compound. The other glove boxes and conveyor

were similarly sprayed with a contamination-fixing compound easily removed by vibratory finishing. The strippable coating on the general-purpose glove box will allow easy removal of the film from the glove box after this glove box is reinstalled as part of the new vibratory finisher system. The coating on the other glove boxes and conveyor will be removed during decontamination in the vibratory finisher.

Contamination levels were relatively uniform throughout the glove box line and conveyor system. Initial contamination levels were on the order of 2×10^7 dis/min·100 cm². After coating the interior contaminated surfaces with the contamination-fixing compounds, the smearable contamination was generally less than 10^4 dis/min·100 cm². The surfaces near the joints, which were to be broken for removal, received special attention and were reduced to 4000 dis/min·100 cm² as they would be the most crucial areas for the subsequent work.

The normal procedure for the removal of plutonium-contaminated glove boxes is to construct a small temporary containment structure around the point where the glove box integrity will be breached. The construction of this containment structure is time-consuming. Moreover, working within the confined space of this structure significantly reduces worker effectiveness.

Since the primary contamination control technique during removal of the glove boxes and conveyor system was the contamination-fixing coatings, the normal procedure was not used. Instead, the floor of the room in which the glove boxes and conveyor were located was protected by application of strippable coatings. Three strippable coatings were applied side by side in the room (Figure 5.9) to allow the compounds to be directly compared for such properties as

ease of application, durability and ease of removal. In addition, application methods were compared. The three compounds selected were a polybutyl dispersion, a waterborne vinyl, and a fiber-reinforced, waterborne vinyl. The methods of application and the resulting film thicknesses are shown in Table 5.1. This table shows that film thicknesses vary considerably for each application method. The polybutyl dispersion film remained intact throughout the entire thickness range. The waterborne vinyl films failed where they were <0.010 in. The most effective and rapid means of application were spraying and squeegee. Brush application was slow and tended to produce a thinner film with brush marks. These brush marks caused the film to tear along these marks during removal, making its removal very difficult and time-consuming.

The fiber-reinforced, waterborne vinyl film showed the least durability. Numerous penetrations of the film resulted from the work to remove the glove boxes (Figure 5.10). The polybutyl dispersion showed the greatest durability, with no penetrations of the film during the entire operation. The nonreinforced waterborne vinyl film received only a few penetrations of the film, and these occurred where there was heavy stress such as a ladder placed on the film or heavy objects dropped. The polybutyl dispersion film and the nonreinforced waterborne vinyl film were removed in one sheet. The fiber-reinforced, waterborne vinyl film failed along brush marks during removal as discussed above.

The glove boxes were removed with no spread of contamination. Detailed contamination surveys were taken each time glove box integrity was breached. In addition, constant air monitors equipped with alarms were in use during the entire operation. Work

8000578-11

FIGURE 5.9. Protective Coatings Used on Floor During Preparation and Removal of Plutonium-Contaminated Glove Boxes

TABLE 5.1. Comparison of Application Methods for Contamination-Fixing Films and the Resulting Film Thickness for Horizontal Surfaces

Compound	Method of Application	Film Thickness, in.
Polybutyl dispersion	Spray	0.002 - 0.020
Waterborne vinyl	Squeegee	0.008 - 0.100
Fiber-reinforced waterborne vinyl	Brush	0.001 - 0.040

8000578-14

FIGURE 5.10. Detail of Fiber-Reinforced Waterborne Vinyl Coating, Showing Numerous Tears in the Film Caused by Preparation and Removal of Glove Boxes

time required in the radiation zone to perform the work was reduced significantly by allowing unrestricted working space around the glove boxes. The removal of the glove box with the vapor degreaser required the removal of the glove box bottom. Sectioning was done with a reciprocating saw. The contamination control provided by the stabilizing coatings permitted the sawing of this heavily contaminated glove box to be performed by personnel not wearing respiratory protection.

The removal of these glove boxes illustrates the high degree of contamination control provided by the use of contamination-fixing coatings. The time required was significantly reduced by eliminating the need to construct temporary containment structures and by eliminating the usual restricted working space provided by these structures. Additionally, the ability to work without respiratory protection further increased worker effectiveness. Finally, this operation demonstrated the use of these same contamination-fixing films as protective coatings for noncontaminated surfaces, and allowed comparison of the properties of three compounds that could be used for these protective coatings.

Plasma Arc Torch

Plutonium-contaminated stainless steel was successfully sectioned using a manipulator-held plasma arc torch. Operation of the torch in this manner was effective for flat material. Approximately 20 ft² of stainless steel 3/16 in. thick was sectioned into 6-in. squares using the manipulator-held torch.

However, it was difficult to follow irregular surfaces using the manipulator without extinguishing the torch. About 50 to 70% of the stainless steel from a typical Hanford glove box could be sectioned using a manipulator-held plasma arc torch with current techniques. Development of an effective spacing guide for the plasma arc torch could increase the range of shapes that can be sectioned using a manipulator-held plasma arc torch.

RELATED PROJECTS

An annular, high-production vibratory finisher with 12 ft³ capacity and an integral media separation screen was used with chemical decontamination techniques to decontaminate 1380 kg of uranium-contaminated molybdenum (Figure 5.11). A fast-cutting ceramic medium and a commercial deburring compound were used during this test. Up to 270 kg of molybdenum were processed per batch. The typical processing time was 1 hr per batch. The contamination levels were reduced to less than 2200 dis/min·100 cm², which allowed unrestricted release of the material. This illustrates the use of the advanced decontamination techniques developed by this program to reclaim valuable materials.

Sixty stainless steel animal cages (Figure 5.12) were decontaminated to background by immersion electropolishing. The animal cages, about 12 by 18 by 8 in. high, were contaminated with ²¹⁰Pb. Initial contamination levels were 700 to 2800 dis/min·100 cm². Decontamination time was generally 16 min per cage.

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FIGURE 5.11. Uranium-Contaminated Molybdenum Before and After Decontamination by Vibratory Finishing and Chemical Treatment

5.14

765330-2

FIGURE 5.12. ^{210}Pb Contaminated Stainless Steel Animal Cages
Decontaminated to Background by Electropolishing

6. KRYPTON SOLIDIFICATION

G. L. Tingey - Project Manager

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

SUMMARY

Sputter-deposited iron-yttrium alloys containing up to 9 at.% krypton have been prepared which also contain 0.1 at.% rubidium. The chemical form of the rubidium is not currently known. These samples will be used to determine the effect of small concentrations of the ^{85}Kr decay product, ^{85}Rb , on krypton release and other deposit properties.

A sputter-deposited amorphous alloy containing about 60 at.% zirconium, 34 at.% iron, and 6 at.% krypton has been prepared and tested. Krypton release occurs at about 1000°C . This sample, however, can be readily ignited and burns vigorously. Other amorphous alloys with zirconium content of about 19 at.%, and iron-yttrium or nickel-yttrium alloys could not be ignited.

ION IMPLANTATION OF KRYPTON DURING SPUTTER DEPOSITION - E. D. McClanahan and G. L. Tingey

A concern in radioactive krypton (^{85}Kr) storage is the effect of the decay product rubidium on the storage medium. Rubidium is a highly reactive alkali metal, and thus corrosion reactions appear likely. To investigate this phenomenon, we are currently investigating the possible effects of rubidium

on a sputter-deposited alloy of nominal composition, $\text{Fe}_{0.79}\text{Y}_{0.12}\text{Kr}_{0.09}$. If this solid were loaded with krypton of a composition generated in light-water reactor fuels (6% ^{85}Kr in krypton), the rubidium content after one half-life (11.7 years) would be about 0.27 at.%.

The most direct method of preparing samples containing the rubidium is to load with ^{85}Kr to obtain the ^{85}Rb decay product. Such an approach, however, would require 11.7 years to obtain the desired level of rubidium. Using krypton enriched in ^{85}Kr would decrease the time to about 6 months for fully enriched ^{85}Kr . Fully enriched ^{85}Kr is not currently available, and the increased care required for handling ^{85}Kr has provided the incentive for us to attempt to sputter rubidium directly into the structure of the sputter-deposited sample. The development of techniques to sputter rubidium into the matrix was described previously.^(1,2)

We have recently prepared two deposits by sputtering from an iron target containing slugs of yttrium metal spaced throughout. In addition, a series of holes were drilled around the center line of the target and filled with a mixture of iron powder and rubidium chloride. The first of these two

deposits has now been analyzed by x-ray fluorescence and samples prepared for gas release measurements. The analysis of the deposit taken from a position about midway between the ring of rubidium chloride and the end of the deposit contained about 0.1% rubidium, with a similar quantity of Cl^- . At present it is not known whether the rubidium is alloyed with the iron or combined in compound form with the Cl^- . We had hoped that the Cl^- would be largely eliminated from this area of the sample because it would be sputtered as a negatively charged atom and thus repelled and be deposited in a small band directly opposite rubidium chloride-filled holes, but apparently this expectation was not realized. Electron microscopy and x-ray photoelectron spectroscopy will be used in an attempt to observe the chemical state of the rubidium in the deposit. Gas release measurements have not been completed on the present samples, but results from the sample prepared earlier⁽²⁾ containing somewhat smaller concentrations of rubidium showed no detectable effect on the rate of krypton release.

Sputtered Zirconium-Iron Alloys

One alloy of interest for storage of krypton is a mixture of iron and zirconium. We have reported previously⁽³⁾ the results from an alloy of composition $\text{Fe}_{0.76}\text{Zr}_{0.19}\text{Kr}_{0.05}$. We have recently prepared a deposit using a target of composition $\text{Zr}_{0.64}\text{Fe}_{0.36}$. This

material sputtered very well, yielding a highly dense amorphous metal containing about 6 at.% krypton. Krypton release from these samples occurred at a temperature of 900 to 1000°C, with <0.01% of the krypton released below 650°C.

Other laboratories have observed that amorphous metal deposits, especially those high in zirconium, sustain combustion. Therefore, we have tested several alloys to determine their flammability. The present sample containing about 60 at.% zirconium was ignited and burned vigorously. However, we were unable to ignite the sample containing only 19 at.% zirconium or the iron-yttrium or nickel-yttrium alloys even with a propane oxygen flame.

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

7. THERMAL OUTGASSING

L. L. Burger - Project Manager

The objectives of the Thermal Outgassing Program are to:

1. *develop a method for the safe and effective removal of volatile fission products from irradiated fuels*
2. *evaluate the use of thermal outgassing using various sweep gases or vacuum outgassing for the removal of ^3H , ^{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 literature survey is complete, and evaluation of the reference material has begun. The search has identified volumes of data related to fission gas release during irradiation and during loss-of-fluid accidents. No significant data have been found related to sweep-gas interaction. The use of DOE facilities identified last quarter, using equipment already developed by HEDL for studying reactor transients, has been delayed by about 4 months because of unexpected building modifications. Initial hot cell tests on Shippingport UO_2 fuel will be completed on schedule but will require minor equipment modifications and a facility change to meet the third-quarter milestone.

THERMAL OUTGASSING - L. A. Bray and
L. G. Morgan

C. A. Hinman, HEDL, has reviewed his data on ex-reactor transient fission gas release⁽¹⁾ as an example of the type of experimental

results to be obtained in future outgassing studies. He determined instantaneous xenon and krypton release rates of 2 to 4%/sec over a temperature range of 1400 to 1800°C for UO_2 (PNL-2-4 fuel pin, 39,000 MWd/MTHM) heated to 2800°C at 200°C/sec.

The potential use of sputter-deposited UO_2 that contains trapped fission gas is being investigated by E. D. McClanahan. Gas-release mechanisms as a function of temperature and sweep-gas composition and analytical techniques to determine fission gas composition could then more easily be studied to complement the more expensive irradiated fuel tests.

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

REFERENCE

1. Hinman, C. A. and O. D. Slagle, May 1978. Ex-Reactor Transient Fission Gas Release Studies, Fuel Pin PNL-2-4, HEDL-TME-77-83, Hanford Engineering Development Laboratory, Richland, WA.

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

Ethylene proved to be ineffective as a regeneration agent for silver zeolites. To date, elemental hydrogen is the only material shown to remove iodine from the silver zeolites. It was also shown to be effective in reacting with pure AgI coated on sodium mordenite.

Thermogravimetric analysis and differential scanning calorimetric analysis were performed on iodine-loaded silver sorbents. These analyses indicated that with >25% Ag use iodine is released in air at $\sim 300^\circ\text{C}$ for silver mordenite, reduced silver mordenite, and silver faujasite. Of the iodine-free materials, only silver nitrate-impregnated silicic acid (AC6120) showed any of the characteristic endothermic changes of silver nitrate, silver oxide, or silver carbonate; none of the iodine-loaded materials had the endotherm characteristic of silver iodide.

Using carbon tetrachloride Soxhlet extraction for iodine-loaded silver sorbents, with 12 to 93% Ag use we found <1% iodine removal from reduced and as-received silver mordenite, 70 to 14% removal from silver faujasite (the lower percentage at the highest loading), and 76 and <1% from AC6120 (the lower percentage at the highest loading).

The retention of methyl iodide on silver zeolites will be examined in the presence of $\text{NO}_2(\text{NO})$, H_2O , and O_2 . It was observed

that NO_2 decomposed CH_3I , forming I_2 in the presence of light, and thus probably in the presence of any radiation. Brief studies showed that although the reaction is significant, it was too slow to be of practical importance.

Rockwell Hanford prepared iodine sodalite samples in vacuum and in helium. The samples are being characterized by x-ray emission spectroscopy and x-ray diffraction.

REGENERATION OF SILVER ZEOLITES -

K. D. Wiemers

To avoid the ambiguity of iodine volatilization from the loaded zeolite materials, recent experiments have employed silver iodide-coated silica gel or sodium mordenite. The reaction of ethylene at temperatures from 250 to 450°C was negligible. To date, elemental hydrogen is the only reagent shown to react with silver iodide.

IODINE-LOADED SILVER SORBENT CHARACTERIZATION -

R. D. Scheele and K. D. Wiemers

Differential scanning calorimetry (DSC), thermogravimetry (TG), and differential thermogravimetry (DTG) were used to determine the thermal behavior, and CCl_4 Soxhlet extraction was used to examine the elemental iodine content of various iodine-loaded silver sorbents, silver faujasite

(AgX), silver mordenite (AgZ), reduced silver mordenite (Ag^oZ), and silver nitrate-impregnated silicic acid (AC6120). Iodine loading levels varied from 12 to 93% silver use, assuming a maximum Ag:I ratio of 1:1.

The various iodine-loaded silver sorbents exhibited slightly different thermal characteristics as a function of iodine loading.

AgZ, Ag^oZ, and AgX showed similar thermal behavior. These materials loaded to ~25% Ag use showed little or no iodine loss below 600°C. Any additional iodine loaded onto these materials volatilized beginning at ~300°C. Figure 8.1 presents the group of TGA (TG and DTG) runs for Ag^oZ. The DSC's up to 550°C for AgZ, Ag^oZ, and AgX show none of the characteristic endotherms due to crystal changes, melting, or decomposition of AgNO₃, Ag₂O, or Ag₂CO₃. The TGA's for AgX loaded to 47 and 71% Ag use show a rapid weight loss occurring at 850°C; this weight loss is absent for AgZ. The DSC's for AgZ, Ag^oZ, and AgX show none of the characteristic endotherms of AgI.

AC6120 differs from the silver-exchanged zeolites because it is silver nitrate-impregnated silicic acid with a 12 wt% Ag content. Figure 8.2 presents DSC's of AC6120 loaded to different iodine loadings, 0 to 71% silver use, or 0 to 100 mg I/g AC6120. AC6120 had all the endotherms characteristic of AgNO₃. The decomposition peak at ~470°C was much broader for the sorbent, however. Figure 8.3 presents the TGA's for AC6120. In both the TGA's and DSC's higher iodine loading reduced the magnitude of the weight losses and endotherms, respectively, due to silver nitrate. In addition, endotherms characteristic of AgI were absent in the DSC's. A small weight loss at ~400°C was evident for the 100 mg I/g

AC6120. The composition of the released material is unknown.

Extraction with CCl₄ in a Soxhlet apparatus was employed in an attempt to determine elemental iodine present on the silver sorbents. The results are presented in Table 8.1. Some differences exist between the extraction results and the thermoanalytical results. Both AgZ and Ag^oZ had <1% iodine extracted for all iodine loadings, yet thermoanalytical results indicated that iodine, loaded to about 25% Ag use, is present as chemically bonded iodine, and the remainder is easily volatilized. The percent of iodine extracted from AgX and AC6120 decreased as the iodine loading increased, contrary to the thermoanalytical results for AgX. A possible explanation is that the pores of the matrix become blocked to the CCl₄.

ALTERNATIVE FIXATION - G. A. Wolf, W. I. Winters, and W. W. Schulz, (RHO)

Four samples of sodalite were prepared using the clay process and temperatures and pressures described by D. M. Strachan.⁽¹⁾ Two of these samples were prepared in a vacuum and two in helium.

X-ray diffraction analysis of one sample prepared in a vacuum showed two phases, sodalite (Na₈(AlSiO₄)₆·I₂) and albite (NaAlSi₃O₈). Total iodine content is being determined by x-ray emission spectroscopy.

Thermogravimetric analysis of the materials of preparation showed weight losses between 500 to 600°C and 900 to 1000°C. The low-temperature loss can be attributed to the loss of the water of crystallization of the clay; the high-temperature loss, however, is currently unexplained.

FIGURE 8.1. Thermogravimetric Analysis of Iodine-Loaded Ag^0Z

FIGURE 8.2. Differential Scanning Calorimetry Analysis for AC6120

FIGURE 8.3. Thermogravimetric Analysis for AC6120

TABLE 8.1. Percent Iodine Extracted Using CCl_4

Sorbent	Iodine Loading, mg I/g Sorbent	Silver Use, %	I_2 Extracted, %
AgX (silver faujasite), 3.34 mmol Ag/g	50	12	70
	100	24	69
	150	35	75
	200	47	34
	300	71	14
AgZ (silver mordenite), 1.67 mmol Ag/g	50	24	<1
	100	47	<1
	150	70	<1
	200	93	<1
Ag ⁰ Z (reduced silver mor- denite), 1.67 mmol Ag/g	50	24	<1
	100	47	<1
	150	70	<1
	200	93	1
AC6120, 1.11 mmol Ag/g	70	50	76
	100	71	<1

ORGANIC IODIDE REMOVAL BY SILVER ZEOLITES -
K. D. Wiemers

Studies measuring methyl iodide decomposition in the presence of NO_2 , air, water, and light showed an increase in the decomposition rate when NO_2 was present, but

this rate for 1% CH_3I , 200 ppm/hr, is insignificant compared to the residence times in the reprocessing facility.

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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

A physical model of one-dimensional flow of water and radionuclides through geologic media has been used to determine cobalt and tritium migration. Results have indicated a higher K_d for ^{60}Co -EDTA than was originally determined using small laboratory columns. Tritium migration occurred as expected. Field monitoring of tritium migration at a field site has shown significant transport of tritium upward through the geologic media from a depth of 60 cm to the atmosphere. Geologic logging results of ^{60}Co -EDTA from the same site have shown no significant transport.

LABORATORY ANALYSIS - G. W. Gee and
A. C. Campbell

A laboratory analysis report was published this quarter that covers physicochemical analysis of partially saturated geologic media transport.

PHYSICAL MODELING - A. C. Campbell

Physical models are used to evaluate the migration of radionuclides and water. These models consist of large sediment columns used under controlled laboratory conditions to

simulate field conditions. These models are also applied in evaluating the performance of field monitoring transducers. Studies continued with the layered soil column used for determining the flow of water and radionuclides under drainage conditions. A sandy soil (91.7% sand, 7% silt and 1.3% clay) was packed at an average density of 1.75 g/cm^3 into a column 56 cm in diameter and 176 cm long. A 12-cm layer of coarse sand ($>200 \mu\text{m}$) was placed at the 116-cm depth in the column. Cobalt-60 complexed with ethylenediamine tetraacetic acid (EDTA) (0.1 mCi) was used as the radionuclide tracer in a soil layer 1 cm thick (4.71 kg). The layer was placed at the 60-cm depth. Periodic applications of water were monitored for their influence on water content and gamma activity through the column profile.

To characterize water and solute movement through the mobile-immobile water fractions of the large column and to provide additional water as a carrier for the ^{60}Co -EDTA, water traced with tritium was applied at the top of the column. Approximately two pore volumes of tritiated water were applied, followed by two pore volumes of water to flush the tritium out of the column. Pore volume is the equivalent volume of void space in the total sample volume. Void space for the large column was calculated as 50.87 liters. For

31 days, 6.3 liters were applied daily. Column outflow was collected and analyzed for tritium and cobalt activity. Water content and gamma profiles were determined from soils sampled at different depths of the column.

Tritium movement occurred simultaneously with the water through the column. A plot of the effluent concentration, C , relative to the influent concentration, C_0 , as a function of effluent volume indicates that the column's pore volume is 47.5 liters. One pore volume corresponds to the volume of effluent at which the relative concentration (C/C_0) is 0.5. The experimental pore volume value includes variables within the layered column that were not initially accounted for.

No increase in cobalt concentration in the column outflow was detected. The updated cobalt effluent activity plot is given in Figure 9.1. The volume of effluent corresponds with 4.3 pore volumes. Increased concentrations of cobalt were expected at 2.3 pore volumes, with an unsaturated distribution coefficient (K_d) of 0.1 as indicated from batch K_d tests. Recent column evaluations indicate a K_d range from 0.8 to 2.7, which corresponds with breakthrough pore volumes of 11.8 and 37.3, respectively. Movement within the column is occurring, but the major portion of cobalt has not moved (Figure 9.2). Samples taken above the cobalt layer show cobalt concentrations at <1 pCi/g. Samples

FIGURE 9.1. Effluent Activity as a Function of Outflow from Large Column

FIGURE 9.2. Radionuclide Content as a Function of Depth Within Physical Model

taken below the cobalt layer range from 1 to 13 pCi/g.

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

Monitoring systems are being developed to evaluate the transport of radionuclides and water at arid-region radioactive waste burial sites. Monitoring systems for shallow-land burial disposal facilities are necessary to

measure ambient environmental conditions and to determine when remedial actions will be needed.

Monitoring systems and methodologies for measuring radionuclide transport and water migration in the partially saturated zone are currently being tested at a buried waste test facility (BWTF). The second 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.

The BWTF field caissons containing 1-cm layers of geologic media traced with tritium and ^{60}Co (EDTA) were sampled in mid-February. A plug 2 cm long was removed from each sampling port in the tracer caissons. Laboratory analysis determined the radionuclide concentrations of the samples. Results were then compared with the October sampling results.

Cobalt was not detected in any sample. Insufficient water had moved through the caissons for transport of the cobalt from the original placement depth of 60 cm to the nearest sampling port at 15.24 cm. Downward movement of ^{60}Co will be detected first in the irrigated control caisson, which receives twice the precipitation of the ambient caisson.

Tritium was detected at lower concentrations and throughout more of the caisson profiles at the February 1980 sampling than at October 1979 sampling. Increased moisture had moved the tritium downward. As before, more downward movement was evident in the control irrigated caisson than in the ambient caisson. It is possible, however, that the higher concentrations of the October 1979 sampling are due to edge effects of the caisson. Tritium profiles are given in Figures 9.3-9.6

Numerical integration of tritium concentration versus depth of the control (irrigated) and the ambient caissons between the October 1979 and February 1980 sampling results indicates a -20.8 and -33.0% change

in concentration, respectively. This suggests significant migration of tritium through the caisson, probably under vapor phase transport upward through the geologic media into the atmosphere.

Two techniques were compared for the detection of tritium associated with small geologic media samples. Samples <15 g were collected, subdivided and weighed. The "a" samples were mixed directly with 15 ml of liquid scintillation (LS) cocktail (a toluene-based LS cocktail used for aqueous and nonaqueous, and soluble organic samples) for direct counting. To the "b" samples 5 ml of distilled water was added; the mixture was shaken and centrifuged; and a 250- μl aliquot of the remaining liquid was taken and added to the 15-ml LS cocktail. Dilution and energy calibration corrections performed on the LS raw data indicated little difference between techniques for obtaining sample values. Although the direct addition of soil sample to LS cocktail was faster, the error associated with counting the samples was greater. Sample self-attenuation results in lower counting efficiencies, which correspond with higher errors. This toluene-based LS cocktail extracts water from soil; therefore the direct-counting results were superior to those with other LS cocktails. Further analysis for tritium in geologic media samples will be done by the leaching technique.

Logging of cobalt-contaminated caissons by means of a sodium-iodide multichannel analyzer has continued to measure the rate of transport of ^{60}Co -EDTA at the BWTF. Figures 9.7 and 9.8 provide vertical logs of counts per minute versus depth of the controlled irrigated and the ambient caissons. At the 60-cm depth ^{60}Co is highest because this is the depth of original emplacement. The counting results show a decrease in

FIGURE 9.3. BWTF Caisson Sampling - 10/29/79 Tritium Profiles

FIGURE 9.4. BWTF Caisson Sampling - 2/14/80 Tritium Profiles

FIGURE 9.5. BWTF Ambient Caisson Sampling Tritium Profiles

FIGURE 9.6. BWTF Irrigated Caisson Sampling Tritium Profiles

FIGURE 9.7. Sodium-Iodide Well Log of $^{60}\text{Co-EDTA}$ Concentration Versus Depth at the BWTF Ambient Caisson

FIGURE 9.8. Sodium-Iodide Well Log of $^{60}\text{Co-EDTA}$ Concentration Versus Depth at the BWTF Irrigated Caisson

count rate below and above the 60-cm layer because of the geologic media's attenuation coefficient to the ^{60}Co gamma peaks (1.332 and 1.173 MeV). Thus there is no evidence of migration of ^{60}Co in either the controlled irrigated or the ambient caisson.

Numerical integration of the controlled irrigated caisson and the ambient caisson count rate versus depth for August 1979 and March 1980 shows no significant difference

in centimeters times counts per minute for either caisson within counting error bounds. Equivalent pore volume input from natural precipitation in the ambient caisson and the controlled irrigated caisson if all precipitation reached the 60-cm depth would equal 0.67 and 1.16, respectively. Thus no transport would be expected until significantly more water flux downward through the 60-cm layer occurs.

10. WELL-LOGGING INSTRUMENTATION DEVELOPMENT

R. L. Brodzinski - Project Manager

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

SUMMARY

A paper entitled "A Well-Logging Technique for the In Situ Determination of ^{90}Sr ," by R. L. Brodzinski and H. L. Nielson, has been accepted for publication in Nuclear Instruments and Methods.

The detailed research plan for completion of the ^{90}Sr neutron activation analysis experiments has been updated.

Conceptual development of the tritium logging device has been continued, and equipment requirements for the system are being defined.

Results of the photon detection well-logging experiments are detailed. This technique appears to have substantial merit, and field testing will be undertaken to more closely define its range of applications. Laboratory calibrations indicate detection limits as low as 5 nCi cm^{-3} for ^{239}Pu in gamma-ray free environments.

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

A paper entitled "A Well Logging Technique for the In Situ Determination of ^{90}Sr ," by R. L. Brodzinski and H. L. Nielson, has been accepted for publication in Nuclear Instruments and Methods.

The detailed research plan for completion of the ^{90}Sr neutron activation analysis experiments has been updated.

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

Professor Clarence Menninga from Calvin College will continue work on the development of the tritium logging device again this summer. Dr. Menninga is assembling a list of all component parts required for construction and testing of the system.

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

All transuranic isotopes emit photon radiation. However, in most cases, these photons are fairly low energy and extremely low yield. Consequently, the detection and measurement of transuranics by gamma-ray spectroscopy has been possible only when relatively large quantities of the actinides are present and in the absence of high yield gamma-ray emitting interferences, such as fission products. This report describes the sensitivities and detection limits for determination of actinides homogeneously distributed in sediments as a function of counting

period and concentration of gamma-ray emitting interfering radioactivities. The applicability of this technique as a well-logging system is discussed and compared to other methods of transuranic detection.

A 102 cm³ intrinsic germanium (IG) diode gamma-ray spectrometer system capable of logging nominal 6 in. dia or larger wells was used in these experiments. A newer, omnidirectional 107.6 cm³ intrinsic germanium diode spectrometer capable of logging wells as small as 3 in. in diameter is currently available and promises to provide even better sensitivity than the 102 cm³ diode.

The sensitivity of this well-logging technique for the determination of transuranics in typical fission product activities was obtained using sources of various radionuclides in a calibration facility filled with Hanford sediments. Data representing homogeneous distribution of the activities in an infinite volume of soils were obtained by normalizing each calibration measurement to unit concentration of radioactivity in concentric spherical shells and summing over all significant shells. For the gamma-ray energies involved in this work, this integration procedure effectively interrogates sample volumes ranging from 0.22 to 3.9 m³. The details of this calibration technique and verification of its accuracy have been given elsewhere^(1,2) and will not be repeated here. Data were obtained using the sources described in Table 10.1. Distinctive gamma-ray lines were identifiable for ²³⁹Pu, ²⁴¹Am, ²⁴³Am(²³⁹Np), and ²⁴⁴Cm. The other actinides listed in Table 10.1 could not be identified in the photon spectra. More than one gamma-ray line was attributable to each of the identifiable actinides, but a single photon energy was chosen to represent each based on overall sensitivity and freedom from interferences. The gamma-ray lines at 278, 414, and 816 keV

TABLE 10.1. Transuranic and Fission Product Sources Used To Determine Sensitivities

Source	Isotope	Activity
PuO ₂	²³⁸ Pu	9.872 Ci
	²³⁹ Pu	4.414 Ci
	²⁴⁰ Pu	4.301 Ci
	²⁴¹ Pu	525.0 Ci
	²⁴² Pu	7.390 mCi
	²⁴¹ Am	2.749 Ci
AmO ₂	²⁴³ Am (²³⁹ Np)	397 mCi
Am ₂ O ₃	²⁴³ Am (²³⁹ Np)	12.6 nCi
Cm ₂ O ₃	²⁴² Cm	391 pCi
	²⁴⁴ Cm	7.47 mCi
	²⁴⁴ Cm	3.74 mCi
Mixed	¹⁰⁶ Ru	89.88 μCi
	¹²⁵ Sb	4.543 μCi
Fission Product	¹³⁴ Cs	7.252 μCi
	¹³⁷ Cs	582.2 μCi
	¹⁴⁴ Ce	27.86 μCi
	¹⁵⁴ Eu	1.167 μCi

appear to be uniquely attributable to ²⁴³Am, ²³⁹Pu, and ²⁴⁴Cm, respectively, in isotopic mixtures normally encountered. The 414 and 816 keV lines are from the direct decay of ²³⁹Pu and ²⁴⁴Cm while the 278 keV line is from the decay of ²³⁹Np, the secular equilibrium daughter of ²⁴³Am. Although many photons could be identified in the decay of ²⁴¹Am, all suffered from poor resolution or potential interferences. The 722 keV line was finally chosen as providing the greatest sensitivity, although it may be necessary to correct this photon peak if large amounts of ¹⁵⁴Eu are present.

In addition to the gamma-ray lines from the transuranics and fission products, the 1461 keV line from ⁴⁰K in the sediments was observable in every spectra and served as an internal standard for verification of the reliability and operation of the electronic equipment.

TABLE 10.2. Calibration Factors for the Determination of Transuranics in Sediments with a 102 cm³ Intrinsic Germanium Diode Spectrometer

Isotope	Gamma-Ray, keV	Counts/sec/nCi cm ⁻³
²³⁹ Pu	414	$(2.20 \pm 0.11) \cdot 10^{-3}$
²⁴¹ Am	722	$(6.89 \pm 0.38) \cdot 10^{-4}$
²⁴³ Am	278 (²³⁹ Np)	168 ± 32
²⁴⁴ Cm	816	$(9.8 \pm 1.6) \cdot 10^{-5}$

The experimental calibration factors are given in Table 10.2. The sensitivity for measuring ²⁴³Am is many orders of magnitude greater than for the others due to the high-yield gamma-emitting daughter product. This condition does not exist for the other actinides of interest. Table 10.3 lists the expected relative activities of these four transuranic isotopes for both new and aged (30 years) weapons grade plutonium and pressurized water-reactor fuel originally enriched to 3.3% ²³⁵U and exposed to 33,000 MWDT burnup. Multiplying the relative activities from Table 10.3 and the calibration factors from Table 10.2 shows that detection of the 414 keV gamma-ray of ²³⁹Pu provides the most sensitive measurement of weapons grade plutonium regardless of its age. However, for high-exposure power reactor fuels, the detection of the 278 keV gamma-ray from ²⁴³Am(²³⁹Np) provides the most sensitive measure of plutonium concentration if there has been no segregation of transuranic activities.

In many instances the transuranics to be measured are in the presence of fission product activities, which reduce the sensitivity for actinide detection due to copious interfering gamma radiations. The magnitude of this interference was investigated using a source of typical fission product activities that is described in Table 10.1. Detection limits for the transuranic activities as

TABLE 10.3. Relative Transuranic Activities from Various Source Materials

Source	Relative Activity			
	²³⁹ Pu	²⁴¹ Am	²⁴³ Am	²⁴⁴ Cm
New weapons grade Pu	1	0	0	0
Aged weapons grade Pu	1	0.14	0	0
New 33,000 MWDT fuel	1	0.26	0.055	8.0
Aged 33,000 MWDT fuel	1	8.3	0.055	8.0

a function of fission product concentration are shown in Figures 10.1 through 10.4 for counting periods of 10, 100, 1000, and 10,000 seconds. These detection limits were obtained according to the method of Coop et al.,⁽³⁾ which can be summarized by the following equation.

$$MDTA = k_A \sigma_A + k_B \sigma_B \quad (1)$$

where MDTA = the minimum detectable TRU activity,

k_A and k_B = probability constants for the chosen occurrence frequency of deviations based on a Gaussian distribution (in this work $k_A = k_B = 1.645$ for the chosen 90% confidence limit),

σ_A = the standard deviation of the actinide activity, and

σ_B = the standard deviation of the baseline activity, which includes the background and Compton events from the fission product activity.

Substituting in Equation (1) above,

$$MDTA = \frac{1.645}{t} \left[\sqrt{A \times t} + \sqrt{(b+fp) \times t} \right] \quad (2)$$

where A = the actinide count rate,

b = the background count rate,

fp = the fission product count rate in the area of interest, and

t = the length of the count.

FIGURE 10.1. Detection Limits for Measuring the 414 keV Gamma Ray from ^{239}Pu in Soil Contaminated with Fission Products Using a 102 cm^3 Intrinsic Germanium Diode

FIGURE 10.2. Detection Limits for Measuring the 722 keV Gamma Ray from ^{241}Am in Soil Contaminated with Fission Products Using a 102 cm^3 Intrinsic Germanium Diode

FIGURE 10.3. Detection Limits for Measuring the 278 keV Gamma Ray from $^{243}\text{Am}(^{239}\text{Np})$ in Soil Contaminated with Fission Products Using a 102 cm^3 Intrinsic Germanium Diode

FIGURE 10.4. Detection Limits for Measuring the 816 keV Gamma Ray from ^{244}Cm in Soil Contaminated with Fission Products Using a 102 cm^3 Intrinsic Germanium Diode

The most sensitive indicator of transuranic activities is provided by the measurement of the ^{239}Pu 414 keV gamma ray in weapons grade plutonium and the measurement of the ^{243}Am (^{239}Np) 278 keV gamma ray in high-burnup power reactor fuel regardless of the concentration of interfering fission products or the length of the count. This can be seen from a combination of the relative transuranic activities listed in Table 10.3 with the detection limit data depicted in Figures 10.1-10.4.

Comparison of the sensitivity level of this technique to other measurement techniques should be made here. A ^{90}Sr concentration of only 10 nCi cm^{-3} can be measured in a fission product gamma field of 100 nCi cm^{-3} in a counting period of only 10 sec with the same IG detector,⁽⁴⁾ whereas the corresponding detection limit for weapons grade plutonium is $15,000 \text{ nCi cm}^{-3}$. Even if the count time is extended to 10,000 sec, the ^{239}Pu detection limit is reduced only to 440 nCi cm^{-3} . Obviously, this technique provides insufficient sensitivity for plutonium monitoring under these circumstances. However, if the plutonium is from unseparated, high-burnup material and the ^{243}Am analog can be measured, as little as 5 nCi cm^{-3} of ^{239}Pu can be inferred in 10 sec. In an environment free of interfering gamma radiation, as little as 5 nCi cm^{-3} of ^{239}Pu can be measured directly by photon analysis in $<3 \text{ hr}$. This compares favorably with the detection limit observed for a passive neutron detection technique developed earlier.⁽⁵⁾ The neutron detection technique, however, is completely unaffected by any level of gamma radiation. The use of a phoswich detector for in situ analysis of transuranics⁽⁶⁾ can be shown to be inferior to use of an IG diode by at least a factor of 40.

Since the photon detection technique described here appears to have substantial merit for application to transuranic measurements, at least in relatively low gamma-ray environments, field tests will be initiated to evaluate the usefulness, accuracy, reliability, and versatility of the technique. This will also provide a cross calibration opportunity with the neutron detection technique developed earlier.

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

J. A. Franz - Project Manager

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

SUMMARY

In this quarter, desorption of reduced technetium from Hanford soil by sodium citrate has been examined for the ^{99}Tc concentration range 10^{-6} to 10^{-9}M . Very little desorption of the reduced technetium was observed even at citrate/technetium ratios of 10,000:1--89% of the reduced technetium remained sorbed for the concentration range 10^{-6} to 10^{-8}M . The amount of reduced technetium sorbed at the 10^{-9}M level dropped to ~75%, possibly because of a solubility phenomenon. Comparison of the data from the desorption of reduced technetium by EDTA and citrate indicates similarities in the non-desorbing behavior of both ligand systems of reduced ^{99}Tc . Possible explanations for this observed behavior are discussed.

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

Desorption studies of reduced ^{99}Tc on Hanford soil by sodium citrate have been completed. The metal concentration ranged from 10^{-6} to 10^{-9}M ; each metal concentration was treated with five sodium citrate concentrations so that the following citrate/Tc molar ratios resulted: 1:1, 10:1, 100:1, 1000:1 and 10,000:1. Water/soil ratios were

30:1; TcO_4^- was reduced by hydrazine in the presence of soil; shaken for 3 days; citrate was added; and the contents were shaken for 10 days. As in the previous quarter, necessary precautions were taken to exclude air throughout the study. Solution pH was not controlled, TcO_4^- solutions exhibited pHs of ~7.5 to 7.8; reduced TcO_4^- of ~10.6 to 10.7 (pH increases due to hydrazine), and reduced TcO_4^- + citrate ~10.3 to 9.9. Table 11.1 summarizes the calculated K_d s for the study. In general, no sizable changes in sample K_d s are observed for the citrate/Tc molar ratios examined. Very little of the reduced ^{99}Tc is being desorbed by the citrate. In fact, the sample K_d s in most cases are somewhat larger than those observed for reduced technetium (no citrate), suggesting possibly further reduction of the reduced technetium by citrate. A more meaningful way to examine the data from this study is to look at the percent of ^{99}Tc that remains sorbed as the concentration of the desorbing ligand increases. These data are presented in Table 11.2. Very little desorption of the reduced technetium is observed. The reduced ^{99}Tc appears to be effectively sorbed on the soil (85-89%) even at citrate/Tc ratios of 10,000:1. No sizable differences in the value of technetium sorbed are observed between reduced

TABLE 11.1. Calculated K_{ds} for Desorption Study of Reduced ^{99}Tc by Na_3 Citrate(a)

Concentration Tc	Reduced Tc No Citrate	Reduced Tc + Na_3 Citrate, Cit/Tc Molar Ratio				
		1:1	10:1	100:1	1000:1	10,000:1
$1 \times 10^{-6}\text{M}$	404.00	599.45	453.98	509.87	511.12	161.20
$1 \times 10^{-7}\text{M}$	194.20	399.20	445.51	305.99	250.20	253.76
$1 \times 10^{-8}\text{M}$	52.07	423.66	261.68	200.00	221.64	207.84
$5 \times 10^{-9}\text{M}$	52.23	109.84	102.67	82.38	26.63	19.67

a. TcO_4^- reduced by hydrazine. Duplicate runs performed on each sample.

TABLE 11.2. Desorption Study of Reduced(a) Tc by Sodium Citrate (expressed as percent ^{99}Tc still sorbed on soil)

Concentration ^{99}Tc	Reduced Tc No Citrate	Reduced Tc + Na_3 Citrate, Cit/Tc Molar Ratio				
		1:1	10:1	100:1	1000:1	10,000:1
$1 \times 10^{-6}\text{M}$	93	96	93	95	95	85
$1 \times 10^{-7}\text{M}$	87	93	94	91	89	89
$1 \times 10^{-8}\text{M}$	63	93	88	86	88	87
$5 \times 10^{-9}\text{M}$	64	76	77	73	61	39

a. TcO_4^- reduced with hydrazine.

technetium and the test samples, suggesting that citrate does not or cannot interact with the sorbed reduced ^{99}Tc . A likely and somewhat obvious explanation might be that citrate is not a strong enough ligand to desorb the reduced technetium via complex formation and that perhaps a stronger ligand is needed. Examination of reduced ^{99}Tc desorption by EDTA (discussed in the last quarterly) seems to indicate, however, that a stronger ligand is not the answer. These data are presented in Table 11.3; again, more meaningful information is derived by examining the percent of technetium sorbed. As in the citrate study, very little difference is observed in the percent of technetium sorbed values between the reduced technetium with no EDTA and the test samples with EDTA. Possible explanations for this behavior in both ligand systems might be that:

1. Other metal ions present in the soil, such as Fe^{+2} , Mg^{+2} , Ca^{+2} , etc., are competing effectively for the desorbing ligands. Ca^{+2} readily forms complexes with both citrate and EDTA, with the EDTA complex being more stable [log of the formation constant⁽¹⁾ for $\text{Ca}(\text{EDTA})^{2-}$ is ~11 compared to ~5 and 8 for $\text{Ca}(\text{Hcit})^-$ and $\text{Ca}(\text{Hcit})_2^{2-}$]. $\text{Ca}(\text{EDTA})^{2-}$ exhibits maximum stability in the pH range 7 to 9. Hanford soil is known to contain Ca^{+2} and Mg^{+2} . Unfortunately, stability-constant data are not available for technetium complexes.
2. Something else in the soil has a greater affinity for the reduced technetium than the desorbing ligands, or through some cation exchange mechanism in the soil the reduced technetium is rendered inaccessible.

TABLE 11.3. Calculated Sorption Coefficients (K_d s) and Percent Tc Sorbed in Desorption of Reduced(a) ^{99}Tc by Na_2EDTA

	Concentration Tc	Reduced Tc No EDTA	Reduced Tc + Na_2EDTA EDTA/Tc Molar Ratio		
			1:1	5:1	10:1
K_d	$1 \times 10^{-5}\text{M}$	2947.30	1022.00	374.70	281.40
Percent Tc sorbed		99	98	93	91
K_d	$2 \times 10^{-6}\text{M}$	847.20	1217.10	647.60	317.20
Percent Tc sorbed		97	98	96	92
K_d	$4 \times 10^{-7}\text{M}$	45.70	79.00	67.00	31.90
Percent Tc sorbed		62	72	69	61

a. TcO_4^- reduced by hydrazine. Duplicate runs on each test sample.

The decrease in the percent of technetium sorbed that is observed in the lower technetium concentrations for both the EDTA and citrate studies might be a solubility phenomenon. On the basis of the observed data for both the citrate and EDTA systems, it appears that mobilization of sorbed reduced technetium will not occur in a basic pH medium (8 to 10).

A long-term desorption study (1 month) with citrate as the desorbing agent is nearing completion. It will be of interest to the program to compare those results with those of the 10-day study.

A few more technetium/soil experiments will be conducted before starting europium and samarium desorption studies (which should commence soon). These technetium/soil experiments will include soil interaction of Tc(IV)EDTA and Tc(V)DTPA and examination of the ability of humic acids to reduce TcO_4^- .

REFERENCE

1. Sillen, L. G. and A. E. Martell, 1964. "Stability Constants of Metal-Ion Complexes." Special Publication No. 17, The Chemical Society, London.

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

A report, Summary of Non-U.S. National and International Radioactive Waste Management Programs 1980 (PNL-3333), was published.

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

A report, Release Consequence Analysis for a Hypothetical Geologic Radioactive Waste Repository in Hard Rock, was completed and delivered to the International Atomic Energy Agency. Work began on recasting some of the reports prepared by PNL in support of the International Nuclear Fuel Cycle Evaluation's Working Group 7 as PNL reports.

The Human Affairs Research Centers (HARC) continued work on the six discrete tasks to be performed under this program this fiscal year, including the development of a social sciences research plan for DOE's Office of Nuclear Waste Management (NEW). In March HARC was also assigned an additional task to provide support to MITRE Corporation in a public participation program related to the development of a National Plan for Radioactive Waste Management.

Two reports prepared under contracts by Teknekron, Inc., were published: Nuclear Waste Management Issues: A Multidisciplinary Evaluation Framework (PNL-3078) and A Depth Optimization Study for Geologic Isolation of Radioactive Wastes (PNL-3079).

A draft report, Waste Management Databook (PNL-3392), containing LWR fuel cycle data was sent to ORNL.

Agreement was reached with North Carolina State University on the technical scope of

an effort to develop information on technical aspects of waste management in a form understandable to the lay public.

A report, Commercial Nuclear Reactors and Waste: The Current Status (PNL-3317-1), was prepared as the first in a series to track implications to DOE's commercial waste management program due to the steady decline in the commercial nuclear power industry in the U.S.

INTERNATIONAL NUCLEAR FUEL CYCLE EVALUATION (INFCE)

Camera-ready mats for a report entitled Release Consequence Analysis for a Hypothetical Geologic Radioactive Waste Repository in Hard Rock (INFCE/DEP/WG.7/21) were sent directly to the IAEA, which will publish the report. Copies of the report were sent to DOE-RL, DOE-HQ, the Swedes, Canadians, and U.S. groups, the Office of Nuclear Waste Isolation (ONWI), Lawrence Berkeley Laboratory (LBL), and the Basalt Waste Isolation Project (BWIP). This completed PNL's support of INFCE WG.7.

In support of INFCE WG.7, PNL developed several reports that have been logged into the IAEA depository along with all the other background reports. To make the PNL information available to a broader spectrum of the interested public, PNL is planning to recast two of those reports and publish

them as PNL documents. The report on the waste arisings from three LWR fuel cycles (INFCE/DEP/WG.7/11) will be rewritten to reflect U.S. waste management assumptions. The salt (INFCE/DEP/WG.7/16) and the hard rock (INFCE/DEP/WG.7/21) release consequence analyses reports will be summarized in one report. Carl Cooley, DOE-HQ, has been advised and sees no conflict with INFCE WG.7. We are coordinating the waste arisings report with Oak Ridge National Laboratory (ORNL) and the release consequence report with ONWI.

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

Following resolution in January of the package of tasks to be undertaken by HARC in FY-1980, task teams were organized for the six identified tasks. Task 1 is to develop a long-range plan for social science research in the area of nuclear waste management. The first activity was to partition the field of potential social science contributions into appropriate substantive areas. Then a conceptual framework was developed for carrying out the task. The framework calls for developing a model of waste management activities, identifying points in the model where social science research applies, determining which type of social science work applies for the relevant aspects of the model, assessing the existing state of social science knowledge, and assessing where research gaps exist. An assembly and review of waste management technical program plans was undertaken.

Task 2 involves a survey of perceived comparative risks of various potentially hazardous facilities, including waste management, and of areas of specific public concern

regarding a nuclear waste repository. During the past quarter the sampling methodology and the data collection technique (mail surveys) were selected. The sample of potential respondents and their addresses was then drawn and is currently being typed into the word processing machines. In addition, the survey questionnaires were finalized subject to technical review, which will occur in April.

Task 3 involves an analysis of factors contributing to the preservation of information about nuclear waste management over long time periods. The literature review was carried out last quarter, and analysis will begin next quarter.

Task 4 is an identification of remaining technical problems in nuclear waste management that will serve as a basis for later analysis of the linkage between technical problems and nontechnical waste management issues. Because of other commitments, only one planning meeting was held on this task the last quarter. The major work on this task will begin next quarter.

Task 5 involves consulting with experts on the applicability of environmental mediation techniques in the siting of nuclear waste facilities. This past quarter, the principal investigator attended a meeting in Palo Alto devoted to the evaluation of the applicability of various mediation procedures for resolving disputes arising from waste management siting issues.

Task 6, the update of topical reports, was begun in the first quarter but will not be completed until April.

In March, an additional task, Task 7, was added to HARC's Waste Management Systems Studies contribution. HARC will assist 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. Two HARC staff members attended a meeting with MITRE in March to help in the planning.

ASSESSING NUCLEAR WASTE MANAGEMENT OPTIONS* - R. G. Bradley (Teknekron, Inc.)

A report entitled Nuclear Waste Management Issues: A Multidisciplinary Evaluation Framework (PNL-3078), which was prepared under contract by Teknekron, Inc., was published.

WASTE REPOSITORY COST/SAFETY OPTIMIZATION** - M. Thadoni (Teknekron, Inc.)

A report entitled A Depth Optimization Study for Geologic Isolation of Radioactive Wastes (PNL-3079), which was prepared under contract by Teknekron, Inc., was published.

WASTE MANAGEMENT DATABOOK*** - R. W. McKee

A report entitled Waste Management Databook (DRAFT), March 1980 (PNL-3392), was sent to ORNL for comments. ORNL is expected to use the information in connection with their task of developing a computerized waste management data base for the Planning and Analysis Branch of the Division of Management Support of NEW.

Review of the high-temperature gas reactor data prepared by North Carolina State University for the databook has been deferred pending discussions with ORNL regarding how these data fit with their plans on their data base efforts.

J. V. Robinson attended the third meeting of the ORNL Data Base Steering Committee in

* For background information see PNL-3000-3 (Section 6) in this series.

** For background information see PNL-3000-1, pp. 7.7-7.9.

*** For background information see PNL-3000-4, the prior report in this series.

Seattle on February 14 and 15, 1980, and gave an overview presentation of PNL systems analysis activities. No specific tasks were assigned to PNL other than that mentioned earlier regarding the LWR section of PNL's Waste Management Databook.

WASTE MANAGEMENT INFORMATION FOR THE LAY PUBLIC - R. Murray, North Carolina State University

Dr. Raymond Murray of North Carolina State University and Dr. Frank Pittman, Consultant, visited PNL on February 4 to reach agreement on the scope of work on the task to develop basic waste management information for communicating with the public. Dr. Murray subsequently submitted a detailed scope of work and budget to PNL. Arrangements are being made to draft a new contract with North Carolina State University. It is planned that Dr. Margaret Maxey, Assistant Director of the Energy Research Institute, Dr. Pittman, and HARC will participate.

WASTE FROM THE COMMERCIAL NUCLEAR POWER INDUSTRY - A. M. Platt and J. V. Robinson

A draft PNL report entitled Commercial Nuclear Reactors and Waste: The Current Status (PNL-3317-1), March 1980, was developed as the first of a series to track implications to waste management due to changes (decline) in the declared size of the commercial light-water reactor nuclear power industry in the U.S.

Based on the declared* size of the nuclear power industry in the U.S. as of January 1, 1980, the report shows the installed capacity will peak at 162 GWe in the year 2000 and that two repositories of about 100,000

* Reactors either operating, in construction or announced.

MTU storage capacity each would be sufficient to store the fuel discharged through the year 2060.

The report was sent for comment to members of the Steering Committee for ORNL's

Integrated Data Base project. Several members, including those representing ONWI and BWIP, have encouraged early publication. We plan to submit the report to DOE-RL for formal comment and to publish it in April.

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

A state-of-the-art survey of systems safety analysis methods was begun this quarter. This survey will examine both safety assessment methods and their application to waste management systems. A brief study on ^{14}C dispersion/accumulation tradeoffs was initiated. A review of ^{14}C recovery techniques has been completed.

METHODS SURVEY - P. J. Pelto

A survey was initiated to identify the state-of-the-art of modern predictive system safety analysis methods. Methods currently being used in the assessment of waste management activities are emphasized. Expected outcomes and intended uses of these assessments will be identified along with methods and approaches that appear to be of special utility. This survey is expected to identify some additional needs for methodology development in waste management safety. Some potential examples include areas such as occupational exposure, uncertainty propagation, common cause failures, and operator

error. An issue paper discussing and prioritizing methodology development needs will be prepared. This paper will provide recommendations for high-priority development needs to be addressed in FY-1981.

DISPERSION/ACCUMULATION TRADEOFFS -

P. J. Mellinger

A study was begun on tradeoffs for ^{14}C release versus recovery. A brief review of ^{14}C recovery techniques has been completed. Through use of a simplified environmental pathway analysis, individual radiation exposures to members of the general public are being calculated. The cases of recovery and no recovery are examined, and comparisons will be made with the ^{85}Kr study⁽¹⁾ where appropriate.

REFERENCE

1. P. J. Mellinger et al., ^{85}Kr Management Trade-Offs: A Perspective to Total Radiation Dose Commitment. PNL-3176, Pacific Northwest Laboratory, Richland, WA, January 1980.

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

Work continued to concentrate on improving the release scenario model and developing a finite-element model that couples ground-water flow as well as energy transport and solute transport. Studies continued also on various aspects of uncertainty and geostatistics research related to the ground-water flow and contaminant transport equations. Negotiations began with ONWI and Intera, a new ONWI contractor, concerning the transfer of computer codes. All reports on the data system and the scenario, hydrologic, transport and dose computer codes in use by AEGIS were submitted to clearance, and most were printed.

The salt dome RSIA report (PNL-2955) was distributed to 33 scientists for peer review, with a written response requested from each by May 1, 1980. Subsequent to the peer review, the salt dome RSIA report will be revised as needed prior to general distribution.

Based on the balance of thermal energy fluxes, brine temperatures in the solution-mine scenario using spent fuel are estimated to approach that of the dry host salt prior

to the hypothetical breach. However, estimating of the temperature of dry salt that surrounds a high-level waste (HLW) inventory has proved to be more difficult than expected because the available data show an anomaly between repository size, quantity of stored waste, and thermal loadings.

A written agreement to coordinate the AEGIS basalt RSIA (reference site initial assessment) and the BWIP (basalt waste isolation project) site characterization report (SCR) as a team effort was completed and signed on January 30, 1980. The geology integration report (RHO-BWI-ST-4) and the hydrology integration report (RHO-BWI-ST-5) were transmitted by Rockwell to AEGIS on February 5. The basalt RSIA conceptual model and mathematical modeling plan were presented to Dr. R. A. Deju and other members of the Rockwell technical staff on March 25. A working paper describing the basalt conceptual model will be available for review in April.

Regional hydrologic modeling has received the most attention this quarter. The overall strategy is to develop a regional model of the major portion of the Columbia Plateau Basalt that serves as a source of recharge waters or otherwise influences flow of

circulating ground water within the more local Pasco Basin where the hypothetical repository will be sited. Different modeling strategies have been selected for the regional and local model. The regional modeling effort will use the multi-aquifer, two-dimensional VTT hydrologic code, and the local model will use the fully three-dimensional FE3DGW hydrologic code. Interpretations of potentiometric distributions and transmissivity distributions on a regional scale, including measurement locations and the associated discrete values, have been digitized. Methods for calculating distribution of areal recharge have been identified, and the process for gathering additional needed data and implementing the calculational scheme have begun.

Basalt release scenarios are being developed using expert opinion based on sub-model categories contained in the basalt release scenario model. Analysis of the natural disruptive phenomena suggests that only tectonic phenomena such as faulting and folding are potential natural causes for a breach of the repository host rock. A working paper describing the release scenario analysis for basalt is in progress.

METHODOLOGY DEVELOPMENT - D. J. Silveira

Issues Analysis - D. J. Silveira

Additional information to determine the potential for organic compounds to influence the transport rate of radionuclides was obtained, and a status report will be prepared next quarter. Work also continued on a brief white paper to describe PNL ground-water models, and writing began on the AEGIS integrated methodology (AIM) report, which will provide a thorough presentation of the AEGIS methodology.

During this quarter, the geochemistry effort to determine the chemical environment of the host rock-repository system at the time of a breach was transferred into the issues analysis task from the scenario methodology development task. Chemical changes from the present conditions will be estimated based on anticipated response to the various breach scenarios. The addition of geochemical modeling to the radionuclide transport models is being evaluated. This effort may incorporate the organics work at a later date. At present the geochemistry effort has compiled about 350 publications related to waste isolation in geologic media in support of both AEGIS and WRIT research.

Scenario Methodology Development -

J. T. Zellmer

Work this quarter resulted in changes in conceptualization of the ground-water system. Studies by the U.S. Geological Survey and our consultants suggest that it may be possible to represent the regional ground-water system by a two-dimensional, cross-sectional model. The regional ground-water systems appear to be recharged both to the northeast and southwest of the Pasco Basin. The ground water appears to discharge into the Columbia River and to a shallow, unconfined aquifer system upstream of Wallula Gap. The release scenario model simulates this system by a series of flow tubes having flow characteristics like those of the actual aquifers. This simulation method is much simpler than that used previously.

A hydrology submodel is also being added to the release scenario model. This submodel uses the revised ground-water conceptualization outlined above and also consolidates all the hydrologic calculations previously dispersed throughout several submodels.

The draft of the scenario model user's manual (PNL-2892-2) was printed, and copies were sent to our consultants for review. A response was requested by April 4, 1980.

Guidelines were prepared for generating density curves needed for stochastic operation of the model and were sent to consultants for independent review.

Surface-water models from the U.S. Army Corps of Engineers were studied to simulate river flooding, erosion and deposition.

The input and output programs became operational and were linked to the release scenario model. Consequently, the release scenario model can be used in the test-bed mode as a deterministic model to generate release scenarios.

The statistical team continued studying methods to increase the efficiency of the model, reduce run time, organize, simplify and evaluate input and output data, and reduce variance. Much of this effort was directed toward implementing the model's Monte Carlo aspect. Areas of investigation related to the stochastic operation of the model include splitting, killing runs incapable of producing breaches, and methods of biasing to more efficiently examine rare events.

Preliminary work to devise screening methods began in order to help determine the sensitivities of the model parameters.

The statistical team is evaluating the work still to be done, determining the best approach for each task, and preparing a schedule for each major task.

Geologic and hydrologic data continue to be collected for additional testing and refinement of the model. This includes collecting and analyzing several hundred references, contacting consultants and other experts, and visiting federal, state and local agencies and other private or public sources of data.

Transport Methodology Development - R. W. Nelson

Computer mesh generators have been developed as an auxiliary utility code for CFEST to reduce the time, labor, and the amount of data otherwise required to produce a finite-element grid.

Work continued on determining media properties such as permeability and porosity distribution from information about the potential. This is inverse to the usual problem of determining the potential conditions and distributions from the initial boundary conditions and distributions of porous media properties. This problem has been difficult to solve because the solutions to equations describing this inverse problem may not be continuous with small changes in input data.

It has been observed that stochastic variations are being omitted from recent technical papers on subsurface uncertainty modeling. Instead, only the mean or expected values from previous time frames have been incorporated into the model.

The additional stochastic terms have been incorporated, however, into the development effort at PNL. This ensures that the small approximations are all correct through second order. However, some added numerical steps are involved in the numerical solution when the additional terms are included. Specifically, a combination of time-step control and re-initialization is being examined to handle the added numerical complexity.

The time-step control and re-initialization strategy was defined using an updating procedure that simplifies the computation and data storage requirements. This procedure has been incorporated into the one-dimensional code. The question of frequency of re-initialization is being studied. One

answer is to re-initialize every time step; another is to re-initialize at the largest number of time steps permitted by the approximation constraints. The optimum probably is somewhere between these two. A similar updating procedure is currently being incorporated into the two-dimensional code.

The two-dimensional code has been modified to include an interrupt-restart capability. This feature allows the user to resume computation from previously saved data. A substantial amount of computing is required to obtain coefficients used in advancing the solution in time. This restart facility will permit bypass of this initial computation. It also allows emergency interruptions to occur with minimal cost and inconvenience. The restart procedure is reasonably general and includes appropriate security measures to insure restarting from the desired data files.

Dose Methodology Development - J. K. Soldat

Work continued on documenting the computer codes ARRRG and FOOD while the PABLM report has gone to printing.

SITE APPLICATIONS - F. H. Dove

Salt Dome RSIA

The salt dome RSIA report (PNL-2955) was distributed to 33 scientists for peer review. A written response was requested from each by March 15. Several reviewers indicated a desire to respond but requested a longer time for review. Consequently, the review period was extended to May 1, 1980. So far, comments have been received from ten reviewers. Most of them agreed with the need for the analysis, the general approach, and the over-

all conclusions. There were many comments on details of the analyses; preliminary evaluation indicates that they will not affect the overall conclusions. Subsequent to the peer review, the salt dome RSIA report will be revised as needed prior to general distribution. A presentation of the salt dome RSIA was given to the National Academy of Sciences Review Panel for WIPP (waste isolation pilot plant).

Other activity concerning the salt dome analysis related to the set of calculations using the same scenario and repository design as in PNL-2955 but with an inventory of glass incorporating reprocessed high-level waste rather than an inventory of spent fuel. Early calculations indicated that HLW glass would result in a higher dose to the population than would spent fuel. However, subsequent considerations indicated the temperatures assumed for leaching may have been excessive. Thus, staff from the Waste-Rock Interactions Technology (WRIT) and AEGIS programs independently derived formulations to estimate the effective leaching temperature that should be expected for the particular scenario under consideration. These calculations lead to two disparate results: that the temperature would be near the ambient temperature of the incoming water or that the temperature would be near the temperature of the host salt surrounding the repository in the dry condition. The discrepancy was resolved, based on a better understanding of the particular scenario conditions, and a consensus was reached that the temperature would approach that of the dry host salt. This is based primarily on the balance-of-energy flows from the waste to the salt, from the salt to the water in the cavity, from the water being transported to the surface, and on the exchange of thermal energy from the effluent water to

the influent water via the concentric piping in the solution mine.

Calculations are presently under way to estimate the salt temperatures at 100 and 1000 years post-closure from a repository containing HLW glass in quantities consistent with the amount of spent fuel in the reference repository design. Once those temperatures are estimated, a leach rate will be assigned for each isotope that is a primary dose contributor, a source term for each will be calculated, and resultant dose burdens to individuals and to the surrounding population will be modeled.

Basalt RSIA

A written agreement to coordinate the AEGIS basalt RSIA and the BWIP site characterization report (SCR) as a team effort was completed and signed after review and comments. The technical interface between AEGIS and BWIP was discussed at a meeting on January 21, and the geology integration report (RHO-BWT-ST-4) and the hydrology integration report (RHO-BWI-ST-5) were transmitted by Rockwell to AEGIS on February 5. The basalt RSIA conceptual model and mathematical modeling plan were presented to Dr. R. A. Deju and members of the Rockwell technical staff on March 25. A productive technical discussion ensued, and several items were identified for more detailed examination in informal groups. Completion of a working paper describing the basalt conceptual model has been delayed until mid-April to incorporate modifications suggested by Rockwell.

Plan of Analysis

A schematic diagram of the AEGIS analysis to be followed in the basalt RSIA is shown

in Figure 15.1. Information contained in Federal publications, state publications, Rockwell reports, selected university studies, local consultant reports, and other sources are used to establish the data base and initial hydrologic and geologic interpretations for the site-specific application.

Because an understanding of the dynamics of ground-water flow is essential in developing both release scenarios and consequence analyses, a key step in the assessment is the systems characterization contained in the conceptual model. Regional and local ground-water movement patterns are defined with the aid of hydrologic computer models before initiation of any contaminant transport modeling. Hypothetical release scenarios are developed and evaluated by a process of expert opinion and by a process involving a stochastic scenario computer model to obtain credible release scenarios (if there are any). The release scenarios are used to forecast future boundary conditions for the hydrologic models and to aid in the determination of radionuclide leach concentrations during a simulated repository breach. After the radionuclide concentrations are mathematically introduced into the ground-water movement patterns, waste movement patterns are outlined over elapsed time. Contaminant transport results are summarized both by the profile of point-source concentration versus time and by curves for concentration versus arrival distribution for significant radionuclides hypothetically released to the biosphere. When appropriate, dose models are used to calculate radiation doses to man directly or to man through his food chain.

Description of Conceptual Model

A working paper describing the basalt conceptual model is in preparation and will

FIGURE 15.1. Schematic Diagram of AEGIS Analysis

refer to the various interpretations of the dynamics of ground-water flow. Initial modeling for release scenarios and consequence analyses will be based upon steady-state representations of the surface and ground-water flow dynamics. Initial modeling for release scenarios and consequence analyses will be based upon steady-state representations of the surface and ground-water systems. After a few simulations have been made on the PNL interactive computer system, a better understanding of the possibilities for ground-water flow may result in a more knowledgeable consideration of the transient phenomena. The steady-state approach has been recommended by Dr. J. W. Crosby of Washington State University and is also the basis for

regional modeling by the U.S. Geological Survey in Tacoma, Washington.

The overall strategy for hydrologic modeling is to develop a regional model of the major portions of the Columbia Plateau Basalt that serve as a source of recharge waters or in other ways influence the flow or movement of circulating ground waters within the more local Pasco Basin where the hypothetical repository will be sited. Different modeling strategies have been selected for the regional and local model. The regional modeling effort will use the multi-aquifer, two-dimensional VTT hydrologic code, and the local model will use the fully three-dimensional FE3DGW hydrologic code.

Regional Hydrologic Model

The regional modeling effort has received the most attention this quarter and has been more extensive than anticipated. Based on our conceptual model of the regional system, we have elected to use a three-layer implementation of the VTT code. The grid system selected consists of a 55 X 55 regular grid for each of the three layers. The grid is oriented along the true north-south, and the grid spacing is 3 miles. The center of the (1,1) grid block lies at a longitude of -120.343° and a latitude of 45.855° . The top layer of the three-layer system consists of all held-potential nodes. The potentials in these nodes are held at actual river, lake or seepage face elevations. In areas where there are significant unconfined aquifer systems in surface sediments that lie either in significant recharge or discharge areas, these nodes are held according to known water-table elevations. The held potential nodes in this top or surface layer are connected to the appropriate underlying basalt aquifer systems (Saddle Mountains, Wanapum or Grand Ronde) via an interaquifer transfer coefficient. Since this interaquifer transfer coefficient accounts for the transfer area as well as the conductivity and thickness of the transfer layer, the values can be adjusted to account for the actual transfer area of the river lake when they are less than 3 miles by 3 miles. The second layer of the system consists of the Saddle Mountain-Wanapum basalt aquifer system. The third layer is the Grand Ronde basalt aquifer system. Since the distribution of the potentials in the regional system indicate that some regional discharge is occurring in the Pasco Basin, which is overlain by a water table aquifer consisting of surface sediments, the discharge from the basalt systems

is probably upward into the more highly permeable sediments and then laterally through this system to the river. Seepage faces from the basalt systems along the north are handled by holding the surface potential at the outcrop elevations and adjusting the interaquifer transfer coefficient to account for the actual seepage face area.

Potentiometric and Transmissivity Distributions

Potentiometric distributions and transmissivity distributions on a regional scale (including measurement locations and the associated discrete values) have been digitized. Various interpretations and the discrete values were compared, and a new composite interpretation for the transmissivity distribution in the Wanapum was developed. The transmissivity distribution for the Saddle Mountain aquifer system was used to develop a transmissivity-weighted, composite potentiometric map for the combined Saddle Mountain and Wanapum aquifer system. Because data on the deeper Grande Ronde system is scarce to nonexistent, the transmissivity distribution for the modeled aquifer was initially assumed to be a constant 10,000 gallons per day per foot (gpd/ft), and the areal distribution will be modified during the model calibration process. A map showing the areal distributions of groundwater withdrawals from the regional basalt is nearly complete.

Methods for calculating distribution of areal recharge have been identified, and the gathering of additional needed data and implementing of the calculational scheme have begun. Some initial scoping calculations indicate that recharge to the regional system probably occurs entirely within the

modeled region. The method for calculating recharge is as follows: In areas where the sedimentary water table aquifers being modeled exist, the recharge and discharge (other than pumping) will be self-calculating and can be checked for consistency against other data sources. Recharge from precipitation in other areas will be estimated from precipitation, surface runoff, soil types (from general soils maps), temperatures and vegetative cover (LANDSAT). Lack of the required precipitation and temperature data will force determination of some regression analysis between existing weather stations to account for elevation effects on both temperatures and precipitation. Recharge in areas outside the area of modeled sediments that receive imported surface water for irrigation will be accounted for by crop water requirements and appropriate infiltration estimates.

Release Scenarios

Several weeks have been spent obtaining information and developing release scenarios for the basalt RSIA. The scenarios are being developed by using expert opinion based on submodel categories contained in the basalt release scenario model. Although the release scenario model is capable of generating scenarios in the deterministic mode, the model was not used directly because it does not yet incorporate several modifications considered important. When these modifications are incorporated, the model will be used in the deterministic mode so that the computer-generated scenarios and the expert-opinion scenarios can be compared. At the end of FY-1980 the release scenario model will be capable of generating release scenarios in the stochastic mode.

Analysis of the natural disruptive phenomena for the Columbia Plateau Basalt and prep-

aration of release scenarios continues. The scenarios developed include a human-intrusion-related scenario and two tectonically related scenarios. A working paper describing the release scenarios for basalt is in progress.

The analysis suggests that only tectonic phenomena such as faulting and folding are potential natural causes for a breach of the repository basalt. The definition of "breach" is under investigation from the viewpoint of quantifying a threshold value for ground-water flow through the repository basalt. The tectonic scenarios involve initiating or increasing ground-water flow through the repository by increasing the hydraulic conductivity or creating flow zones in the repository. This is accomplished by faulting through the repository or by fracturing the repository rock by folding or other tectonic stresses.

The human-intrusion scenario assumes that an irrigation or exploration well is drilled through the repository. The well connects aquifers above and below the repository and allows water to flow from one aquifer, through the repository and into the other aquifer, thus contaminating it.

Other Site Studies

Coordination was initiated with ONWI and ONWI geologic contractors with respect to future data needs from the Paradox bedded-salt region in Utah.

TOPICAL REPORT PROGRESS

Several papers were prepared for journals and conference presentations. Final preparation of the following reports occurred this quarter:

To Clearance

PNL-3209 A Computer Program for Calculating Accumulated Radiation Dose from Radionuclides in the Environment. B. A. Napier, W. E. Kennedy, Jr., and J. K. Soldat.

PNL-2928 Perspectives on the Geological and Hydrological Aspects of Long-Term Release Scenario Analysis. J. A. Stottlemire.

PNL-2862 The Feasibility of Computer Interrogation of Experts for WISAP. L. H. Wight.

To Clearance and Cleared

PNL-2891-2 A Conceptual Simulation Model for Release Scenario Analysis of a Hypothetical Site in Columbia Plateau Basalts - A User's Manual. G. M. Petrie.

PNL-3179 Multicomponent Mass Transport Model. J. F. Washburn.

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.

Cleared

PNL-2854 Geologic Factors in the Isolation of Nuclear Waste: Evaluation of Long-Term Geomorphic Processes and Catastrophic Events. S. J. Mara.

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

Printed

PNL-2636 Simulation of the Long-Term Accumulations of Radio-contaminants in Crop Plants. R. G. Schreckhise.

PNL-2782 Test Case Release Consequence Analysis for a Spent Fuel Repository in Bedded Salt. J. R. Raymond, C. R. Cole, and F. W. Bond.

PNL-2903 An Evaluation of Kriging Techniques for High Level Radioactive Waste Repository Site Characterization. P. G. Doctor.

PNL-3070 Comparison of Intera and WISAP Consequence Model Application. C. R. Cole and F. W. Bond.

PNL-3160 Variable Thickness Transient, Groundwater Hydrologic Model. A. E. Reisenauer.

PNL-3161 CIRMIS Data System. D. R. Friedrichs.

16. WASTE/ROCK INTERACTIONS TECHNOLOGY

R. J. Serne - Project Manager

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

- 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 and 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 methodology 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.*

PROGRAM MANAGEMENT - R. J. Serne

A normal field task proposal/agreement covering the years FY-1981 through 1986 was prepared and submitted to the Department of Energy and the Office of Nuclear Waste Isolation (DOE and ONWI).

To facilitate exchange of information and to aid in ONWI's licensing quest, WRIT staff have continued formal interchange with other programs and nations. This quarter included participation in a workshop and critical review of a proposed static leaching test standard with the Materials Characterization Center (MCC). Technical and programmatic exchanges via reports and meetings were made with the High-Level Waste Immobilization Program (HLWIP), Hanford Engineering Development Laboratory (concerning ONWI-funded spent fuel work), Rockwell Hanford Operations (concerning waste package testing and nuclide release modeling of interest to both WRIT and BWIP) and representatives of Swedish and Canadian programs.

At the request of DOE and ONWI, WRIT staff prepared material and participated in 1) the joint Nuclear Regulatory Commission/DOE Waste Package Meeting (January 16-17) to brief NRC on DOE activities in waste package development and testing and 2) DOE critical review meetings on the DOE Draft Statement of Position for NRC Confidence Rulemaking Hearings.

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

Waste Form-Solution Interactions

Static leaching tests at 25 and 75°C on doped 76-68 glass beads are ongoing in three solutions: WIPP B salt brine, sodium bicarbonate ground water and deionized water. Tests at 150 and 250°C have been completed, and a report is being finished.

The neptunium and plutonium solution analyses have been completed for the single-pass continuous flow test at Lawrence Livermore Laboratories. Analyses of neptunium and

plutonium on the outlet filters at 75°C were completed. These were done to check for sorption of neptunium and plutonium on the leaching cell outlet filters. The results (percentages versus the total ^{237}Np and ^{239}Pu that had passed through the filters during the experiment) ranged from 0.0002% to 0.04% of the ^{237}Np and 0.03% to <4% of the ^{239}Pu , indicating that only trivial amounts are caught on the filters. The inductively coupled plasma spectroscopy analyses of the leach solutions have been completed. The 75°C temperature channels clearly show a flow rate effect for boron, sodium, silicon, iron and uranium that is the reverse of that observed for neptunium and plutonium. That is, the slow-flow channels show the highest concentration of these elements in the leachate while the fast-flow channels show the lowest.

Results of uranium, plutonium and neptunium leached from simulated waste-glass under anoxic conditions at Argonne National Laboratory are given in Table 16.1. Analyses are under way on the leach solutions from PNL's parallel test under oxic conditions. The results of the two tests cannot yet be compared and discussed.

Waste Package Interactions

Six static waste package tests were begun during the quarter. Three of these are being conducted in 850-ml autoclaves with direct solution sampling capability and are still in progress. The other three were conducted in 125-ml Teflon[®]-lined digestion bombs at 250°C for 30 days. They have recently been completed, and some of the preliminary results are presented below.

[®]Teflon is a registered trade name of the E.I. Du Pont de Nemours Co., Delaware, MD.

The three digestion bomb experiments consisted of a cylindrical minicanister of 304 stainless steel, about 1-1/2 in. long by 1/2 in. ID, filled with UO_2 -doped 76-68 glass. These minicanisters were open at one end and had a 1/8-in. vertical cut through the canister, exposing the glass to simulate a fracture. A machined rock pellet was placed on top of the open end of the canister, and the entire canister plus rock pellet was surrounded by crushed rock material (<200 mesh). The rock materials used in the three separate tests were NTS granite, Umtanum basalt (BWIP), and Carlsbad bedded salt from near the WIPP site. About 50 ml of DI water was added to the granite and basalt packages. About 50 ml of salt brine (prepared by saturating DI water with crushed Carlsbad salt at 50°C) was added to the salt package. The bombs were placed in an oven at 250°C for 30 days, after which they were removed and immediately quenched by submersion in cold water. The solutions were immediately extracted and analyzed for dissolved metals, and the solid package components were removed and dried.

Extensive recrystallization of salt occurred during this run. The initial pulverized salt recrystallized into crystals up to 8 mm on an edge, and recrystallization fused the original salt pellet to the salt matrix. Some effects are observed in the change in elemental final solution concentrations. The most soluble constituents will remain in the liquid phase while the less soluble elements will tend to be partitioned in the recrystallized phase. Consequently, the liquid phase becomes enriched in elements such as magnesium, boron, sodium, and cesium but depleted in calcium, strontium and, to some extent, potassium. Moreover, elements that tend to form strong chloride complexes such as zirconium, lead, iron,

TABLE 16.1. Results of Anoxic Leach Measurements in g/cm² day^(a)

Medium	Temperature, °C	Element	2 days	32 days	106 days
Deionized Water	23	Np	$(3.2 \pm 0.4) \times 10^{-6}$	$(0.73 \pm 0.05) \times 10^{-6}$	$(0.46 \pm 0.03) \times 10^{-6}$
	23	Pu	$(0.43 \pm 0.03) \times 10^{-6}$	$(0.03 \pm 0.001) \times 10^{-6}$	$(0.009 \pm 0.0005) \times 10^{-6}$
	23	U ^(b)	0.45×10^{-6}	0.014×10^{-6}	0.028×10^{-6}
	75	Np	$(3.8 \pm 0.7) \times 10^{-6}$	$(0.11 \pm 0.03) \times 10^{-6}$	$<0.007 \times 10^{-6}$
	75	Pu	$(0.54 \pm 0.02) \times 10^{-6}$	$(0.034 \pm 0.002) \times 10^{-6}$	$(0.006 \pm 0.0003) \times 10^{-6}$
	75	U ^(b)	2.1×10^{-6}	1.48×10^{-6}	0.81×10^{-6}
0.03M NaHCO ₃	23	Np	$(6.5 \pm 2.5) \times 10^{-6}$	$(3.28 \pm 0.09) \times 10^{-6}$	$(0.94 \pm 0.08) \times 10^{-6}$
	23	Pu	$(1.95 \pm 0.3) \times 10^{-6}$	$(0.24 \pm 0.009) \times 10^{-6}$	$(0.068 \pm 0.003) \times 10^{-6}$
	23	U ^(b)	$<0.15 \times 10^{-6}$	2.6×10^{-6}	1.93×10^{-6}
	75	Np	$(17 \pm 3.5) \times 10^{-6}$	$(0.63 \pm 0.06) \times 10^{-6}$	$(0.19 \pm 0.019) \times 10^{-6}$
	75	Pu	$(1.25 \pm 0.05) \times 10^{-6}$	$(0.02 \pm 0.002) \times 10^{-6}$	$(0.004 \pm 0.0002) \times 10^{-6}$
	75	U ^(b)	7.25×10^{-6}	81.25×10^{-6}	28.8×10^{-6}
Waste Isolation Pilot Plant	23	Np	$(4.75 \pm 0.35) \times 10^{-6}$	$(0.84 \pm 0.08) \times 10^{-6}$	$(0.40 \pm 0.02) \times 10^{-6}$
	23	Pu	$(0.68 \pm 0.02) \times 10^{-6}$	$(0.6 \pm 0.002) \times 10^{-6}$	$(0.027 \pm 0.0009) \times 10^{-6}$
	23	U ^(b)	0.27×10^{-6}	0.47×10^{-6}	0.31×10^{-6}
	75	Np	$(2.3 \pm 1.5) \times 10^{-6}$	$(2.78 \pm 0.13) \times 10^{-6}$	$(1.53 \pm 0.08) \times 10^{-6}$
	75	Pu	$(0.71 \pm 0.03) \times 10^{-6}$	$(0.05 \pm 0.003) \times 10^{-6}$	$(0.014 \pm 0.002) \times 10^{-6}$
	75	U ^(b)	0.16×10^{-6}	$0.15 \times 10^{-6(c)}$	0.51×10^{-6}

Total activity $\times 10^6$

a. Calculated from (activity per gram) (total area)

b. No allowance has been made for uranium that might have remained on vessel walls; in this sense, the results are preliminary and the analytical errors (generally <6%) are not given.

c. Analysis suspect, experiment being duplicated.

nickel, and copper will tend to be enriched in the liquid phase.

The solution composition is a function of both whole rock composition and mineral phases present. The most mobile elements, such as sodium, potassium, and boron, tend to concentrate in the liquid phase. It is also interesting to compare cesium, calcium, and silicon between the two rock types. The SiO_2 content of "granites" (of the Nevada Test Site Climax Stock type) is about 70% while that of basalt is about 50%. Granites tend to be enriched in alkalis, and their primary mineral is alkali feldspar. Basalts tend to be enriched in iron and magnesium, and their primary mineral is plagioclase feldspar (sodium-calcium bearing). Furthermore, there is little or no glass in granites while basalts such as the Umtanum can contain up to 30% intercrystalline glass, which is generally an iron-bearing alkali silicate. Accordingly, the cesium content of the granite solution is because of its generally higher alkali content. The calcium composition of the granite solution as compared to basalt is probably the result of calcium being more tightly bound in a plagioclase as compared to an alkali feldspar. The alkali and silica content of the basalt water probably is largely the result of basalt glass dissolution.

The surfaces of the rock pellets in contact with the glass from the minicanisters were examined by electron spectroscopy chemical analysis (ESCA). In all three cases in runs conducted in Teflon digestion bombs there was no observed migration of glass components into the rock. In all cases, the waste package was submerged during the run and was probably under a relatively reducing environment.

TRU Leaching studies

Modified IAEA and static leach testing has continued at Brookhaven National Laboratory on Portland type I cement specimens containing plutonium-contaminated incinerator ash waste.

Modified IAEA leach tests in demineralized water, WIPP brine B and sodium-dominated ground water have been analyzed at 53 days of leaching. These results are reported as a cumulative fraction release of plutonium times (V/S), where V is the nominal specimen volume and S is its external geometric surface area. The term (V/S) is a normalizing factor that makes leaching from a semi-infinite medium independent of specimen size and geometry. For these specimens, (V/S) is 0.51 cm. After 53 days, cumulative fraction plutonium releases of 8.7×10^{-7} and 1.3×10^{-7} were observed respectively for leaching in demineralized water and for leaching in WIPP brine B. The cumulative fraction plutonium release for leaching in synthetic sodium-dominated ground water (0.04M NaCl) was 6.8×10^{-7} after 46 days of leaching.

Static leach test data are available for Portland cement waste forms leaching in demineralized water and WIPP brine B after 2 days, 4 days, 8 days, and 16 days at 25°C. As found in modified IAEA testing, release rates are lower for leaching in WIPP brine B than in demineralized water. Cumulative fraction plutonium releases of 7.1×10^{-7} and 2.3×10^{-7} after 16 days of static leaching in demineralized water and in WIPP brine B, respectively, are higher than those observed after a similar period of modified IAEA leaching. Similarly, incremental leach rates are also generally higher for static leaching over this period. The rapid initial

decrease in incremental release rates observed for modified IAEA testing were not, however, observed for static leach testing. This is partially a result of not taking a 1-day leach aliquot in the static test. Efforts are currently under way to compare these results with those from glass-leaching experiments.

Surface Science Studies

Comparison of ICP solution data to elemental releases calculated from the depth profiles indicates from mass balance principles that the gel layer of 76-68 glass withdraws from the surface during leaching. ESCA analyses of gamma-irradiated 76-68 glass samples imply (based on increased lanthanide dissolution) that a leaching mechanism different from that of unirradiated samples may occur.

The most significant difference between the irradiated and unirradiated samples was the nature of the neodymium and cerium. In the unirradiated sample, both were increased in the surface region, as were iron, titanium, zinc, and zirconium. However, no increase of cerium or neodymium was observed in the irradiated sample, while iron, titanium, and zirconium profiles resembled those of the unirradiated sample.

Reaction of the irradiated glass was more extensive than in the unirradiated glass, as shown in Table 16.2. It must be concluded that dissolution of neodymium and cerium is enhanced by the presence of gamma radiation. The mechanism for this enhanced lanthanide dissolution may involve radiolysis of water, leading to peroxide and other reactive species formation.

TABLE 16.2. Leach Solution Analyses, (a)
Values in ppm by Weight

Element	Gamma Irradiated	Unirradiated ^(b)
Na	5.0	1.8
Cs	(c)	0.13
Ca	0.8	0.18
Ba	0.19	0.03
Sr	0.14	0.03
Sb	6.5	1.44
B	1.1	0.26
Mo	0.1	0.13
Zn	2.0	0.17

- a. Glass 76-78; temperature 50°C; solution deionized water; gamma field 2.4×10^6 R/hr; time 5 days.
b. Unirradiated but otherwise identical conditions to irradiated experiment.
c. Not enough sample to analyze.

Spent Fuel Special Studies

Spent fuel fragments from the Zorita Reactor (54,500 MWd/tU) and Quad Cities I Reactor (9000 MWd/tU) were examined with a shielded electron microprobe to determine whether burnup affects elemental distribution. The concentration of cesium, zirconium, iodine, tellurium, ruthenium, cerium, barium, technetium and plutonium were measured.

In the low-burnup fuel fragment (Quad City), concentrations from edge to center are all near constant except for plutonium, which appears higher at the outer edge. In the high-burnup fuel (Zorita), the concentrations of all the selected elements are higher at the edge than toward the center of the fragments. The large cesium gradient indicates that this element had migrated toward the pellet-cladding interface and that the material left on the cladding removed from the pellets may have contained significant

amounts of cesium. Thus leach rates reported from the unclad fragments may be lower than one would expect for an equal exposed surface area of spent fuel in a breached repository. The lack of a burnup effect on leach rate reported in PNL-2983, Spent Fuel Leach Tests, may have been due to the selection of fuel sample fragments. Transversely cut clad fuel samples would give surfaces compositionally more representative of the actual spent fuel.

UO₂ oxidation experiments are being performed to identify probable leaching mechanisms for spent fuel that lead to release of radionuclides during contact with an aqueous solution. More specifically, we intend to study the leaching mechanisms related to dissolution of UO₂ matrix material under various oxidation conditions.

Oxidation of single crystal UO₂ surfaces was studied in air and in a solution containing H₂O₂. Air oxidation converted the UO₂ surface into UO_{2+x} where $x = 0-0.33$ at between 100 and 285°C. The oxidation was caused by diffusion of oxygen into the UO₂ lattice, and scanning electron microscopy (SEM) of the sample cross-sections indicated no diffusion boundary created by the diffusion process. However, we observed by x-ray Lang topography a slight movement of the subgrains at the initial oxidation stage. This movement, which terminated after the UO₂ was converted into UO_{2.33}, suggested rapid diffusion of oxygen through the subgrain boundary. On the other hand, oxidation and dissolution of UO₂ surfaces in water containing 300 ppm H₂O₂ at room temperature resulted in UO₃·2H₂O scale nearly 5 μm thick forming within 3 days. SEM showed that the scale was porous and contained numerous cracks, possibly formed after the sample was removed from the solution. In another experiment with 3000 ppm H₂O₂ at 75°C, a single

crystal UO₂ surface formed UO₃·2H₂O and UO₄·4H₂O scale and the single crystal was disintegrated into several fragments. In both cases, we have demonstrated that UO₃·2H₂O scales can be readily formed in the presence of H₂O₂ and accompanied with rapid dissolution.

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

Evaluation of Experimental Methodology

Column elution experiments at Los Alamos Scientific Laboratory (LASL) continued. These have been comparing retardation factors predicted from batch K_d tests with experimentally determined retardation factors obtained with columns of crushed granite, tuff and argillite. Only one peak has been eluted since January 1980 (the rest are still being eluted). The eluted ⁸⁵Sr peak from Nevada Test Site yielded a retardation factor of about one-third the value expected from batch tests. The lower K_d or retardation factor from the column experiment compares with results reported the previous quarter. No conclusive explanation has yet been found for the batch/column disagreement.

LASL has reported unusual results for ¹³⁷Cs on two columns of crushed granite and for both ⁸⁵Sr and ¹³⁷Cs on a column of crushed tuff. The radionuclide tracers on these columns have been eluting at a slow but uniform rate and no peak has been observed. The low but constant radionuclide concentrations may indicate that mineral phases form in the column that incorporate the tracers and limit their solubility.

Investigators at Argonne National Laboratory (ANL) reported results for the sorption of ¹³⁷Cs by Bandelier tuff. Batch K_d values

were larger for desorption than for adsorption, and both batch K_d values were larger than the values calculated from column experiments with intact tuff cores. Their data can easily be fit to a Freundlich type equation:

$$S = k C^N \quad (1)$$

where S is the solid phase concentration of cesium (moles per gram), C is the solution concentration of cesium (moles per milliliter) and k and N are constants determined from a linear regression of $\log(S)$ on $\log(C)$. Equation 1 is commonly used to describe the sorption isotherms for cation migration in soils and may be a useful form for the safety assessment of deep geologic nuclear waste repositories.

The ANL data show a dependence on the direction of the sorption reaction (adsorption $K_d <$ desorption K_d) and the state of the rock used for the experiment (K_d on crushed rock $> K_d$ for intact core). The difference between adsorption and desorption K_d values could be due to nonequilibrium conditions (e.g., a K_d that increases with time) or to a change in solution composition caused by dissolution of the tuff constituents in the fresh surfaces exposed by crushing. Column K_d values are probably lower in this case because of the lower specific surface area exposed in the intact tuff cores compared to the surface area of crushed tuff. Work will continue to obtain a better understanding of the differences between intact core K_d s and batch or crushed column K_d s.

A study of americium and plutonium sorption on Nevada Test Site tuff at 22 and 70°C has shown no trend with temperature change. The observed distribution coefficients varied more with the method for adding tracer to solution than with temperature. Sorption K_d

values for ground waters prepared with dried tracer stock solution were an order of magnitude higher than K_d s determined with ground water made with tracer stock solution added directly (no drying). Sorption K_d s were greater than desorption K_d values for ground waters prepared with dried tracer. Experiments run using ground water prepared by direct addition of liquid tracer exhibited the opposite behavior, with desorption K_d values being greater than adsorption K_d values. These experiments point out a need to understand the solution chemistry behavior of a radionuclide. Americium and plutonium K_d s varied over two orders of magnitude (1×10^2 to 4×10^4 ml/g and 7×10^1 to 8×10^3 , respectively). Precipitation, sorption and redox reactions may be acting simultaneously to reduce the radionuclide concentrations in these systems. Accurate quantitative predictions of their migration behavior can be made only after these three mechanisms can be described separately.

Sorption experiments with plutonium and four rocks under atmospheric conditions have shown a high K_d for plutonium on Teflon centrifuge tubes. Teflon tubes sorb less plutonium than do polycarbonate tubes, but the loss of plutonium from solution in containers without rock is significant. The plutonium adsorbed by tubes with rocks was found to increase as the rock K_d decreased. For quantitative study of the sorption of plutonium, blank corrections should not be used for calculating K_d values if a gamma-emitting isotope such as ^{237}Pu is available. If only alpha emitters are available, the solution and tube walls must both be assayed and a K_d determined by mass balance. Whichever method is used, the radioisotope concentration should be below the solubility limit to prevent precipitation and erroneously high K_d values.

Mechanism Studies

Sorption experiments carried out at Oak Ridge National Laboratories (ORNL) with strontium on powdered SiO_2 , silica gel and powdered apatite $[\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6]$ have shown that $\log [K_d(\text{Sr})]$ has a linear dependence on pH of the form: $\log(K_d) = k + \text{pH}$ at low strontium loadings on the adsorbent material. At higher loading of the apatite (greater than about 10^{-4} M Sr/kg apatite) the K_d drops sharply and the above pH dependence is no longer valid. Each sorption isotherm for apatite (constant pH and temperature) follows the behavior expected from adsorption by an ion-exchange mechanism.

The minerals used by ORNL researchers can exist at equilibrium in aqueous suspensions while the crushed rocks used at Rockwell Hanford Operations (RHO) and ANL are likely to undergo dissolution reactions and formation of new amorphous or crystalline mineral phases. Aquifer material from a specific site should be investigated to determine whether it is at equilibrium with the existing ground water. The RHO and ORNL data also emphasize the need to investigate the effects of pH, radionuclide concentrations and ground water chemistry on tracer sorption.

Adsorption of ^{239}Pu by different minerals from aerated $5 \times 10^{-3} \text{ M}$ CaCl_2 solutions containing $7.3 \times 10^{-9} \text{ M}$ Pu(VI) was studied at PNL. Sorption experiments were carried out at pH 7 for comparison with previous quarter results at pH 4. Initial ^{239}Pu concentrations added to the mineral suspensions were about 22 times the maximum permissible concentration (MPC) in unregulated water as established by the Nuclear Regulatory Commission. However, the ^{239}Pu concentrations in pH 7 effluents that had contacted the selected minerals were near or lower than the MPC. This significant (>90%) removal

of plutonium was also found for vermiculite, biotite, and hematite at pH 4. These results combined with the fact that most geomedias around deep repository sites are expected to be alkaline and more reducing than the present experimental conditions indicate that plutonium in general [and Pu(VI) specifically] would be relatively immobile in geomedias not containing significant quantities of complexing ligands.

The sorption behavior of cesium, strontium, barium, cerium and europium were studied at LASL under controlled atmospheric conditions ($<0.2 \text{ ppm O}_2$ and $<20 \text{ ppm CO}_2$) on Climax Stock granite, Eleana argillite and Yucca Mountain tuff (all from the Nevada Test Site). Contact times of 3 to 12 weeks and a pH range of 8 to 9 were used. Observed K_d values for cesium, strontium and barium on the granite were essentially the same as those values observed under atmospheric conditions. On argillite, K_d values for these were smaller in the controlled atmosphere than under normal atmospheric conditions. Both cerium and europium had higher K_d s under controlled atmospheric conditions on granite and argillite. Only the barium and a few strontium K_d values were altered on the tuff in the controlled atmosphere (lower by a factor of 2) than air-equilibrated sorption tests.

Adsorption of technetium on the same rocks (tuff, granite, and argillite) under controlled atmospheric conditions tended to be higher than in air. The observed K_d values also increased with time, and desorption K_d values were significantly higher than adsorption K_d s. The increase of $K_d(\text{Tc})$ with time indicates that technetium is reduced slowly to a more highly adsorbed species. The rate-limiting step for reduction of technetium seems to be the slow release of a reducing agent from the rocks.

The sorption behavior of multivalent elements (cerium, technetium) in anoxic or controlled atmospheres shows the need to determine redox conditions in the geomeidia surrounding a deep geologic repository. Observed decreases in K_d values for cesium, strontium, and barium under controlled atmospheric conditions also warrant study to determine whether the rocks are altered or the lack of CO_2 affects their sorption behavior.

Naturally weathered basalt samples were obtained by RHO researchers from the Hanford Reservation. These were separated into 0.5 to 1 mm and <0.5 mm size fractions and equilibrated with basalt ground water. Sorption of cesium, strontium, neptunium, and americium were studied on these samples for comparison with earlier results obtained with freshly crushed basalt and basalts weathered artificially in air and nitrogen atmospheres. Table 16.3 shows that sorption K_d values in air for both naturally and artificially weathered basalts are higher than those found on the freshly crushed rock. The high K_d for cesium on naturally weathered basalt is thought to be caused by claylike material found in vesicles. The claylike material will be separated from the rock for addi-

tional sorption studies and characterization. Rocks, such as basalt, that tend to dissolve in water can be covered by a coating of secondary minerals. Artificial weathering of these rocks in the laboratory may not produce the same weathering products as found in natural rocks. Sorption studies for the licensing of a repository should concentrate on the material found in expected flowpaths (aquifer material), not on material that serves as an aquitard.

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 done last quarter by AEGIS personnel on this subtask concentrated on collecting field data and performing thermodynamic calculations on the expected range of chemical composition for deep basaltic aquifers on the Hanford Reservation. Efforts are under way to obtain thermodynamic models capable of predicting ground-water compositions.

TABLE 16.3. Distribution Ratios for Fresh and Altered Basalts

Basalt Rock Type	$K_d, (a) \text{ ml/g}$			
	Cs	Sr	Np	Am
Fresh	350 $\pm$ 40	108 $\pm$ 20	10 $\pm$ 1	6.2 $\pm$ 2.3
Naturally altered, <0.5 mm	14,000 $\pm$ 1,600	1,100 $\pm$ 500	17 $\pm$ 2	6,000 $\pm$ 1,500
Naturally altered, 0.5 - 1.0 mm	12,000 $\pm$ 1,400	400 $\pm$ 100	20 $\pm$ 4	10,000 $\pm$ 5,000
Weathered in air	1,500 $\pm$ 300	500 $\pm$ 100	49 $\pm$ 16	18,000 $\pm$ 17,000
Weathered in N_2	1,400 $\pm$ 150	34 $\pm$ 2	37 $\pm$ 4	>116,000

a. Mean of three replicates. Error shown is 1σ .

Nuclide Solution Chemistry

TcO₄ Reduction Under Defined Eh-pH Conditions

Bondietti and Lee (ORNL) observed the reduction of pertechnetate under controlled pH and redox potentials. The redox potentials were controlled by using 10^{-6} M concentrations of 2,6-dichlorindophenol, theonin, and Nile blue. The pH of the solutions was adjusted to 8.2.

The redox potentials measured with the platinum electrode agreed well with the calculated potentials. At Eh's of about -0.03 volts (1% Theonin), Tc(VII) at $\leq 10^{-9}$ M was found to be reduced, assuming that the loss from the solution upon filtration signifies reduction. If one assumes that the result of reduction of Tc(VII) is the formation of TcO₂ solid and that the reported thermodynamic values for the solubility of this solid are correct, the equilibrium Eh for a system with 10^{-9} M TcO₄ and pH = 8.2 would be -0.085 volts. Fe(II) was used to reduce the dyes, and some residues may have been present when the dyes were reduced. The 1% oxidized theonin data indicate that the reduction occurs at a more oxidizing Eh than the theoretically calculated Eh (-0.085 V) for TcO₂(s) solubility. In a second experiment no evidence for reduction of technetium was found at -0.16 volts (Nile blue), or even lower, except when the dye had been almost completely reduced (-0.24 volts). Thus in this case TcO₄⁻ reduction appears to necessitate a lower Eh than theoretical calculations. These conflicting results suggest that the electron transfer from the dye to Tc(VII) may be restricted (kinetics) and that just having a low Eh may not be adequate to reduce TcO₄⁻. This evidence indicates that an ion pair like

[Fe(II)-Tc(VII)] may be needed for electron transfer. Further experimentation is under way.

Solubilities of Compounds

²³⁷NpO₂ Solubility Studies

To develop methodology, preliminary studies of ²³⁷NpO₂ solubility in dilute salt solutions (0.003N CaCl₂) under oxic conditions were begun last quarter. Under oxic conditions, the reaction which will most likely characterize the NpO₂ dissolution is given by

To determine the equilibrium constant for the above reaction, it is imperative that accurate activities of NpO₂⁺ and e⁻ are known. Radioanalytical techniques were used to determine the total concentration of neptunium in solutions. Solvent extraction techniques, thenoyltrifluoroacetone (TTA) in 0.5M xylene, were used to determine Np(III+IV) and Np(V+VI). The electron concentration (pe) was calculated from the redox measurements with a platinum electrode. A redox buffer (quinhydrone) was added to some of the NpO_{2(c)} suspensions to fix the redox potential.

It has been shown (Reinschmidt, Sullivan, and Woods 1973) that in quinhydrone solutions Np(VI) is rapidly reduced to Np(V). The TTA extractions of all the solutions contacting NpO₂ showed the solutions to contain <1% Np(III+IV).

Results on the solubility of ²³⁷NpO₂ in solutions equilibrated from 3 days up to 123 days are obtained. The log K^C values for contact times of 3 days or more are very similar, indicating that equilibrium is

attained rapidly. The values of the $\log K^C$ calculated from these studies compare very favorably with the $\log K^C$ values -15.34 (Burney and Harbour 1974) and -13.59 (Burney and Harbour 1974; Fuger and Oetting 1976) calculated from the reported thermodynamic data.

The $\log K^C$ values for the high pH suspensions are generally slightly higher than those for the low pH suspensions. This may suggest the presence of Np(V) species other than NpO_2^+ , such as NpO_2OH . Experiments are planned to evaluate this hypothesis.

Solubility of ^{237}Np -Doped Glass Beads

Studies were conducted to determine whether neptunium concentrations in solutions contacting doped glass beads are governed by a solid material of these elements and whether these solid mineral phases can be identified.

Neptunium-doped glass beads were contacted with a dilute salt solution (0.0015M CaCl_2) containing a quinhydrone (a redox buffer). The suspensions of crushed glass beads and the salt solution were adjusted to pH values ranging from 3 to 8. It was difficult to maintain the pH of these suspensions at 8, and the pH tended to decrease below 7.

The concentrations of neptunium in 0.015 and $0.0018\text{-}\mu\text{m}$ filtered solutions were determined by α surface barrier detectors. The pH and Eh were measured with a glass and a platinum electrode, respectively.

The results indicate that the concentration of neptunium in solutions contacting glass beads and those contacting $\text{NpO}_{2(\text{c})}$ are similar under the similar pe values. These results strongly suggest that the glass beads may contain $\text{NpO}_{2(\text{c})}$ and thus the concentrations in glass leachate solutions may be predictable based on crystalline phases.

PREDICTIVE MODEL DEVELOPMENT - W. K. Kuhn

Data Banks and Data Reduction

Graphics and output software were largely completed this quarter for the Sorption Information Retrieval System (SIRS).

The output software is written for a PDP 11/45, on which the main program on a PDP 11/55 may be queried for results of data manipulation requests. The results can either be put into a specific format, such as rows and columns in a table, or left in an informatted form for rapid scrutiny of output files on a screen or printer.

The output software is also designed to call graphics routines. A graphics package has been written to provide for plotting of linear, semilogarithmic, and polynomial "fits" to data, and for histogram displays. The data plots can show data points and a computed correlation as a line. The graphics package is expected to be especially useful for presenting and explaining leach data.

The separate development of software for analysis of leach data has been suspended; we now expect SIRS to be the preferred software for this purpose. Moreover, we now expect that Analysis of Large Data Sets (ALDS) software being developed independently at PNL will become a preferred and very powerful tool for future WRIT data base management needs.

Empirical Model Development

The FY-1979 annual report on adaptive Learning Networks produced under subcontract with Adaptronics, Inc., was critically reviewed. Comments were incorporated, and the final report will appear in PNL-SA-8571 about May.

Mechanistic Model Development

A subcontract was let to Lawrence Livermore Laboratory to modify and update the

EQ3/EQ6 thermodynamic modeling software. Activities this fiscal year will include data base evaluation and modification and output software modification.

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Reinschmiedt, K., J. C. Sullivan and M. Woods, 1973. "Kinetic Study of the Oxidation of p-Hydroquinone and p-Tolhydroquinone by Neptunium(VI) in Aqueous Perchlorate Media." Inorganic Chemistry 12(7):1639-1641.

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

Documentation of the reference salt site barriers analysis was completed in draft form. The dispersion effects evaluation was completed and is now being analyzed to determine what modification may be needed in the conclusions presented in last quarter's report.⁽¹⁾ The SAI (Science Applications, Inc.) Task 3.1 report was drafted, reviewed and completed and will be issued early next quarter. The SAI efforts have been somewhat redirected to emphasize release rate-limiting aspects of partially failed barriers.

CONSEQUENCES ANALYSIS

The evaluation of flow-field dispersion effects (as opposed to convective dispersion effects) was completed for a reference salt site case. The results of the evaluation are being analyzed to determine what the implications of these effects are on the tentative conclusions, listed in last quarter's report,⁽¹⁾ regarding engineered barriers performance. Initial indications are that the effects tend to reduce the incentives for providing low-leach waste forms and/or other release rate-limiting barriers. The draft

reference salt site analysis topical report was compiled and is currently being revised to include the flow-field effects.

The set of parameters for scoping calculations for the reference granite site was completed and is now being reviewed to determine whether the granite site results will differ enough from the reference salt site results to change the overall conclusions regarding incentives for engineered barriers.

The reference basalt site definition is being modified based on new data recently developed at the Hanford Reservation. Too few descriptive data are available to adequately define a reference shale site, so the analysis for the shale will be modified and generalized considerably.

BARRIERS PERFORMANCE ASSESSMENT

The SAI Task 3.1 interim report was compiled as a draft, reviewed by PNL, and finished during the reporting period, and will be issued early next quarter. The follow-on work has been redirected to emphasize the nuclide release rate-limiting capability of partially failed barriers. This redirection primarily affects the development of

the release rate modules of the BARIER assessment model.

Assessment Model Development

Changes to the main program to accommodate new subroutines have been completed and compiled. Some debugging is still in progress but nearing completion. The revised code is being run with new stress analysis and temperature subroutines.

Revision of the material degradation model has been completed. Some additional study will be done on the role of diffusion resistance of the backfill or partially failed barrier elements. Under certain conditions corrosion rates could be totally controlled by transport rates of corrosion agents or products into and out of the package. The current model assumes that the rate is characteristic of immersion. Bulk corrosion, pitting corrosion, and crack propagation are included as mechanisms. Data on temperature dependency have been disappointing. A fixed value at the highest temperature will probably be used.

Development of a nuclide release rate model was begun during March as part of the new program direction. A preliminary model has been formulated that gives a nuclide-specific release rate as a function of time and accounts for dissolution rate, transport resistance of partially failed barriers, and sorption in the backfill. While the equations have been formulated, some difficulty with numerical problems is expected. The mathematics has some of the same difficulty encountered in running other sorption codes. The necessary iteration of some simultaneous equations may tend to be unstable. Sample calculations are in progress to pinpoint trouble areas and solve implementation problems. The model is currently undergoing internal review to ensure technical correct-

ness. Some scoping calculations indicate very high resistance in failed packages, giving large attenuation to nuclide leaching and greatly reducing source terms.

Some data on water exclusion backfills have been obtained, and work will begin in that area during April. Current thinking centers on inserting a delay time before corrosion begins to account for slow permeation of water into the package. Effects on corrosion rate are also being considered.

Work on the radiation subroutine was started during March and is expected to be completed early next quarter.

Applications

Work is beginning on developing the design cases to be run in the new model. Some preliminary test cases are being used for debugging. Effort will be increased in April and May to identify candidate design cases. As cases are identified, input files will be prepared so that cases can be run as soon as the new BARIER version is fully operational.

SUMMARY OF REPORT PROGRESS THIS QUARTER

In Preparation or Draft Issued

Cloninger, M. O., C. R. Cole, and J. F. Washburn, 1980. An Analysis of the Use of Engineered Barriers for Geologic Isolation of Spent Fuel in a Reference Salt Site Repository. PNL-3356, Pacific Northwest Laboratory, Richland, WA, DRAFT.

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Stula, R. T., S. E. Donelson, and D. H. Lester, March 1980. System Study on Engineered Barriers, Task 1 Interim Report. SA101379-1070LJ, Science Applications, Inc., La Jolla, CA.

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1. Platt, A. M. and J. A. Powell, compilers, November 1979. Nuclear Waste Management Quarterly Progress Report July Through September 1979. PNL-3000-4, Pacific Northwest Laboratory, Richland, WA.

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.

CRITERIA DEVELOPMENT: GENERAL SUPPORT -

R. D. Widrig

Draft criteria documents ONWI-33(2) and ONWI-33(4) were reviewed and comments submitted for ONWI and DOE consideration. Support for criteria discussions with the Nuclear Regulatory Commission was also provided.

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

Calculations have been performed to determine the minimum critical mass (MCM) of irradiated fuel materials in homogeneous, water-moderated and reflected spheres. Effects of other moderators have also been scoped. Neutron absorption by fission product isotopes has been ignored in the calculations because the leaching and dissolution properties of fission products may differ considerably from those of the actinide elements. Calculations assumed the presence of isotopes of uranium, plutonium, neptunium, americium, and curium.

A base case for calculations was chosen, having 3.5% enriched PWR fuel 10 yr after discharge. Variations included 4.5% enriched extended burnup PWR fuel and 2.5% enriched BWR fuel. The calculated MCMs increase slowly with exposure until a significant fraction of the fuel design life is exceeded.

A single PWR fuel assembly has a mass of about half a ton of uranium and a design life of roughly 33,000 MWd/MTM. For the base case the MCM increases slowly from an initial value of 60 kg at zero burnup to 500 kg at 28,000 MWd/MTM. Beyond this burnup the MCM increases rapidly as k_{∞} approaches unity. Similar results were found for the other enrichment fuels as burnup varied from zero to design lifetimes.

For geologic disposal of spent fuel assemblies the chief importance of these results is that the MCM is less than the fuel mass contained in a single fuel assembly for most of the design life of the fuel. In fact, the MCM is <50% of the assembly mass for the base case during almost two-thirds of its design lifetime. This demonstrates the importance of considering variations of fuel burnup from design values in assessing the criticality safety of geologic disposal of spent fuel.

Effects of radioactive decay have been investigated for base case fuel exposed to 30,000 MWd/MTM. The MCM of homogeneous, water-moderated and reflected spheres of this material increases during the first century, then decreases until 30,000 years after discharge. The increase is due to decay of fissionable ^{241}Pu , and the decrease is because of decay of ^{241}Am and ^{240}Pu to nuclei with lower neutron absorption values. At 30,000 years

the MCM is 73% of its value 10 yr after discharge. At longer times the MCM again increases because of the decay of ^{239}Pu to ^{235}U .

A significant increase in MCM was found for base case fuel homogeneously mixed with an optimal "soil"-water mixture containing 80 wt% SiO_2 and 20 wt% Al_2O_3 . This material lacks strong neutron absorbers. For base case fuel exposed to 20,000 MWd/MTM and moderated by 60 vol% soil plus 40 vol% water, the MCM was increased to 1280 kg from the water-moderated value of 208 kg.

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

A computer search of the literature has been completed, and pertinent documents are being reviewed as they become available. An

outline of the final report has been completed in draft form for review and comment. Individuals having background and specific information relevant to the study have been identified, and contacts have been initiated.

To develop a perspective of the natural background radiation compared to radiation of a waste repository, data on the occurrence of uranium have been collected. The inventory of ^{238}U in the earth's crust actually or potentially available to the environment in the United States is about 10^{12} Ci, or 34 million times greater than a single 24,000-Ci waste repository. Uranium present in currently mineable grades totals about six million curies, equivalent to 264 repositories. If the activity of radium in equilibrium with uranium is included, the inventory is doubled. Information on the inventory of uranium in single deposits is currently being collected for comparison with a waste repository.

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 world survey of spent fuel storage experience is under way, sponsored jointly by the BEFAST* committee and the International Atomic Energy Agency (IAEA). The survey requested information on the following topics:

- characteristics of the spent fuel inventory stored in water pools: e.g., length of storage, highest burnup, storage behavior
- type and behavior of spent fuel pool components
- pool water chemistries and radio-chemistries
- methods for controlling radioactive species
- useful techniques in spent fuel pool operation.

Questionnaires were returned from 14 countries; several other countries are expected to respond. The steering committee that will interpret the survey has representatives from: IAEA, NEA, Austria, Belgium, United Kingdom, and USA. The committee met in Vienna, March 17-20, 1980, to assess and summarize the survey results.

*BEhavior of Fuel Assemblies in SStorage, organized under the Nuclear Energy Agency (NEA) of the Organization for Economic Cooperation and Development (OECD)

The results will be assembled into a draft report for review and publication. Issue of the final report is projected for March 1981.

ACQUISITION AND EXAMINATION OF SPENT FUEL

Negotiations are under way for fuel assemblies that will be factored into the Department of Energy's spent fuel surveillance program. Acquisition of two Zircaloy-clad assemblies (one partial) from the Shippingport Reactor has been negotiated. Arrangements for shipment and examination of the fuel are in the advanced stages of negotiation, with shipment to a hot cell for non-destructive and destructive examination planned to occur in May 1980. The fuel includes rods from the world's oldest Zircaloy-clad fuel, stored in water since 1959. Characteristics of the fuel were summarized in the prior quarterly report.⁽¹⁾

Negotiations also are in advanced stages to obtain and ship a well-characterized PWR fuel assembly that contains stainless steel-clad fuel rods. The assembly has a burnup of 32,151 MWD/MTU and has been stored about 5 years in boric acid pool chemistry. Negotiations for examination of the fuel at the BCL hot cell facilities are in advanced stages.

A Zircaloy-clad Turkey Point (PWR) assembly, characterized under another DOE

program,^(2,3) has been identified as being available for the surveillance program. It is presently at the Battelle Columbus hot cell facility. Formal transfer of the assembly will be arranged as soon as a storage site is identified.

Once the surveillance fuel has been placed in an away from reactor (AFR) pool, it will be subjected to periodic surveillance, chiefly visual and nondestructive. Surveillance on the relatively few well-characterized surveillance assemblies will be supplemented by random selection of assemblies from the AFR inventory.

BEHAVIOR OF FUEL POOL COMPONENTS

Sections have been requested from spent fuel pool components exposed in the Zion (PWR), La Crosse (BWR), and receiving basins for offsite fuel (AFR) spent fuel pools.

MECHANISM STUDIES

Mechanism studies are under way at PNL to investigate stress corrosion cracking that

developed on 304 stainless steel spent fuel pool piping at the Three Mile Island No. 1 Reactor. The mechanism studies include constant extension rate (CERT) testing of 304 stainless steel specimens cut from the failed TMI pipe. Also, U-bend specimens will be exposed to simulated boric acid pool chemistries. The mechanism studies will be conducted also in deionized water.

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3. Davis, R. B. and V. Pasupathi, 1979. Data Summary Report for the Destructive Examination of Rods G7, G9, J8, I9, and H6 from Turkey Point Fuel Assembly B17. IC-1540.

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

Since DOE published estimated spent fuel storage and storage plus disposal fees in DOE/ET-0055, Preliminary Estimates of the Charge for Spent-Fuel Storage and Disposal Services, many of the program assumptions have changed. During this quarter, calculations were performed to determine the effects of these changes in the spent fuel management fees. The key assumptions that have changed are:

1. Storage and disposal fees are separate.
2. The first repository is delayed to the mid or late 1990s.
3. Several repository geologic media are to be evaluated.
4. Discount rate is increased.

The computer programs used to compute the spent fuel fees have been modified to include decommissioning costs directly. Modifications are also being made to allow calculating the revolving loan fund balance for the program under various fee assumptions.

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