Nuclear Waste Management Quarterly Progress Report January Through March 1979

**A. M. Platt
J. A. Powell**

May 1979

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NUCLEAR WASTE MANAGEMENT
QUARTERLY PROGRESS REPORT
JANUARY THROUGH MARCH 1979

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

May 1979

Prepared for
the U.S. Department of Energy
under Contract EY-76-C-06-1830

Pacific Northwest Laboratory
Richland, Washington 99352

FOREWORD

This document is one of a series of technical progress reports designed to report on commercial radioactive waste management programs at Pacific Northwest Laboratory. These programs are funded by the Department of Energy's Office of Nuclear Waste Management. The Commercial Radioactive Waste Immobilization Program is reported elsewhere. These reports are issued on a quarterly basis.

The prior report in this series is Nuclear Waste Management Quarterly Progress Report October Through December 1978, PNL-2378-4.

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1.0 DECONTAMINATION AND DENSIFICATION OF CHOP-LEACH CLADDING RESIDUES

T. M. Lambright - Project Manager

Fuel element cladding residues from the chop-leach head-end process constitute a low-density, high-surface-area metallic waste with a substantial actinide element contamination. The objective of this study is to develop methods for removal of long half-life transuranics from fuel cladding residues and to consolidate the decontaminated cladding into a dense, chemically unreactive form for efficient storage or burial. The study includes:

- 1. demonstration of a prototype system for combined descaling and densification of unirradiated scrap fuel cladding*
- 2. development of engineering data to provide the basis for scaleup to a production system*
- 3. evaluation of ground water corrosion tests conducted on samples of alloyed ingots previously produced by the densification process.*

SUMMARY

A prototype system for decontaminating and densifying chop-leach cladding residues has been assembled in a building operated by the Pacific Northwest Laboratory. Pilot-scale chemical decontamination equipment and an Inductoslag ingot melting furnace are set up on a simulated hot cell floor plan for eventual combined nonradioactive demonstration. Autoclaved, unirradiated scrap cladding pieces will be descaled in the decontamination prototype with HF/Ar followed by an aqueous rinse and then melted in the induction furnace to produce ingots.

Initial tests of the chemical decontamination equipment showed that ~50% of the outside-diameter surfaces and ~10% of the inside-diameter surfaces of the unirradiated scrap cladding were descaled when the HF gas was applied at only 16% of the desired rate. Several components were modified to refine equipment operation. A rotating air lock is being prepared to replace the gate valves between the HF reactor and the aqueous washer/

rinser. The gate valves, which were repaired after being damaged by cladding pieces in previous operating tests, allowed water vapor to leak into the HF reactor. The rotating air lock is expected to eliminate the problems encountered with the gate valves.

Corrosion tests are under way to determine the corrosion resistance of various zirconium and stainless steel alloy samples taken from ingots produced in previous Inductoslag furnace melting tests. Seven alloys are being exposed to ground water from the Hanford site, ground water modified by the addition of fluoride ion, and two different brines.

DECONTAMINATION PROCESS

The Pacific Northwest Laboratory's pilot-scale decontamination equipment is designed to "decontaminate" (descale) about 2 kg of chop-leach cladding residues per hour. Operating tests of the prototype equipment have been made to check out concurrent operation of all subsystems, which include an HF

gas reactor, the HF reactor furnace, HF and argon gas supply systems, an aqueous washer/rinser, associated process solution tanks and piping, and control instrumentation, including the safety circuits. The basic components of the system have been described and diagramed in previous reports.⁽¹⁻³⁾

Autoclaved, unirradiated scrap cladding pieces served as feedstock for two descaling tests made this reporting period. About 50% of the outside-diameter surfaces and 10% of the inside-diameter surfaces of the scrap tubing were descaled when the HF gas was supplied to the reactor at only 16% of the desired rate. The two descaling tests led to equipment refinement in several areas.

Better HF cylinder heating coils were installed after the first test because the HF cylinders were not supplied enough heat to vaporize the HF at the rate necessary for effective descaling. A heat tape was applied to the HF supply manifold to prevent condensation of HF gas in the flowmeter, thereby providing reliable flow indications.

After the first test, the electro-pneumatic transducer in the reactor pressure control system was isolated from vibrations induced by the cladding feeder. The vibrations caused the transducer to receive and generate false signals that resulted in problems with reactor pressure control.

A newly installed filter prevents clogging of the reactor gas exhaust system with zirconium fluoride powder. The fine powder prevented proper operation of the reactor pressure controller during the first test. The powder also caused problems with the O-ring seals in the two gate valves that separate the HF reactor from the aqueous washer/rinser.

A temperature increase detected in one zone of the HF reactor during the second test was attributed to water vapor leaking through

the gate valves. Water vapor in the presence of HF gas and zirconium causes an exothermic reaction that produces various combinations of ZrF_4 , $ZrOF_2$, and ZrO_2 . A rotary air lock will be installed to replace the two gate valves. An argon purge below the rotary air lock will prevent transfer of water vapor into the HF reactor during valve rotation. Three microswitches were installed to activate two cladding feeders and the rotary air lock at appropriate times.

A full report on the development of the chemical decontamination process is now being prepared.

DENSIFICATION PROCESS

The Inductoslag ingot melting furnace is the densification portion of the decontamination-densification equipment set up for processing chop-leach cladding residues. The furnace is located on a hot cell floor plan with the prototype chemical decontamination equipment, where the two systems will eventually be operated in nonradioactive demonstrations of the combined decontamination-densification process. To date, 21 melts have been made in the Inductoslag furnace. Various alloys of Zircaloy, stainless steel and Inconel have been cast as described in previous reports.^(1,2,4) The furnace has been inactive since these initial tests, awaiting the final readiness of the chemical decontamination equipment. A report on the development and operation of the Inductoslag furnace is now in preparation.

In the absence of melting activities, corrosion tests of ingots produced in previous melting heats are in progress. Seven different alloys, representative of expected ingot compositions, are being tested in a water bath to determine their corrosion resistance. Alloys will be exposed to four

different solutions. Two of the solutions are typical Hanford ground water; one of these is modified by the addition of 2 ppm fluoride ion. The other two solutions are brines: one consists of primarily

sodium ions; the other is a mixture of sodium, magnesium, and potassium ions. The water bath maintains the solutions and ingot samples at a constant 80°C.

REFERENCES

1. A. M. Platt and J. A. Powell, comps., Nuclear Waste Management Quarterly Progress Report January through March 1978. PNL-2378-1, Pacific Northwest Laboratory, Richland, WA, August 1978.
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2.0 MONITORING METHODS FOR PARTICULATE AND GASEOUS EFFLUENTS FROM WASTE SOLIDIFICATION PROCESSES

R. W. Goles - Project Manager

The objective of this program is to develop reliable and accurate techniques for process monitoring and stack emission monitoring for future waste solidification facilities.

SUMMARY

Sampling of gaseous and particulate effluent associated with the vitrification of high-level liquid waste was successfully completed.

SAMPLING - R. W. Goles and D. C. Hamilton

The sampling phase of this monitoring program was successfully completed during this reporting period. Of the two vitrification campaigns that occurred during this quarter, only the final one could be effectively used for sample collection because of interfering shearing and dissolution activities accompanying the first glassification effort. Nevertheless, all sampling systems designed to identify and measure the process effluent listed in Table 2.1 were fully deployed during the final vitrification campaign. In addition, isokinetic sampling for particulates was also accomplished using a 0.4- μ membrane filter. Examination of this filter, utilizing scanning electron microscopic techniques,

will provide a detailed description of particle sizes most likely to escape in cell cleanup devices. Laboratory analysis of all collected samples is currently under way.

TABLE 2.1. Important Process Effluents

Gaseous Effluents

^3H as HTO, TH and organics
 ^{14}C as CO, CO₂ and organics
 ^{129}I as I₂, HOI and organics
 NO_x

Semivolatile Effluents

^{79}Se
 ^{99}Tc
 ^{106}Ru
 ^{125}Sb , ^{126}Sb
 $^{125\text{m}}\text{Te}$, ^{127}Te
 ^{134}Cs , ^{135}Cs , ^{137}Cs

Particulate Effluents

Fission products including $^{144}\text{CePr}$
 Activation products
 Heavy elements

3.0 TRU WASTE IMMOBILIZATION PROGRAM

C. R. Palmer - Project Manager

The objectives of this program are to adapt high-level waste immobilization technologies to selected transuranic wastes, and to demonstrate that suitable waste forms can be produced routinely for these wastes.

SUMMARY

Laboratory experiments during the quarter addressed two candidate waste forms: borosilicate glasses and sintered ceramic pellets. Low-temperature glasses were developed for high-alumina waste residues (specifically for ashes received from Rocky Flats and from LASL) which exhibit good performance characteristics and remain compatible with the in-can melting process. Except for possible modifications to improve chemical durability in acidic leachants, a glass composition was selected for process tests. Verification of the composition in pilot-scale equipment will be made during the fourth quarter.

A variety of sintered ceramic pellets, prepared last year using two different transuranic wastes and three trial additives, were characterized for porosity, impact behavior and chemical durability. This work will be completed and reported during the third quarter.

Glass development experiments will now emphasize higher-temperature borosilicate glasses and will attempt to improve the flexibility of the composition to variations in the waste feed.

GLASS DEVELOPMENT - G. B. Mellinger and L. A. Chick

Laboratory development of borosilicate glasses has concentrated during this reporting period on consolidation of dispersible incinerator residues. The ultimate objective is to develop formulations which can accept a mixture of several transuranic wastes at high waste loading and remain relatively insensitive to expected variations in feed composition.

As described in the last progress report, glass compositions were developed for an ash composition expected from the Rocky Flats incinerator (identified as waste 5108). These compositions were improved with respect to leach resistance in pH4 solutions by decreasing levels of Al_2O_3 , B_2O_3 , and Na_2O in the frit. The resulting glass composition, 79-14, and its precursor, 5325, are shown in Table 3.1.

Midway through the quarter a bulk quantity of ash was received from Rocky Flats which will be used in a pilot-scale process test during the fourth quarter. The chemical analysis indicated the bulk ash (designated TRU-RFP-1) had significantly more alumina present than waste 5108 (see Table 3.2).

TABLE 3.1. Chemical Composition of Laboratory TRU Waste Glasses, wt%

Component	Glass			
	5325	79-14	79-116	79-X
Waste 5108	63.0	65.0	-	-
Waste TRU-RFP-1	-	-	50.0	40.0
SiO ₂	-	5.3	14.0	25.0
B ₂ O ₃	14.7	8.8	10.5	8.0
Na ₂ O	12.3	8.8	11.5	9.0
TiO ₂	0.2	-	4.1	5.0
K ₂ O	-	2.6	4.1	5.0
CaO	-	2.6	4.1	6.0
Li ₂ O	-	1.8	1.7	2.0
ZnO	4.8	2.6	-	-
Al ₂ O ₃	5.0	2.5	-	-
Total	100.0	100.0	100.0	100.0

TABLE 3.2. Chemical Composition of Two Incinerator Residues, wt%

Compound	TRU Waste	
	5108	TRU-RFP-1
Al ₂ O ₃	6.1	33.0
B ₂ O ₃	2.3	0.1
BaO	0.4	1.1
C	-	7.1
CaO	4.9	1.0
Cr ₂ O ₃	2.5	-
CuO	0.4	0.1
Fe ₂ O ₃	9.0	3.2
H ₂ O	-	2.8
K ₂ O	0.4	0.7
MgO	1.9	0.2
MnO ₂	0.1	-
NaCl	-	0.5
Na ₂ O	0.9	0.9
Na ₂ SO ₄	-	1.1
Nd ₂ O ₃	1.6	-
NiO	0.7	-
PbO	0.5	-
P ₂ O ₅	1.7	0.5
SiO ₂	62.3	41.3
TiO ₂	4.3	4.0
ZnO	-	2.4
Total	100.0	100.0

Thus it was necessary to modify glass 79-14 to accommodate this high-alumina waste so that performance and processing requirements could be met.

An intermediate glass composition that meets all development objectives for TRU-RFP-1 waste except pH4 chemical durability was developed (79-116, Table 3.1) which incorporates 50% waste by weight. A consequence of the high alumina concentration of the waste is that B_2O_3 , Na_2O , and K_2O levels in the glass frit were significantly increased. Titania was also increased to partially compensate for the poorer chemical durability because of high alkali and boron concentrations. The significance of the relatively high acid leach rate is not clear because acidic ground water may be less likely in proposed repositories than a neutral or basic environment. Nevertheless, efforts are under way to improve durability by reducing the waste loading somewhat, together with reducing levels of boron and sodium. A series of glasses approximating the proposed glass composition shown in Table 3.1 (79-X) will be prepared and characterized.

The next phase of TRU glass development will emphasize higher temperature glasses to permit more flexibility in accepting refractory residues at high waste loadings. Current high-level waste continuous melting technology can accommodate glasses up to about 1250 C, and a new developmental system is designed for operation about 1400 C. Glass compositions melting within both temperature regimes will be examined.

CRYSTALLINE WASTE FORMS - J. M. Rusin

All sintered ceramic pellets have been impacted, and the particle size distribution was determined. The residues after impact were ground to a uniform size, and comparative leaching analyses were initiated. The samples are being contacted with deionized water at 90°C for 72 hr. The leachates and filter residue will be quantitatively analyzed by inductively-coupled plasma emission spectroscopy. Impact behavior and leaching data were not available at the time of this report, but will be presented in the next progress report, together with recommendations regarding future development of these waste forms.

4.0 KRYPTON SOLIDIFICATION

G. L. Tingey - Project Manager

The objective of this program is to develop alternative techniques for storing radioactive krypton in a solid matrix. Two techniques are currently being investigated: 1) dissolution of krypton in low-density glass followed by densification at high temperatures and 2) entrapment of krypton in solids during ion sputtering.

SUMMARY

Several potential metal matrices have been examined for entrapment of krypton during sputtering deposition of a metal film. Krypton entrapment is enhanced in an amorphous metal containing a relatively large secondary atom (i.e., yttrium, zirconium). Retention of the krypton appears to be enhanced by increasing the melting point of the deposit.

Krypton has also been dissolved or trapped in low-density SiO_2 at pressures of 34 MPa and 900°C . The krypton content of up to 6 cm^3 of $\text{Kr}(\text{STP})/\text{g}$ of SiO_2 is retained in the glass to a temperature of about 900°C .

KRYPTON ENTRAPMENT DURING SPUTTERING -

E. D. McClanahan, M. A. Bayne, and
G./ L. Tingey

Sputter deposition using Kr^+ as the sputtering ion has been shown⁽¹⁾ to be effective in trapping krypton in the deposit. This phenomenon has potential for preparing a solid for long-term storage of the radioactive krypton generated in nuclear fuels.

Initial studies were conducted on single-element crystalline metals (i.e., Fe, Ni, Al, Ti) with a negative bias voltage (2500 V) applied to the substrate. In these crystalline

systems, up to 5 atom Kr ($\sim 20 \text{ cm}^3$ of $\text{Kr}(\text{STP})/\text{g}$ of metal) is incorporated in the metal deposit. We later observed that two or three times the krypton could be trapped in an amorphous deposit than in the crystalline metals. Furthermore, the gas trapping occurred at a much lower substrate voltage (250 V) and the need for pulsing the voltage was eliminated.

Since the krypton trapping efficiency and the retention are both very dependent upon the metal composition, we have undertaken a study to determine the optimum metal for this application. Some of the criteria for determining the optimum alloy include: 1) high krypton loadings achievable, 2) ease of sputtering, 3) materials cost, and 4) gas retention.

The overall results of this series of depositions are presented in Table 4.1. The composition was determined by x-ray fluorescence analysis. Materials with grain sizes $<30 \text{ \AA}$, as determined by x-ray diffraction peak width and exhibiting conchoidal fracture, are considered glassy while the deposits with $>30 \text{ \AA}$ grain size were considered to be crystalline. The compositions listed as "mixed" are those showing a broad x-ray diffraction peak with a narrow peak superimposed upon it.

TABLE 4.1. Summary of Experiments in Developing Glassy Alloys
for Use in ^{85}Kr Storage

Materials	Structure	Coefficient 225 eV, atoms/ion	Net Sputtering Yield 2.5 KeV, g/amp-hr	Deposition Rate, nm/sec	Average(a) Krypton Content		Material Origin
					cm^3/g	at%	
$\text{Fe}_{0.89}\text{Y}_{0.09}\text{Me}_{0.02}^{(b)}$	Glassy	0.25	5.3	13	31.9	9	A-108 steel, Y plugs
$\text{Zr}_{0.64}\text{Fe}_{0.35}\text{Me}_{0.01}$	Glassy	0.18	3.2	11	22.1	9	Zircaloy IV, Steel plugs
$\text{Ni}_{0.82}\text{Y}_{0.18}$	Glassy	0.14	5.7	11	27.1	8	Ni-200, Y plugs
$\text{Fe}_{0.78}\text{Zr}_{0.20}\text{Me}_{0.02}$	Mixed	0.10	5.4	16	18.5	5	A-108 steel, Zircaloy II plugs
$\text{Fe}_{0.61}\text{Cr}_{0.20}\text{Y}_{0.10}\text{Ni}_{0.06}\text{Me}_{0.03}$	Mixed	0.10	5.1	12	17.5	5	316 stainless steel, Y plugs
$\text{Fe}_{0.73}\text{Zr}_{0.18}\text{Ta}_{0.07}\text{Me}_{0.02}$	Glassy	0.05	6.1	11	15.7	5	A-108 steel, Zircaloy II plugs
$\text{Fe}_{0.95}\text{Y}_{0.03}\text{Me}_{0.02}$	Crystalline	0.03	5.1	7	(c)	(c)	A-108 steel, Y plugs
$\text{Fe}_{0.67}\text{Si}_{0.24}\text{Ta}_{0.03}\text{Me}_{0.06}$	Mixed	0.02	3.3	≤ 21	0.6	<1	Duriron Ta wafers
$\text{Fe}_{0.69}\text{Si}_{0.25}\text{Me}_{0.06}$	Crystalline	<0.03	5.0	14	<0.1	<1	Duriron
$\text{Fe}_{0.67}\text{Si}_{0.24}\text{Cr}_{0.04}\text{Me}_{0.05}$	Experiment aborted: Deposit peeled badly						Durichlor-51
$\text{Fe}_{0.48}\text{Mo}_{0.30}\text{Cr}_{0.14}\text{Ni}_{0.05}\text{Me}_{0.03}$	Glassy	<0.01	5.5	19	<0.9	<1	316 stainless steel, Mo plugs
$\text{Ni}_{78}\text{Mo}_{21}$	Crystalline	<0.01	7.5	20	<0.2	<1	Ni-200, Mo plugs

a. Determined from Kr uptake and metal deposited.

b. Me implies minor or impurity elements.

c. Not calculable due to experimental problems.

• Duriron and Durichlore are tradenames of the Duriron Company, Inc.

In general, the materials which deposited in the amorphous state and had a large secondary atom (i.e., Y, Zr) had relatively high loadings when deposited with a low substrate bias (250 V). This indicates a high Kr^+ sticking coefficient. On the other hand, deposits not containing a large ($>1.5 \text{ \AA}$ metal radius) secondary atom did not trap significant quantities of krypton at this low-bias voltage. Materials with the mixed phase (both crystalline and amorphous phases) and having a large metal atom in the structure trap intermediate quantities of krypton in the matrix.

At present it appears that metals containing ~10% Y or Zr will be most likely to trap larger quantities of krypton. Gas retention properties of the krypton are also of interest. It now appears that the higher melting alloys give greater retention of the krypton. These criteria will be considered in selecting a reference material for gas trapping.

DISSOLUTION OF KRYPTON IN LOW-DENSITY GLASS -

G. L. Tingey and W. J. Gray

Earlier results⁽²⁾ have shown that krypton can be dissolved or trapped in low-density, high-surface-area glass rods. We have recently heated low-density glass rods to 900°C in 34 MPa (5000 psi) of krypton. Using these techniques we have achieved

loadings of up to 6 cm^3 of $Kr(\text{STP})/\text{g}$ of SiO_2 . Gas retention measurements from such samples are excellent, with essentially no krypton release at temperatures below 900°C. Evaluation of the diffusion coefficient of krypton and comparison with that reported earlier⁽³⁾ shows a gas release rate in the calculated range. Higher pressure loadings will be required for storage of ^{85}Kr by this technique. Therefore experiments will be conducted at 170 MPa (25,000 psi) at INEL to test potential loadings in SiO_2 under the higher pressure conditions. Extrapolation of current experimental data to 170 MPa yields a potential krypton content of about 25 cm^3 of $Kr(\text{STP})/\text{g}$ of SiO_2 .

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5.0 CARBON-14 AND IODINE-129 FIXATION

L. L. Burger - Project Manager

The objective of this program is to develop and demonstrate the technology needed to safely and effectively immobilize ^{129}I and ^{14}C released from treatment of irradiated fuels.

SUMMARY

A leaching study was conducted to determine the effects of seven factors on the leach rate of iodide from iodide-impregnated cement. Collection and statistical evaluation of the leach data are under way.

The effects of carrier gas composition, temperature, and zeolite pretreatments on iodide loading efficiency of silver-exchanged mordenites exposed to methyl iodide were investigated. Temperature and pretreatment processes had significantly affected the iodine loading efficiency. Tests using nitrogen carrier gas, with O_2 concentrations < 5 vppm, suggest that O_2 is not necessary in the methyl iodide loading mechanism.

The system used for measuring HI trapping efficiency of aqueous scrubbers was modified to decrease the decomposition of HI to I_2 .

STUDIES ON LEACHING - K. D. Wiemers

The first two phases in the study of the leaching of iodine from iodine-impregnated cement involved a parametric investigation of dynamic leaching methods and a screening study of factors affecting the iodine as iodate leach rate.⁽¹⁻³⁾ This quarter a second screening study, Phase III, began; it is designed to determine the influence of seven factors on the iodine, as iodide, leach rate from cement. Phase III will identify

the major influential factors, their relative magnitude, and the direction of their effect. The factors for Phase III were selected based on Phase II results⁽³⁾ and potential differences in chemical behavior between iodide and iodate compounds in cement. Table 5.1 lists the selected factors and their respective experimental levels. These seven factors are described below:

1. Solubility - To determine the effect of the fixation material's solubility in water on the iodide leaching mechanism, MgI_2 and HgI_2 were selected as the fixation compounds. Their solubilities at 25°C are 10.64 and $1.3 \times 10^{-4} \text{ M I}^-$, respectively.
2. Concentration of iodide - To evaluate a practical range for the amount of fixation material to be incorporated in a given amount of cement, levels of fixation material equivalent to 0.03 and $0.10 \text{ g iodide/g dry cement}$ were selected for study. These levels were based on results from Phase II and the practical limitations of cement mixing.
3. Addition of silver ion - The presence of a minimal amount of silver ion in the cement may decrease the amount of iodide solubilized into the free water of the cement system by forming the less soluble silver iodide compound. Silver ion was added as silver nitrate at a concentration equivalent in moles to 10% of the lowest concentration of iodide added.

TABLE 5.1. Factors Selected for Screening

Factor	Experimental Levels	
	Minimum	Maximum
Iodide solubility in water, I, M at 25°C	1.3×10^{-4}	10.64
Concentration of iodide, g/g dry cement	0.03	0.10
Addition of silver ion, g/g dry cement	0	0.0026
Addition of barium ion, g/g dry cement	0	0.0077
Addition of bentonite, g/g dry cement	0	0.05
Addition of sodium resinate, g/g dry cement	0	0.0003
Curing environment, CO ₂ , % by volume	0.033	100

4. Addition of barium ion - The addition of barium ion to the cement may decrease the exchange between the iodine fixation material and the sulfate present in cement by precipitation of BaSO₄. An amount of barium equivalent in moles to 10% of the maximum anticipated sulfite ion concentration was added in the form of barium nitrate. The maximum allowable wt% of SO₃⁻ in Portland Type III cement containing greater than 8% 3CaO Al₂O₃ is 4.5%.⁽⁴⁾

5. Addition of bentonite - Bentonite is an integral waterproofing agent belonging to the class of inert, pore-filler compounds. It also increases the plasticity of cement. Based on the little information available,⁽⁵⁾ 0.05 g bentonite/g dry cement was the chosen addition level.

6. Addition of sodium resinate - Sodium resinate is a recommended air-entraining agent.⁽⁶⁾ Air, properly entrained in cement, alters the formation of capillary channels in such a way as to decrease water diffusion and permeability. This addition also increases the workability of uncured cement. A 5% by volume sodium

resinate solution was prepared and added to the cement to give a final concentration of 0.003 g sodium resinate/g dry cement.

7. Carbon dioxide curing environment - Results from Phase II indicated that the interaction of the cement specimen with CO₂ saturated water significantly decreased the iodate leach rate.⁽³⁾ Studies concerning CO₂ crazing of cement showed that curing environment of 100% CO₂ and 100% humidity would minimize crazing while allowing carbonation reaction appropriate for reduction of reversible water movement.⁽⁷⁾ An apparatus was constructed to permit curing under such conditions.

To screen these seven factors a 12-trial Plackett Burman design⁽⁸⁾ was employed. The 11 factors employed included the 7 listed above and 4 unassigned factors used for estimation of experimental error. Each of the 12 trials consisted of a unique set of factors as defined by the design. Statistical evaluation of the data from the 12 trials provided an estimate of the effect each factor had on the measured quantity, the leach rate.

In this study the variables common to each cement specimen were cement type (Portland Type III), water to cement ratio (0.6 by weight), mixing procedure (time, speed, and type), specimen size (cylinders on the average 2.5 cm dia x 3.5 cm high), curing (10 days in humid environment), leachate (doubly distilled water, 500 ml, 20–25°C), sampling rate (similar to that described in Reference 2), and length of study (23 days).

For the leaching process, the cement specimens were suspended in the leachate by a nichrome wire basket and hanger; a minimum of 2 cm depth of leachate was maintained around the specimen's surfaces. Gentle agitation was provided by placing the leachate containers (Pyrex beakers covered with watch glasses) on a rotating shaker.

Iodide concentrations in the leachate sample will be analyzed using the iodide-specific ion electrode and/or ion chromatography.

To date, insufficient data are available to perform the statistical analysis. Preliminary results for the MgI_2 -impregnated cement in terms of iodide accumulative leach rate,

$$L = \left(\frac{\sum a_n}{A_0} \right) \left(\frac{V}{S} \right),$$

where L = leach rate, cm

a_n = iodide lost during leach period

A_0 = initial iodide present in specimen

V = volume of specimen, cm^3

S = exposed surface area, cm^2

indicate leach rates of an order of magnitude similar to those observed for the iodate leach studies, 10^{-4} cm, during the first day of leaching.⁽³⁾ At this rate, 0.04% by weight of the original fixation material was leached after 24 hr of leaching. If the leaching mechanism is similar to that

observed previously, the leach rate will decrease significantly after the third or fourth day of leaching.

During the initial cement set period those specimens containing HgI_2 were seen to be nonhomogeneous. Bands and pockets of HgI_2 were noted after curing. Tests involving the addition of surfactants to the cement appeared qualitatively, at least, to eliminate this problem.

Collection and statistical evaluation of the leach data will continue next quarter. Tests will be developed to aid in understanding the leaching mechanisms and the interactions of cement with the environment and the iodine fixation material. Once the major influential factors have been identified, a long-term leach study will be conducted.

IODINE RECOVERY - K. D. Wiemers

To further characterize the reactions of metal-exchanged zeolites when exposed to methyl iodide, we investigated the effects of carrier gas composition, temperature, and zeolite pretreatments.

The apparatus is shown schematically in Figure 5.1. A mass flow controller was added to ensure a more constant flow rate. Windows carved out of the reaction vessel's insulation provided observation of color changes. The effluent gas temperature was taken as the loading temperature. Samples of the influent and effluent gas streams were collected in gas sampling bulbs and analyzed by gas chromatography. The method provided a sensitivity of 0.1 vppm CH_3I and detection of possible reaction products, including organic alcohols and ethers.

Previously collected data have indicated a dependence of the iodide loading efficiency

FIGURE 5.1. Methyl Iodide Loading Apparatus

upon both pre-equilibration time and continuity of exposure to methyl iodide.⁽⁹⁾

To minimize these effects, short-term exposures and a standard operational procedure were employed. The operational procedure consisted of the following steps:

1. The reaction bed was equilibrated for 1 hr with the appropriate carrier gas at loading temperature.
2. The methyl iodide generator was operated for 0.5 hr before methyl iodide was introduced to the reaction vessel.
3. The exposure to methyl iodide ranged from 2 to 5 hr, depending on the instantaneous DF value. During loading, the effluent was sampled every 15 to 20 min.
4. Following methyl iodide exposure, the reaction vessel was disconnected and plugged. Three influent samples were collected.
5. The methyl iodide generator was then disconnected. The preheater and manifold were flushed and then reconnected to the reaction vessel for collection of purge samples.

The constant experimental parameters are listed in Table 5.2. Silver-exchanged (18.2%), 1/16-in. extruded mordenite was the initial starting material for all cases except for the run using 1/16-in. extruded sodium mordenite.

TABLE 5.2. Constant Experimental Parameters

Bed diameter, cm	2.5
Bed depth, cm	10.0
Face velocity, m/min	5
Average CH_3I	1
Influent concentration, gm/m^3	

In the nine loading runs, the temperature range studied was 100 to 250°C and the carrier gas was either breathing quality air (21% O_2) or prepurified nitrogen (<5 vppm O_2). The silver-exchanged mordenite was either 1) pretreated with 100% hydrogen at 500°C, yielding a reduced silver form, denoted Ag^{m} , or 2) pretreated with air at 500°C, yielding a mordenite with an unidentified silver form, denoted $\text{Ag}^{\Delta\text{m}}$. In one run the material was treated with air and then treated with hydrogen, both at 500°C, denoted $\text{Ag}^{\Delta\text{m}}$. Untreated silver mordenite, Agm , and sodium mordenite, Nam , were run as references. The experimental conditions for the nine runs are listed in Table 5.3.

For each run the instantaneous decontamination factor, DF, was determined as a function of the amount of iodide loaded. Results from these preliminary runs are summarized in Table 5.4 and described below.

TABLE 5.3. Experimental Conditions

Material	Carrier Gas	
	Composition	Temp., °C
Ag ^Δ _m (a)	N ₂	150
Ag ^{Δ°} _m (b)	N ₂	150
Agm	N ₂	100
Agm	N ₂	150
Agm	N ₂	250
Agm	Air	150
Agm	Air	200
Ag [°] _m (c)	Air	150
Nam	Air	150

a. Material pretreated with air at 500°C.

b. Material pretreated sequentially with air, then H₂, both at 500°C.c. Material pretreated with H₂ at 500°C.

TABLE 5.4. Methyl Iodide Loading Results

Material	Carrier Gas		Loading, mgI/g Metal Mordenite	DF
	Composition	Temp., °C		
A. Effect of Temperature				
Agm	N ₂	250	2.5	>10 ³
Agm	N ₂	150	2.5	>10 ³
Agm	N ₂	100	2.5	<10 ²
Agm	N ₂	250	25	>10 ³
Agm	N ₂	150	25	<10 ²
Agm	N ₂	100	25	<10 ²
Agm	Air	200	25	>10 ³
Agm	Air	150	25	<10 ²
B. Effect of Carrier Gas Composition				
Agm	Air	150	2.5	>10 ³
Agm	N ₂	150	2.5	>10 ³
Agm	Air	150	25	<10 ²
Agm	N ₂	150	25	<10 ²
C. Effect of H ₂ Pretreatment at 500°C				
Ag [°] m ^(a)	Air	150	25	>10 ³
Agm	Air	150	25	<10 ²
D. Effect of Air Pretreatment at 500°C				
Nam	Air	150	1	5
Ag ^Δ m ^(b)	N ₂	150	1	1
Ag ^{Δ°} m ^(c)	N ₂	150	1	1

a. Material pretreated with H₂ at 500°C.

b. Material pretreated with air at 500°C.

c. Material pretreated sequentially with air, then H₂, both at 500°C.

1. Increasing the carrier gas temperature within the tested range increased the DF for a given iodide loading (Table 5.4A).
2. Oxygen concentrations >5 vppm were not required for the methyl iodide loading mechanism (Table 5.4B).
3. At higher iodide loadings the H₂ pretreated silver mordenite had a higher DF than the untreated silver mordenite loaded at the same carrier gas temperature (Table 5.4C).
4. The lowest iodide loading capacity was observed with those samples pretreated with air at 500°C. This pretreatment evidently caused both irreversible chemical and physical changes in the silver mordenite as the iodide loading was less than that observed for Nam and the iodide loading properties were not revived by subsequent treatment with H₂ (Table 5.4D).

Methanol, dimethyl ether, and methyl nitrate have been reported as reaction products of the methyl iodide-silver adsorbent interactions.⁽¹⁰⁻¹²⁾ In our studies, dimethyl ether was the only detectable reaction product. Table 5.5 lists the conditions under which dimethyl ether was first observed, the experimental conditions, and the methyl iodide DF. The following summary of these results demonstrates the apparent inverse relationship between dimethyl ether generation and the loading efficiency of the silver mordenite.

1. In the cases where the iodide loading efficiency onto silver mordenite was poor dimethyl ether was detected immediately (Table 5.5, entries 1 and 2).
2. At increased temperatures, where the iodide loading efficiency was greater, dimethyl ether generation was not detected until higher iodide loadings were obtained

(Table 5.5, entries 3, 4, and 5, and entries 6 and 7).

3. Reduced silver mordenite, whose iodide loading efficiency was considerably greater than the untreated silver mordenite's, did not generate dimethyl ether until a considerably higher iodide loading had been reached (Table 5.5, entries 6 and 8).
4. Although the iodide loading efficiencies in air and N₂ are similar, the interaction between the carrier gas composition and temperature, the iodide loading and dimethyl ether generation was not clear (Table 5.5, entries 4, 6, 5 and 7). Further study is necessary to define this interaction.

The absence of dimethyl ether during exposure of Nam to methyl iodide, even though it had a DF <10 (Table 5.5, entry 9) supports the concept that the chemical nature of the metal may greatly influence the iodide loading mechanism.

Future work includes:

1. revision of the loading apparatus to provide an automated, continuous sampling system and more direct temperature measurements
2. investigation of methods for characterizing loading materials after pretreatment
3. determination of the methyl iodide loading capacity of reduced silver faujasite and silver-impregnated silicates
4. determination of the effect of contaminant gases on methyl iodide loading, and further investigation of product gases
5. determination of lifetime expectancy and iodide loading efficiency in the recycling system
6. investigation of alternative stripping schemes.

TABLE 5.5. Dimethyl Ether Formation

Entry Number	Material	Carrier Gas		Loading at (CH ₃) ₂ O Detection, mg I/g Metal-Mordenite	Decontamination Factor Information
		Composition	Temp., °C		
1	Ag ^Δ _m ^(b)	N ₂	150	0.2	<10
2	Ag ^{Δ°} _m ^(c)	N ₂	150	0.5	<10
3	Agm	N ₂	100	3.6	<100
4	Agm	N ₂	150	6.8	100 at 7 mg I/g Agm
5	Agm	N ₂	250	14.0	>10 ³ at 24 mg I/g Agm
6	Agm	Air	150	3.0	100 at 8 mg I/g Agm
7	Agm	Air	200	(a)	>10 ³ at 23 mg I/g Agm
8	Ag [°] _m ^(d)	Air	150	88.0	100 at 80 mg I/g Agm
9	Nam ^(d)	Air	150	(a)	<10

a. No dimethyl ether was detected during the run.

b. Material pretreated with air at 500°C.

c. Material pretreated sequentially with air, then H₂ at 500°C.

d. Material pretreated with H₂ at 500°C.

HI TRAPPING - R. D. Scheele

If hydrogen reduction is used in the recycle of silver zeolites, a gas stream containing ~0.15 vol% HI will be formed. An alternative to trapping the HI on a less valuable metal zeolite is to absorb it in an aqueous system for subsequent processing for storage.

The results reported in Reference 9 for aqueous absorption indicated efficient removal of HI with laboratory scrubbers. The observed decontamination factors are probably lower than ideal because of oxidation of the HI to I₂. The system has been modified to prevent light-induced decomposition and to allow for a nitrogen purge. Selected experiments are being repeated for comparison.

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6.0 INTERNATIONAL PROGRAM SUPPORT

K. M. Harmon - Project Manager

The objective of this program is to develop and maintain an information system covering nuclear waste management R&D programs and technology in other nations, for use by U.S. government agencies and DOE contractors.

SUMMARY

Collection, review, and summarizing of significant documents continued. The report

PNL-2941, Summary of National and International Radioactive Waste Management Programs (1979), was prepared and cleared for publication.

7.0 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 major effort this quarter has been the documentation of studies done, including the seismic data base; geologic field investigations; and kriging. A report An Evaluation of Kriging Techniques for High Level Radioactive Waste Repository Site Characterization has been issued. It finds this statistical technique to be a useful tool in developing realistic contours of the geologic structure of a potential repository site.

Teknekron, Inc., has completed the methodology for radionuclide migration and population dose commitment. The ground-water transport times have been calculated for multilayered strata in bedded salts, shale, and basalt. Work is being performed at the Virginia Polytechnic Institute in the correlating of mining costs and hazards with depth of repository.

The workshop "Nuclear waste Management: Understanding Social Assessments" was attended at Seattle by government employees and government contractors. Work on risk, conflict, and societal acceptance concerning nuclear waste and its disposition has focused mainly on completing the documentation of studies done, and continuing work on this year's tasks.

A SEISMIC DATA CATALOG AND ASSOCIATED GRAPHICAL CAPABILITIES - T. N. Bishop and H. P. Foote

During the quarter, documentation of the seismic data base was drafted. The report, now being reviewed for use in other waste management studies, is briefly summarized below.

The seismic data base developed by PNL is a collection of computer files of earthquake locations, origin times, magnitudes, and related information received from many sources. Available seismic data sets in the Pacific Northwest area have been merged, and duplicate events discarded. The data file structure has been designed to be flexible enough to accept data from different sources and be updated easily. Use of disc storage and the interactive nature of the PDP-11/45 and 11/55 computers make searches of particular groups of earthquakes, epicenter maps, and statistical studies relatively rapid. The programs designed to analyze and display the data are unique and have proved useful in several applications. Strain release maps of various regions have also been constructed.

The Pacific Northwest region has been used to demonstrate the programs. These techniques are designed to be used also in other areas of the United States to provide needed seismic data and analytical techniques to support nuclear waste management activities.

The standard format of the earthquake files and the various programs that input, sort, select, analyze, merge, and plot the seismic information is also described in the writeup.

GEOLOGIC INVESTIGATIONS IN THE NORTHWEST -

G. A. Sandness and W. M. Phillips

During the quarter, the recently completed geologic studies were summarized

and draft documentation was prepared. Now under review, this material will be incorporated into other waste management studies. The paragraphs below are an abstract.

Reconnaissance field studies of a 270-km long, NE-trending geologic lineament (see Figure 7.1) in the State of Washington initiated by PNL in 1977 have now been completed. The results indicate that the photolineament, clearly visible to Landsat imagery from the Lake Merwin area northeast to the Omak Lake region, possesses a composite structural expression in bedrock ranging from pre- to late-Tertiary age. Faulting of small displacement is present along the lineament trace in the Lake Merwin area. Near Randle an apparent intracanyon basalt flow is evidence of an ancient drainage

FIGURE 7.1. Index Map Showing Location of Study Areas and Lineament Trace. L = Lake Merwin; S = Spirit Lake; R = Randle; B = Bumping Lake; C = Corbaley Canyon; O = Omak Lake

alignment along the lineament trace. In the Corbaley Canyon area the lineament is apparently controlled by folding and jointing in basaltic rocks. Investigation in the Omak Lake-Bridgeport region led to the conclusion that the expression of the photolineament is fortuitous there. The most compelling expression of the lineament is in the Bumping Lake area. There a portion of the lineament lies on a contact between the pre-Tertiary Russell Ranch Formation and the Eocene Puget Formation. A definitive structural analysis of the contact (either a fault or an angular unconformity) was not possible because of a Quaternary basalt flow cover.

A final evaluation of the lineament will require extensive additional field studies of Tertiary volcanoclastic rocks and hypabyssal intrusives that blanket much of the study area.

KRIGING* - P. G. Doctor

A report An Evaluation of Kriging Techniques for High Level Radioactive Waste Repository Site Characterization has been issued. The study evaluates kriging, a statistical method for estimating functions that describe spatially distributed phenomena such as ground-water elevation (potential) and depth to basalt, for its potential use in site selection and safety assessment for permanent storage of high-level radioactive waste.

Kriging produces a contour model of the geologic formation of a potential site with an associated measure of uncertainty and thus may provide a more complete description than can be gained from other contouring methods. Furthermore, given the existing data, kriging

can be used to optimize the selection of additional sampling locations. These features help to reduce the number of core samples taken and could cut data acquisition costs significantly.

In this study the most efficient way found to evaluate kriging was to experiment with the techniques on representative data sets from the Hanford Wells data base. The basic criterion used here is how realistically it contours the water potential and basalt surfaces. The water potential surface is quite well known; hand-drawn contour maps, based on substantive knowledge in addition to well data, are considered the standard. The kriged contours based on only the well data are quite similar to the hand-drawn contours. The kriged water potential map (Figure 7.2) agrees rather closely with the hand-drawn map (Figure 7.3). The kriging standard errors (measure of uncertainty) provide a quantification of the precision of these contours in various locations (Figure 7.4). They can be used to help select additional data sampling locations.

The basalt surface is much less well known than the water potential surface. Consequently, existing top-of-basalt contour maps rely very heavily on substantive knowledge. The presence of discontinuities, such as synclines, necessitates a more complex kriging analysis. The kriged contours (Figure 7.5) based on only the well data and the approximate locations of two major synclines showed good agreement with an existing contour map (Figure 7.6). The basalt kriging standard errors (Figure 7.7) were much larger than those for the water elevation surface, reflecting the more complex spatial structure of the basalt deposits.

The kriging computations are performed using BLUEPAK, a computer package developed by the Paris School of Mines and installed at

* For background information see quarterly progress reports PNL-2378-3 and -4.

FIGURE 7.2. Kriged Contour Map of January 1975 Hanford Water Potential Surface

FIGURE 7.3. Hand-Drawn Contour Map of January 1975 Hanford Water Potential Surface

FIGURE 7.4. Contour Map of Kriging Standard Errors of January 1975 Hanford Water Potential Surface

the DOE-Las Vegas computing facility. It is currently being accessed using a DECWRITER terminal over Federal Telecommunications System lines.

This study concludes that kriging can be a useful tool in developing realistic contours of the geologic structure of a potential repository site. Secondly, the kriging standard errors provide a quantification of the precision of the contours; this can be useful evidential information in developing a rationale for site selection. Thirdly, in-

sights gained from the kriging analyses can contribute to the substantive knowledge of the geologic or hydrologic phenomenon under study; an example is "the inverse problem" in hydrology, which is the derivation of hydraulic conductivity (an areal distribution) from ground-water potentiometric (point) measurements.

Development of kriging into an effective tool for geologic repository site characterization for the licensing process requires an interdisciplinary environment. An immediate

FIGURE 7.5. Kriged Contour Map of Hanford Top-of-Basalt Surface

U.R. = Umtanum Ridge
 G.B. = Gable Butte
 G.M. = Gable Mountain
 C.C.S. = Cold Creek Syncline
 P.S. = Pasco Syncline

FIGURE 7.6. Contour Map of the Topmost Buried Basalt Surface(1)

benefit of this environment would be improvements to the kriged ground-water and basalt surface contours produced in this study. More importantly, the interaction of kriging methodology with the traditional deterministic models of geologic phenomena will contribute to a more defensible repository site characterization; kriging can be used for the statistical evaluation of the physical models, and input from physical models will produce more realistic kriging models.

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

The objective of this study is to optimize repository depth in terms of cost and safety.

The radionuclide migration and population dose commitment methodology has been completed. Using 100,000 MTHM as a basis for waste disposal inventory (50% HLW and 50% spent fuel), Teknekron has calculated the

FIGURE 7.7. Contour Map of Kriging Standard Errors of Hanford Top-of-Basalt Surface

radiological dose commitments as a function of depth for bedded salt and shale repositories. Calculations for basalt are in progress.

Isotopic concentrations of nuclides in the waste were calculated using the ORIGEN computer code. The fuel is assumed to be irradiated to 27.5 MWd/kg over a 3-year period. It is then cooled for 10 years before reprocessing. The high-level wastes from reprocessing are cooled for an additional 5 years before solidification and shipment to a repository. The ORIGEN calculations were completed and the results tabulated as

radionuclide inventories remaining in the spent fuel and the high-level waste as a function of time.

Generic characteristics of the geologic columns were developed by considering the physical processes involved in the formation of the geologic units of interest to waste isolation. The definition of the relative thickness of the realistic stratigraphic units as a function of the depth of a waste repository was based upon the first principles of the physical processes involved in their formation.

After survey of several existing hydrologic and nuclide migration models, a simple one-dimensional hydrologic transport model based upon Darcy's equation of porous flow was selected. This model considers a vertical upward flow through multilayered geologic media and utilizes the vertical component of the hydraulic gradients and vertical hydrologic flow properties of the geologic media.

Applying this model to radionuclide migration, the ground-water transport times were calculated for multilayered strata in bedded salt, shale, and basalt. The nuclide migration times are then calculated using geochemical retardation for bedded salt, shale, and basalt geologies. The peak annual inventory release of the nuclides to the biosphere is calculated assuming a uniform waste dissolution rate of 10^{-4} per year. The total radionuclide inventories that might be released to the biosphere are then calculated by accounting for the further radionuclide decay over the 10,000 years of release to the biosphere.

Work has also proceeded at the Virginia Polytechnic Institute, where studies are being performed correlating mining costs and hazards with depth of repository. The study of repository design concepts was completed for bedded salt, shale, and basalt repositories and the excavation cost developed as a function of depth and geologic media. The study was completed on shaft excavation and hoist system costs for the three geologic media. The results are summarized as dollar costs as a function of repository depth for different shaft cross-section areas. The hoist operating costs are also summarized as a function of load and depth of operation. Ventilation costs are also being correlated with depth. Correlation of total repository costs with the repository depth is under way.

The data available on mining accident injuries and fatalities have been collected, and a regression analysis is under way.

RISK, CONFLICT, AND SOCIETAL ACCEPTANCE CONCERNING NUCLEAR WASTE AND ITS DISPOSITION - S. M. Nealey (HARC)

Task 1 was completed this quarter. The workshop "Nuclear Waste Management: Understanding Social Assessments" was held February 21 and 22, 1979, at the Battelle Seminar and Study Programs facilities in Seattle. About 25 government employees and government contractors attended the meeting.

A major portion of the work on Task 2, dealing with public perception of risk associated with production of electric power, was completed this quarter. Task 3 was completed last quarter, with final approval received on the report A Comparative Analysis of Network Television News Coverage of Nuclear Power, Coal, and Solar Stories.

Task 4, comprising review and completion of FY-1978 reports, was mostly completed during the last quarter. Four of the five reports were finished and cleared. These included: A Comparative Analysis of Print Media Coverage of Nuclear Power and Coal Issues, The Relationship of Human Values and Energy Beliefs to Nuclear Power Attitude, Nuclear Knowledge and Nuclear Attitudes: Is Ignorance Bliss? and Radioactive wastes: Public Attitudes Toward Disposal Facilities.

Work continued on Task 5. The writing task is under way on Task 6, an examination of group and individual involvement in environmental decision-making focusing on nuclear power issues. The literature review continued on Task 7 regarding conflict mediation techniques applicable to the siting of nuclear waste repositories.

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Report RHO-BWI-C-6, Rockwell Hanford Operations, Richland, WA, 1977.

8.0 WASTE MANAGEMENT SAFETY STUDIES

W. K. Winegardner - Project Manager

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

SUMMARY

A report was begun summarizing the initial application of safety indices for the evaluation of waste management implications of alternative fuel cycles; currently under investigation are a once-through and coprocessed UO_2 - PuO_2 fuel cycle. Assessment of ^{85}Kr management, with and without recovery, continued. Accident analyses and development of methods for estimating occupational exposure rates were started for the latter case, i.e., with noble gas recovery. An investigation of reports of failures in nuclear air-cleaning systems was completed.

FUEL CYCLE ASSESSMENT - P. J. Pelto

The evaluation of the once-through fuel cycle and the coprocessed UO_2 - PuO_2 fuel cycle waste management operations continued during the quarter. As described in previous quarterly reports, the analytical approach defines safety indices for a scoping analysis of the pretreatment waste streams. A more detailed approach utilizing checklists and preliminary hazards analyses is used to analyze the waste streams in conjunction with their conceptual management systems. A report summarizing the initial application of this analysis approach to the once-through and coprocessed UO_2 - PuO_2 fuel cycle will

be completed early in the next reporting period. Its purpose is to demonstrate the analytical approach, provide relative comparisons of the once-through and coprocessed fuel cycle waste management operations, and identify the information needed for a more comprehensive analysis.

DISPERSION/ACCUMULATION TRADE-OFF ASSESSMENT - P. J. Mellinger

Assessment of ^{85}Kr management techniques, with and without recovery, is being used to provide insights into tradeoffs between waste management by dispersion/dilution and by accumulation/containment. Equations were derived for calculating cumulative radiation doses for an 80-year period in which the population is increasing. This was done both for persons in the region of a coprocessing plant and the world population. Initial results indicate that the cumulative doses calculated for a growing population from 1980 to 2060 are within a factor of about two of those calculated for a static year 2000 population (presented in PNL-2378-4, the October-December 1978 quarterly progress report).

For the case of recovery, occupational radiation exposure estimates will be based on both laboratory measurements and computer calculations. Radiation exposure rate measurements have been made on three laboratory

cylinders containing ^{85}Kr . Two of these cylinders contained 100 Ci each of ^{85}Kr , and the other 20 Ci. Information from these measurements should aid in estimating the exposure rates from a cylinder containing 130,000 Ci of ^{85}Kr . The computer code ISOSHL D has been used to calculate radiation exposure rates from storage cylinders containing 20, 100 and 130,000 Ci of ^{85}Kr . Although discrepancies have been found between measured and calculated exposure rates, it is believed that accurate estimates of occupational exposures can be made from calculations and extrapolations from measurements. The next step is to mockup situations in the recovery and storage processes to permit the use of ISOSHL D in calculating radiation exposure rates.

Accident analysis for the cryogenic krypton recovery process is also in progress. The following potential accidents have been identified:

Minor

- loss of cooling supply to the cryogenic separator; vaporization and loss of the krypton inventory through the plant stack
- system leak to process cell atmosphere (e.g., loss of compressor seal)
- process gas dryer vents the process gas during the drying cycle

- process lines plugged by freezing and/or foreign bodies.

Moderate

- oxygen recombiner explosion resulting in ground-level krypton release
- process shutdown with krypton venting through plant stack
- cryogenic system explosion with krypton inventory released at ground level.

Similar accident analyses are being initiated for storage of krypton in pressurized bottles and zeolites. An umbrella analysis will follow to identify the commonality in the potential accidental releases.

HEPA FILTER PERFORMANCE – H. K. Elder

HEPA filters are used in the engineered safety features systems for plants where radioactive materials are handled. In an accident air is filtered before release and the HEPA filters provide the final protection preventing contaminated process air in the enclosure reaching the environment. For this reason reliability of the filter system is of great interest in nuclear system safety analyses, and failure data on HEPA filters used in nuclear air cleaning systems were reviewed. Preliminary work indicates a failure rate of about 10^{-4} per year per HEPA filter.

9.0 WASTE ISOLATION SAFETY ASSESSMENT PROGRAM

A. Brandstetter - Project Manager
M. A. Harwell - Assistant Project Manager

The objectives of the Waste Isolation Safety Assessment Program (WISAP) are to:

- 1. develop the capabilities needed to assess the post-closure safety of geologic repositories*
- 2. obtain scientifically defensible generic and site-specific data necessary for safety assessments*
- 3. provide, as needed, studies to further support these data and analyses*
- 4. demonstrate the assessment capabilities by performing analyses of reference sites*
- 5. apply the assessment methodology to assist the National Waste Terminal Storage Program in site selection*
- 6. 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.*

PRELIMINARY INFORMATION REPORT ACTIVITIES

The reference site initial analysis for salt domes was given top priority within WISAP during this quarter, with the goal to provide input to the Preliminary Information Report (PIR).

Because of the importance of the PIR, it was necessary to provide the most thorough scenario analysis possible within the time allowed. The deadline for Task 1 input into the Consequence Analysis Task was moved ahead to March 30, 1979.

Initial work for the salt dome reference site analysis began during the last portion of the preceding quarter. However, in this quarter it was necessary to choose a new reference site for the analysis. In late January the site was chosen by ONWI to be in the northeast Texas basin (Hainesville salt dome).

TASK 1 - RELEASE SCENARIO ANALYSIS -

G. L. Benson

A draft report describing the salt dome release scenario analysis was developed based on the results of the salt dome analysis. The report is based on input from the available literature, WISAP Task 1 internal expertise, the Task 1 expert consultant team, the Geologic Project Manager (GPM) (Law), the Repository Project Manager (RPM) (Bechtel and NUS), and the Texas Bureau of Economic Geology (TBEG).

The process for developing the resulting release scenarios for the PIR was:

1. research and analysis by Task 1 staff
[working closely with Bechtel (BNI), Law, NUS, TBEG]

January-February 1979

2. scenario analysis review by BNI, Law, NUS at PNL

March 5, 1979

3. development of draft report
March 5-16, 1979
4. geotechnical review of draft report by
Law's review consultants and by TBEG
March 22-23, 1979
5. final management review and approval
by ONWI, BNI, and NUS
March 27, 1979
6. input to Task 3 consequence analysis
March 30, 1979.

Salt domes of the Gulf Coast Interior Basins possess many characteristics, such as plastic mechanical behavior and extremely low porosity and hydraulic conductivity, that render them geologically attractive as nuclear waste repositories. The conclusion drawn from the existing information and analysis for the reference salt dome repository is that within the time frame analyzed (1,000,000 years) geologic phenomena alone will not breach the reference site repository. It is important to note that this conclusion is based upon limited data and a preliminary analysis. And it should not be construed to mean that all salt domes in the interior basins are geologically suitable for a nuclear waste repository.

One important result of the salt dome analysis has been to outline areas that require additional basic research. Probably the most significant one for salt domes is that of dome dissolution because this is the most plausible method of breaching a repository over geologic time, especially as it is an ongoing process at many salt domes.

One of the greatest potential weaknesses of any salt formation, in terms of long-term geologic repository stability, is the high solubility of halite in water. But because many Gulf Coast Interior domes have existed for tens of millions of years, massive dissolution by laterally or vertically moving ground waters appears unlikely. However,

this concept must be verified by detailed studies of dome dissolution mechanisms before a definitive safety assessment can be made.

For significant dissolution to occur, domed salt must be in direct contact with flowing ground water, and impervious barriers, such as dense anhydrite caprock, clays, or marls, must be not present. Ground-water flux at the zone of dissolution must be great enough to remove saturated brines and to supply incoming fresh or unsaturated ground waters. Clearly, the greater the ground-water flux of fresh or unsaturated water the greater the potential for salt dissolution. The basic conditions for salt dissolution are potentially fulfilled wherever a salt dome intersects an aquifer system, or where structural features, such as upturned beds and faults, allow vertical ground-water movement along the salt-host interface.

In the northeast Texas basin, two aquifer systems appear capable of promoting active dome dissolution, the Woodbine Formation and the Carrizo-Wilcox Group. Using calculations of dissolution rates based on salt plumes around a group of northeast Texas salt domes, it was shown that an 800-ft salt buffer zone around a repository could be breached in about 2.7 million years. Assuming climatic changes that increase hydraulic gradients, such a breach could be moved up to about 2 million years. Several uncertainties are inherent in this method. Specifically, ground-water parameters are not well known for the near-dome environment.

The most serious potential problem with salt domes is that many of the same reasons that make them attractive as a nuclear waste repository make them attractive for other purposes. In fact, they are intrinsically a resource as a source for salt, storage, and

other uses. The PIR scenario analysis showed inadvertent human intrusion to be an important and plausible breach mechanism.

The primary basis for any inadvertent future human intrusion into a waste repository must be based on the "loss of institutional control" as suggested by EPA's proposed draft criteria. This is interpreted to mean that, at some time following the final closure of the repository, information of the repository is lost. Subsequently, humans inadvertently breach a repository through various possible mechanisms.

One of the most credible methods of future intrusion for a salt dome repository is by solution mining, a process used widely in the United States since the beginning of this century to mine salt from salt domes. In addition to its use to extract the mineral salt it has been used to create cavities for storage of various gases and liquids.

Solution mining is simply the removal of salts and evaporites by dissolution. Fresh water is injected into a salt deposit, and brine is extracted. Although the methods differ with application, the controlling physical processes are the same. It is highly plausible that solution mining after the loss of institutional control would result in the perturbation of a nuclear waste repository located in a salt dome and that such solution mining would intersect the repository, creating a breach. Given these assumptions, a release scenario was developed.

The primary conclusion drawn from this scenario analysis is that geologically a carefully chosen salt dome provides an excellent medium for the long-term disposal of nuclear waste. The potential geologic phenomenon that could plausibly breach a salt dome repository within a 10^6 -year time frame is natural dissolution. To breach the repository within this time, however, even natural

dissolution would require much greater rates than are presently recorded. It is, nonetheless, considered both the most probable and the bounding geologic scenario.

Another important conclusion of this PIR scenario analysis is that much additional work is required to identify and quantify the geologic and hydrologic phenomena associated with salt domes. They are surrounded by a structurally complex system and are themselves complex. In short, the salt dome geosystem is not well understood now and needs further research.

The major Task 1 modeling effort during the second quarter of FY-1979 involved the second-generation repository simulation model for a hypothetical site in the Columbia Plateau Basalts. The user-interactive computer tool is being developed to assist geoscientists in identifying and quantifying the various potential geologic and hydrologic system states a repository site might exist in in the future.

This computer model will assist in reducing a complex, multivariate problem to a set of interrelated but distinct components that can be more easily addressed by geoscientists. The key is to focus the energies of the experts on one segment of the problem at a time and yet have a framework developed for integration of all the components. Factors involved in the model under development are:

- There is significant interaction among disruptive phenomena. For example, climate, precipitation, continental and alpine glaciation, erosion, sedimentation, and ground-water recharge are all synergistic.
- Most of the disruptive phenomena are functions of time, and therefore initiation of breach and consequences cannot always be considered simultaneously.

- Data uncertainties dictate reliance on probability distributions rather than on unique values.
- The sensitivity of the output to variations in the input must be analyzed to optimize time and money expenditures on the waste disposal problem.
- The output of the methodology must be tailored to provide input to the consequence analyses. Additionally, it must estimate the input variable ranges, to bound a parametric consequence study.
- The methodology must explicitly state the assumptions of the geoscience users and in so doing provide a degree of trackability to the study.

The second generation scenario model was made operational in an interactive model. The data included in each submodel are strictly hypothetical; however, the framework is now in place, so that substitution of specific values into each submodel can proceed. Also in progress this quarter was work on a controlling interaction package that will allow more thorough interaction by the geoscientist user with the computer model.

The plans for the Task 1 workshop for FY-1979 have been expanded and will serve as a forum for reviewing the various release scenario analysis methods and many of the technical geologic aspects of such methods. The workshop is slated for the last quarter of this fiscal year, and the agenda is currently being developed.

TASK 2 - WASTE FORM RELEASE RATE ANALYSIS - D. J. Bradley and R. P. Turcotte

A series of milestones for Task 2 were met during this period. Static tests on actinide-doped glass and on spent fuel were started at PNL. Hydrothermal tests were started on cold waste glass.

Also at PNL, spent fuel was located for thermochemistry studies, and oxidation studies were started on spent fuel. Brookhaven National Laboratory (BNL) received Rocky Flats transuranic (TRU) ash, prepared TRU leached samples, and started International Atomic Energy Agency (IAEA) leach tests. The anoxic leach test on actinide-doped glass was started at Argonne National Laboratory (ANL).

Autoclave tests on the doped beads are proceeding smoothly through the 150-experiment matrix. We have concentrated on the cold glass, containing depleted uranium, so that these samples may be examined by existing Auger spectroscopy and by nonradioactive induction-coupled plasma spectrometer (ICP) solution analysis methods.

The problem of leakage through the final cold weld seal of the gold capsules has been satisfactorily remedied by welding the capsules shut with the tungsten arc inert gas welding process (TIG).

The hot cell leaching cabinet has been installed in C-cell and an ambient temperature static leach test started on spent fuel fragments, with a burnup of 28,000 MWd/MTU. Five leach solutions with the following designations are used in the static tests:

1. salt brine solution WIPP "B"
2. simulated calcium chloride ground water
3. simulated sodium chloride ground water
4. simulated sodium bicarbonate ground water
5. deionized water.

A sixth solution, representing a bedded or domed salt site, will be started when the solution composition becomes available.

Chemical distribution studies on spent fuel leaching involve the micro-analysis of spent fuel leach samples. A microprobe analysis is in progress for representative fragments of HB Robinson -2 fuel, with a burnup of 28,000 MWd/MTU. Cursory

examination showed that tellurium, iodine, and barium were concentrated at the outer edges of the transversely sectioned samples. The rest of the detected elements appear uniform from edge to center. Fuel fragments of Zorita fuel (54,500 Mwd/MTU), and Quad City fuel (9,000 Mwd/MTU) will be examined during the next quarter. These three fuels are being leached in the long-term spent fuel leach tests transferred to WISAP Task 2 in January 1979. These spent fuel leach tests are now being summarized.

Spent fuel rods for leaching partially clad fuel samples are being identified for procurement. Two fuel rods with a burnup of 30,000 Mwd/MTU will be transferred from the Nuclear Waste Vitrification Program to WISAP Task 2. Additional fuel rods of differing irradiation history have been located at Battelle-Columbus, and procurement will begin. This supply of fuel will allow some in-situ release studies as well as supply the needs for the chemical distribution effect studies.

Static leach tests have been started on actinide-doped waste glass using the glass PNL 76-68, detailed in the WISAP FY-77 Annual Report and following the details reported in the last quarterly technical progress report (PNL-2378-4). Inspection of cumulative fraction curves shows that ^{237}Np leaches out six to eight times faster than ^{239}Pu for most solutions. Leach solution affects the leach rate generally in the following order: $\text{NaHCO}_3 > \text{H}_2\text{O}$, CaCl_2 , $\text{NaCl} > \text{salt brine}$. The raised pH in the bicarbonate solution probably increases breakdown of the glass structure. The concentrated brine solution tends to retard leaching compared to other solutions.

Actual leachate solutions from the International Atomic Energy Agency's (IAEA) test have been transferred to WISAP Task 4 for sorption-desorption analyses.

The cold rotary kiln incinerator ash (40 kg) and the hot ^{239}Pu -contaminated incinerator ash were received from Rocky Flats in March. Emission spectroscopy has been used to verify the composition of the cold ash and will be compared to the Rocky Flats ash analysis. Work using the cold ash with cement solidification indicates that it behaves much differently than the simulated ash composition used earlier. The difference is believed partially attributable to the physical structure of the ash, involving a larger particle size and high porosity. Acceptable formulations with all solidification agents are anticipated.

The alpha air monitor for the TRU leaching facility has been received. Specimen preparation using the ^{239}Pu -contaminated ash will begin as soon as the air monitor is installed. Leaching with the IAEA solutions will begin next quarter.

The anoxic leach test on ^{239}Pu - and ^{237}Np -doped waste glass has started at ANL. Gamma-ray analysis of glass beads (produced by PNL) and of initial leach solutions indicates:

- Both ^{237}Np and its ^{233}Pa daughter can be effectively measured by their gamma-ray emissions.
- Using a HNO_3 -HF scrub of the leach container, much of the activity removed from the beads is found on the wall of the container.

The feasibility of applying the EXAFS technique to study the local environment of actinides in liquids and solids has been investigated. The results obtained from uranium samples indicate that the technique can be applied, and the information obtained from the experiments is very useful. However, the experiment is relatively difficult to perform. Qualitative comparison of the EXAFS spectra indicated that the uranium atoms have a similar local environment in the

sodium silicate glasses and in UO_3 . Quantitative analysis cannot be performed until knowledge of the k-dependent phase shift and scattering amplitude for uranium atoms has been obtained.

The analysis continued of solutions generated by the continuous flow leach test at Lawrence Livermore Laboratory (LLL). Analysis of bicarbonate and deionized water samples has been completed through day 68. For the WIPP brine solution, analysis has proceeded through day 20 and counting through day 6. The design of the continuous-flow test involving rock material was started.

TASK 3 - RELEASE CONSEQUENCE ANALYSIS -

J. R. Raymond and R. W. Nelson

During this quarter parametric (sensitivity) studies were conducted as part of the Paradox Basin Release Consequence Analysis. Sensitivity analysis aids in assigning confidence limits to inherent uncertainties. The objectives of this study were to determine the degree of influence particular model parameters have on the arrival times and distribution of contaminants into the biosphere and to demonstrate and document the procedure for performing a site-specific sensitivity analysis.

The sensitivity analysis was performed for the parameters of both the hydrologic and transport models. For both models, the base case parameters provided a starting point from which sensitivity comparisons could be made. In performing the study, each parameter was varied over a range of practical values while holding all other parameters constant at their base case values.

The base case parameters considered in the hydrologic model sensitivity analysis include porosity and permeability of the upper aquifer, boundary recharge rate, and fracture

flow rate. The remaining hydrologic model base case parameters (i.e., geologic structure, aquitard thickness, repository site location, lower aquifer permeability, and regional discharge site) are considered to be determinate values and were held constant.

A range of porosities from 1 to 20% was studied. A direct linear relationship exists between porosity and water travel time from the repository to the discharge site.

Fracture flow rate was studied by determining the maximum amount of flow that could move through the fracture and then determining the impact of this maximum flow rate on water travel time. The results indicate that a 63% increase in fracture flow rate (over the base case) results in only a 5% decrease in water travel time.

From the results, we can conclude that the influence of porosity, permeability, and boundary recharge on the water travel time is significant. Halving the porosity results in a decreased water travel time of 50%. Doubling this boundary recharge decreases water travel time by 43%. A twofold increase in permeability results in a similar decrease in water travel time. These influences are certainly significant because often the confidence limits on values of porosity, permeability, and boundary recharge can range by a factor of 10 or higher. The results regarding the fracture flow rate indicate that its influence on water travel time is minimal. No matter how wide or how permeable the fracture becomes, its flow rate is limited by how much water the lower aquifer can supply and the upper aquifer can accept.

Using the transport model, three parameters [the adsorption coefficient, (K_d), soil-to-solution ratio (β), and dispersivity] were studied. Their relationships to both peak concentration and time of peak concentration were determined. Because the

adsorption coefficient and the soil-to-solution ratio are inversely proportional, analysis was based on the retardation factor $(1 + BK_d)$.

Hydrologic model comparisons were made between the WISAP methodology and Sandia's (Intera Environmental Consultants) procedures for the WIPP Site Release Consequence Analysis. The comparisons were made for the high-permeability case (scenario 1). The transport model comparison was not completed because some additional data are still needed. The WISAP hydrologic model assessment agreed closely with the Sandia results when the same ground-water interpretations and release scenario were used.

Release consequence analysis for the salt dome repository was reoriented to provide the required input for the Preliminary Information Report (PIR). Additional meetings were held with BNI and Law to develop the conceptual model for the selected site (Hainesville Dome in East Texas) from available geologic and hydrologic data. BNI and Law provided ground-water potential maps, transmissivity distribution, aquifer top and bottom maps, and base maps/topographic maps. These maps were digitized and stored in matrix form on the data base. Area boundaries were selected, and the preliminary numerical hydrologic model was implemented.

The analytical solution for two-dimensional flow obtained in the first quarter was reduced to nomograph form for rapid, direct use as a hydrologic "front end" for the GETOUT transport code. It provides estimates for the steady flow paths and travel times for water and single trace constituents when data are limited. The results are expressed in terms of dimensionless grounds so they can concisely represent the large range of actual flow conditions described by the analytical solution.

Revision of the PATHS hydrologic model to consider three-dimensional problems continued, with extension of a previously solved three-dimensional line source to a circular rod-shaped source of finite length and radius. An additional analytical solution was obtained during the second quarter. The solution describes three-dimensional flow from a rectangular plant source into a deep aquifer with lateral flow. This solution was derived and expressed in terms of a special compact symmetrical form, which enhances and greatly simplifies the evaluation process. The possibility of expressing the characteristic pathline equations in this form is being carefully considered. If the compact expressions are obtained, it will simplify incorporating this three-dimensional PATHS formulation being provided for the line source solution.

Extension of the 3-D finite element (FE) hydrologic model was completed for coupled solution of flow, energy, and contaminant transport. The extended and revised ground-water model solves the partial differential equations describing single phase flow, energy transport by conduction and convection, and solute transport by diffusion and convection. The model is fully three-dimensional, to simulate large regional multi-layered basins.

The initial comparison of the extended 3-D FE model has been made with simple analytical cases. Work continued on revision and extensions of the MMT transport model code during this quarter. The discrete parcel random walk method of simulating convective-dispersive transport in hydrologic systems involving geologic interactions and transformations of multiple components (MMT-DPRW model) appears to be the most versatile and mathematically powerful method.

During this quarter, these specific advances were made in conceptualizing and implementing the program code for the 1-D MMT-DPRW model:

- An improved use of parcel statistics in describing system exit concentration as a function of time is achieved by keeping track of exact exit time for each nuclide parcel.
- Each nuclide is allowed to traverse the system with independent numbers of time steps (dispersion events).

The continuing work on the inverse problem centered during this quarter around the sample size (scale) problem associated with measuring the hydraulic conductivity distribution in heterogeneous ground-water systems. These factors are being studied using the experimental data set described last quarter. These data were further supplemented with a data set containing much larger changes in hydraulic conductivity.

The tentative conclusions regarding the significance of the dispersion term in the transport equation were reinforced:

- The smaller scale (experimentally verified) dispersivities have minor effects on the predicted final contaminant outflow rates to the environment. Accordingly, ignoring small-scale dispersion introduces little inaccuracy, and such evaluations always provided the worst case results.
- The large-scale dispersion parameters, when used in transport models, significantly reduce the predicted peak contaminant outflow rates. Hence they should not be used without justification.

The stochastic method of kriging, to measure the variance of subsurface flow variables and to be used in uncertainty analysis, is showing considerable promise in providing better, more credible consequence analysis. The expected ranges of variances

for ground-water potential data and hydraulic conductivity data are being obtained through kriging. Progress was sufficient to warrant procurement of BLUEPACK kriging computer code for installation at PNL, with half of the purchase cost borne by the WISAP program.

The CIRMIS data system was used to provide more detailed background maps and to digitize, store, and retrieve equipotential surface maps of the aquifers at the WIPP site.

Additional development was done on the graphic contouring programs to provide rapid plots in isopleth format. Programs were written to provide more versatility in creating, correcting, and plotting digitized background maps.

TASK 4 - SORPTION/DESORPTION ANALYSIS -

R. J. Serne and J. F. Relyea

Various laboratory methodologies are being evaluated using a wide range of geologic materials and nuclide-spiked waters. K_d values are being determined by each method, and evaluations are being performed on precision limitations and on ease of use. The effects of parameters such as particle size and geologic media, pH, Eh, salt composition of water, temperature, and nuclide concentration are being studied. Methods currently being used include static (batch K_d), axial filtration K_d , flow-through column (crushed media), and flow-through contact core (whole rock and fissures).

Acquisition of sorption-desorption data on a wide range of representative geologic materials with numerous ground-water types is a major goal of this task. To evaluate the influence of exchange and surface adsorption on the concentration of radionuclides in solution, empirical sorption distributions (e.g., K_d , retardation factors) of long-lived radionuclides for a large number of

geomedia types are being determined by the WISAP Task 4 subcontractors. Adsorption-desorption distribution is determined by reacting a known concentration of radionuclide with well characterized geomedia and then measuring the radionuclide concentration remaining in solution. These sorption distributions may also reflect the influence of mineral precipitation; however, this effect may be reduced by selecting lower tracer concentrations of the radionuclides. These data may not lend themselves to identifying adsorption mechanisms, but will provide empirical data required to assess migration from repositories. Additionally, equations will be derived to assess the effect of different factors (such as pH, Eh, geomedia type) on adsorption. These equations involve fitting a polynomial to the multidimensional curve that actually describes the sorption distribution.

To understand the reason for selecting a given K_d value for a given set of rock-water-nuclide conditions, many characteristics must be measured. A formal protocol and a coding form for reporting WISAP data have been transmitted to the subcontractors.

Rocks and ground waters appropriate for tuffs, shales, and granites at the Nevada Test Site and for basalt at Hanford are under study. Anhydrites, dolomites, and limestones of utility to bedded and domed salt analyses are also being used.

A quantitative prediction tool capable of estimating the migration rate of a nuclide for any given geologic material and water type is the ultimate objective of Task 4. The data generated, supplemented by literature values, will be quite large. With proper experimental design and media-water characterization, statistical methods can be used to relate the dependent variable (migration rate or K_d) to independent variables (e.g.,

rock type, solution type). Although the derived relationships do not prove causation, they do allow prediction of trends. Thus, from K_d data on a limited number of rock, mineral, and water types, estimates can be made of K_d data on a limited number of rock, mineral, and water types, estimates can be made of K_d values for other rocks and water environments not directly studied.

PNL personnel are responsible for installing all generated data onto a computerized information retrieval system and for coordinating the collation of all subcontractors' work into a set format for use by Adaptronics. Currently ongoing is the final installation of all subcontractor data from FY-1977 and FY-1978. The information retrieval system should be operational on the complete (through FY-1978) data base during the next quarter.

Adaptronics is performing Adaptive Learning Network (ALN), pattern recognition, regression, and correlation studies on the K_d data base supplied by PNL. Output from Adaptronics includes K_d predictor equations expressed as a function of properties of geologic media ground water, and radionuclides.

Short-term laboratory results are being extrapolated and compared with theoretical concepts, such as weathering, ore deposition geochemistry, mineral stability, thermodynamic Eh-pH diagrams, and thermodynamic chemical equilibrium computer codes. During this quarter, work concentrated on completing the installation of thermodynamic chemical equilibrium codes onto computers at Lawrence Livermore Laboratory (LLL) and at Lawrence Berkeley Laboratory (LBL) and on adding thermodynamic data on various nuclides to existing data files.

Several codes are being examined at present to allow cross-checks and to explore different calculational schemes. Test cases

will be used to assess which models have the most versatility and cost effectiveness. The best models will be used to evaluate thermodynamic equilibrium conditions for various hypothesized scenarios and to compare with experimental studies performed in other sub-tasks. The use of these computer models will allow rapid and cost-efficient scoping and validation studies to be performed on sorption-desorption aspects of the overall safety assessment.

Efforts continued to investigate the basic factors and their interactions that control the sorption-desorption by geologic media of actinides, long-lived fission products, and activation products.

Studies are under way at PNL to determine the valence state distribution versus time of plutonium in solution above PuO_2 and plutonium hydroxide solids. These experiments have been ongoing for a year. Early analyses showed Pu(V) to be the predominant species in solution. Preliminary results on the adsorption of Pu(VI) by an acidic sandy soil show high adsorption, apparently resulting from reduction of plutonium by the soil surfaces.

The mobility of nuclide tracers in simulated ground waters is being compared with the mobility of nuclides in actual waste form leachate. Preliminary results reported last quarter on cesium indicated that there are differences caused by particulates formed during waste form leaching. Results obtained

this quarter do not support this conclusion, perhaps because of differences in the amount of cesium present. As noted by Oak Ridge National Laboratory (ORNL), cesium sorption on clay is unusually sensitive to mass loading effects.

Studies on redox sensitivity being performed at ORNL show that under anoxic conditions Np, U, Pu, and Tc may be strongly adsorbed. The mass dependent, time dependent, ferrous-ferric ratio and rock type effects are under study.

Autoradiography techniques are being refined in an attempt to produce an analytical tool capable of identifying individual sorption sites within the rock matrix.

Particle transport studies at Georgia Tech continued. The effect of solution composition on particle migration was studied this quarter.

Outcrop samples from the vicinity of Gulf Coast salt domes were obtained. The samples were dried and crushed to below 20 mesh. Samples were distributed for total chemical analyses, mineralogy, surface area, and cation exchange capacity determinations.

Recipes for two ground waters were developed after consultation with ONWI sub-contractors responsible for salt dome work. These outcrop samples and other generic materials may be used to develop a K_d data base for the PIR.

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J. R. Raymond, chairman, Workshop on Transport Modeling for Safety Assessment Program on Nuclear Waste Isolation, PNL-SA-7468, Pacific Northwest Laboratory, July 25-26, 1977.

B. D. Melber, Understanding Public Perspectives on Nuclear Power and Alternative Energy Options, PNL-SA-7906, American Psychological Association Annual Convention, Ontario, Canada, August 1978.

J. A. Hébert, Anticipating Conflicts in Technological Policy: The Case of Nuclear Waste, PNL-SA-7169, American Psychological Association Annual Convention, Ontario, Canada, August 1978.

S. M. Nealey, Mapping the Public Policy Issues in Nuclear Waste Management, PNL-SA-7170, American Psychological Association Annual Convention, Ontario, Canada, August 1978.

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J. E. Rasmussen, Implications of Social Science Research for Contemporary Energy Policy, PNL-SA-7172, American Psychological Association Annual Convention, Ontario, Canada, August 1978.

D. B. Shippler, J. R. Raymond and P. F. Gnirk, Analysis of Migration Pathways for Geologic Radioactive Waste Repositories, Energy Symposium Sponsored by the U.S. Department of Energy, Washington, DC, October 1978.

10.0 WELL-LOGGING INSTRUMENTATION DEVELOPMENT FOR SHALLOW LAND BURIAL

R. L. Brodzinski - Project Manager

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

SUMMARY

Laboratory experiments were completed for evaluation of a Phoswich-type detector system toward determination of ^{90}Sr from boreholes and cased wells.

A concept involving conversion of water and water vapor to gaseous tritium is being considered as a technique for the in situ well-logging determination of tritium.

Calibrations with the passive neutron detection technique for the determination of actinides were completed.

Three open literature publications describing technology developed in this program were prepared.

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

Experiments were completed to evaluate the applicability of a Phoswich-type detector system to the well-logging determination of ^{90}Sr . Laboratory calibrations with pure standards of ^{90}Sr and mixed standards of ^{90}Sr and typical interfering gamma-ray emitting radionuclides were conducted to obtain sensitivity and detection limit data for this technique. In addition, data were accumulated as a function of well-casing

material and thickness to determine system sensitivities as a function of well construction. This is necessary to define the range of applicability of this logging technique for comparison with the bremsstrahlung detection technique developed earlier. The results of these experiments are currently being evaluated.

An open literature publication entitled "A Well-Logging Technique for the In Situ Determination of ^{90}Sr " by R. L. Brodzinski and H. L. Nielson has been prepared.

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

Various methods for in situ well-logging sampling and analysis of tritium continue to be evaluated for their technical viability, reliability, selectivity, and potential costs. A concept involving the reactive metal reduction of water and water vapor to elemental hydrogen (tritium) is being considered. In this system, the gaseous tritium would be separated and purified by a chemical train and then blended with a suitable counting gas for proportional scintillation spectrometric analysis. A continuous flow, gas proportional counter that would provide tritium analyses on a real time basis is envisioned.

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

Calibrations with the passive neutron detection technique for the determination of actinides were completed. This technique provides a method for quantitative analysis of transuranic activities even in extremely high gamma radiation fields and serves as the basis for a real-time logging system that utilizes neutron detection for determination of actinides. The procedure involves the exposure of metal forms in the wells. Subsequent determination of the neutron-induced activation products in these metals allows the transuranic content of the system to be determined. The primary reactions utilized in this work are:

- 1) $^{63}\text{Cu}(n,\gamma)^{64}\text{Cu}$,
- 2) $^{64}\text{Zn}(n,p)^{64}\text{Cu}$,
- 3) $^{24}\text{Mg}(n,p)^{24}\text{Na}$.

Reactions in titanium, nickel, indium, and cadmium covered metals have also been investigated but have shown no particular advantages.

A detailed description of the theory behind this technique, including the rationale for choosing these particular nuclear reactions as monitors and the calibration techniques employed, has been given elsewhere⁽¹⁾ and will not be repeated here. Reaction 1) (copper) has a $1/v$ capture response and is primarily sensitive to thermal neutrons. Reaction 2) (zinc) has a practical threshold of 2.3 MeV and is thus sensitive to neutrons produced by (α,n) or spontaneous fission reactions that have not undergone appreciable moderation. Reaction 3) (magnesium) has a threshold of 6.2 MeV and provides a measure of only those high-energy neutrons produced in the spontaneous fission process which are above this threshold energy. This reaction

is insensitive to (α,n) neutrons produced in matrices containing oxygen or fluorine--the light elements commonly accompanying transuranics in the nuclear industry. The flux and energy distribution of neutrons emitted by any system can be determined utilizing a combination of these three reactions, and this information in turn can be related to the chemical and isotopic composition of the transuranic content, assuming appropriate calibration data is available. This report presents the results of calibrations performed in matrices of sand, sediments, salt cake, water, and typical dry wastes. The isotopic compositions of the various transuranic sources used in these calibrations are given in Table 10.1.

The thermal neutron flux, as monitored with the copper reaction, can be easily calculated utilizing capture cross sections and standard equations of radioactive growth and decay. The zinc and magnesium reactions are slightly more complex since the (n,p) cross sections vary as a function of the neutron energy. Hence, the integrated product of the neutron flux and cross section, which is simply the reaction rate, is used for these reactions. Calibrations are performed by exposing the metals to known transuranic sources in geometric configurations similar to the field systems to be analyzed. In the case of homogeneous matrices, the flux or reaction rate is determined through known amounts of the material using a point source of transuranic activity. The bulk matrix material is then mathematically divided into concentric spherical shells, and the total flux (reaction rate) is normalized to unit concentration of transuranic activity in each shell and summed over all significant shells. Details of this calibration technique and verification of its accuracy are given elsewhere.⁽¹⁾ Typical

TABLE 10.1. Chemical and Percent Isotopic Composition of Transuranic Sources

<u>PuF₄</u>	<u>PuO₂</u>	<u>PuO₂</u>	<u>PuO₂</u>	<u>Am₂O₃</u>	<u>Cm₂O₃</u>
	²³⁸ Pu-0.021	²³⁸ Pu-0.256	²³⁸ Pu-0.588		
²³⁹ Pu-90.80	²³⁹ Pu-93.998	²³⁹ Pu-78.989	²³⁹ Pu-72.659		
²⁴⁰ Pu-8.84	²⁴⁰ Pu-5.691	²⁴⁰ Pu-16.789	²⁴⁰ Pu-19.373		
²⁴¹ Pu-0.35	²⁴¹ Pu-0.269	²⁴¹ Pu-3.079	²⁴¹ Pu-5.472		
	²⁴² Pu-0.021	²⁴² Pu-0.887	²⁴² Pu-1.907		
²⁴¹ Am-0.153	²⁴¹ Am-0.056	²⁴¹ Am-0.467	²⁴¹ Am-0.866	²⁴¹ Am-0.169	
				²⁴³ Am-99.23	
				²⁴⁴ Cm-0.6	²⁴⁴ Cm-91

flux measurements are shown in Figures 10.1-10.3 as a function of distance through sediments at different moisture levels. These curves represent data from a plutonium oxide (19.373Δ ²⁴⁰Pu) source but are typical of the shape obtained with all sources.

Serious consideration must be given to the definition of unit activity for normalization purposes. Neutrons producing reactions in the copper and zinc monitors come from two different sources, i.e., from (α ,n) and from spontaneous fission (sf) reactions. If the neutrons are considered to arise from only the alpha activity, serious disparities will arise between plutonium sources of different isotopic composition. Similarly, spontaneous fission activity cannot be considered as the only normalizing factor because (α ,n) contributions to the neutron flux are far from negligible. Furthermore, the relative contributions from (α ,n) and sf neutrons are different for the copper and zinc reactions. Obviously, since only sf neutrons contribute to reactions in the magnesium monitor, the (α ,n) component need not be considered in this

case. However, the magnesium reaction rate should change for various spontaneously fissioning isotopes by virtue of the differences in neutron yield per sf event and in the sf neutron energy spectra. Thus, at first glance, it appears hopeless that any common normalizing factor can be found. In actual practice, however, the differences in neutron yields and energy from the spontaneously fissioning isotopes investigated here are too subtle to be detected within the limits of experimental error, and neutrons can be assumed to come from only two sources, either (α ,n) reactions or spontaneous fission, regardless of the isotopes or alpha decay energy.

The relative contributions to the thermal flux and the zinc reaction rate were determined experimentally for the (α ,n) and sf neutron production methods from oxide and fluoride sources. A neutron yield coefficient was determined for each production process, and an (α ,n) equivalent activity which represents the calibration source as if no spontaneously fissioning isotopes were

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FIGURE 10.1. Thermal Neutron Flux from a Point Source of Plutonium Oxide Measured Through Various Thicknesses of Soil Having Different Moisture Contents

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FIGURE 10.2. $^{64}\text{Zn}(n,p)^{64}\text{Cu}$ Reaction Rate from Neutrons Generated by a Point Source of Plutonium Oxide Measured Through Various Thicknesses of Soil Having Different Moisture Contents

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FIGURE 10.3. $^{24}\text{Mg}(n,p)^{24}\text{Na}$ Reaction Rate from Neutrons Generated by a Point Source of Plutonium Oxide Measured Through Various Thicknesses of Soil Having Different Moisture Contents

present was generated for normalizing purposes. These experimental neutron yield coefficients are given in Table 10.2.

Calibration factors for each monitor reaction are given in Table 10.3 for different sediment moisture contents. The normalizing activities for the copper and zinc reactions are the (α ,n) equivalents described above.

The data in Tables 10.2 and 10.3 show that information regarding both the chemical and

isotopic composition of an unknown matrix can be obtained by employing these three neutron monitors. The total quantity of spontaneously fissioning activity is obtained directly from the magnesium reaction. A prior knowledge of the original source of the transuranics might often yield the isotopic composition directly. In lieu of any such knowledge, the total alpha activity of the system can also be determined by utilizing either the copper or zinc monitor, assuming

TABLE 10.2. Relative Neutron Yield Coefficients for Transuranics in Sediments

Source Term	$^{63}\text{Cu}(n,\gamma)^{64}\text{Cu}$ Reaction Thermal Flux, $\text{n cm}^{-2} \text{ sec}^{-1}$	$^{64}\text{Zn}(n,p)^{64}\text{Cu}$ Reaction Reaction Rate, $\text{g}^{-1} \text{ sec}^{-1}$
(α ,n) on fluorine	$2.62 \cdot 10^{-3} / \text{nCi } \alpha \text{ cm}^{-3}$	$5.31 \cdot 10^{-8} / \text{nCi } \alpha \text{ cm}^{-3}$
(α ,n) on oxygen	$3.68 \cdot 10^{-5} / \text{nCi } \alpha \text{ cm}^{-3}$	$5.38 \cdot 10^{-9} / \text{nCi } \alpha \text{ cm}^{-3}$
Spontaneous fission	$1.71 \cdot 10^3 / \text{nCi sf cm}^{-3}$	$2.99 \cdot 10^{-1} / \text{nCi sf cm}^{-3}$

TABLE 10.3. Neutron Reactions in Metal Monitors for Transuranic Sources in Hanford Sediments

H ₂ O Content, %	Source	$^{63}\text{Cu}(n,\gamma)^{64}\text{Cu}$, $\text{n cm}^{-2} \text{ sec}^{-1} / \text{nCi}^* \text{ cm}^{-3}$	$^{64}\text{Zn}(n,p)^{64}\text{Cu}$, $\text{g}^{-1} \text{ sec}^{-1} / \text{nCi}^* \text{ cm}^{-3}$	$^{24}\text{Mg}(n,p)^{24}\text{Na}$, $\text{g}^{-1} \text{ sec}^{-1} / \text{nCi sf cm}^{-3}$
1.1	Fluoride	$(2.28 \pm 0.29) \cdot 10^{-3}$	$(5.17 \pm 0.61) \cdot 10^{-8}$	
1.1	Oxide	$(3.67 \pm 0.39) \cdot 10^{-5}$	$(6.15 \pm 0.76) \cdot 10^{-9}$	$(6.39 \pm 0.13) \cdot 10^{-2}$
8.0	Fluoride	$(2.62 \pm 0.25) \cdot 10^{-3}$	$(5.31 \pm 0.55) \cdot 10^{-8}$	
8.0	Oxide	$(4.46 \pm 0.68) \cdot 10^{-5}$	$(9.0 \pm 1.0) \cdot 10^{-9}$	$(6.2 \pm 2.7) \cdot 10^{-2}$
16	Fluoride		$(4.46 \pm 0.63) \cdot 10^{-8}$	
16	Oxide	$(4.13 \pm 0.79) \cdot 10^{-5}$	$(5.66 \pm 0.30) \cdot 10^{-9}$	$(6.1 \pm 1.1) \cdot 10^{-2}$
42	Oxide	$(2.498 \pm 0.090) \cdot 10^{-5}$	$(2.48 \pm 0.33) \cdot 10^{-9}$	$(3.6 \pm 1.2) \cdot 10^{-2}$
100	Oxide	$(1.105 \pm 0.027) \cdot 10^{-5}$	$(1.64 \pm 0.16) \cdot 10^{-9}$	$(3.6 \pm 1.4) \cdot 10^{-2}$

nCi* = Equivalent alpha activity if all neutrons were from (α ,n) reactions.

the chemical composition of the system is known. Conversely, if the isotopics can be deduced by measuring only the sf neutrons, the chemical composition can be determined from measurements of the (α ,n) neutrons with the copper or zinc monitors. In actual practice, the chemistry will usually be dominated by a single light isotope. For example, unless the fluoride content of a matrix is high enough that the alpha particles have a reasonable probability of striking a fluorine nucleus relative to the probability of striking an oxygen nucleus, a transuranic fluoride dispersed in an oxide matrix will behave like a transuranic oxide.

The calibration factors for the three monitor reactions are plotted as a function of moisture content of the sediments in Figures 10.4-10.6 for transuranic oxides. Only relatively minor changes occur in the normal range of moisture values, and the calibration factors are essentially constant. These same curves can be used for transuranic fluorides in sediments of normal moisture values (with the proviso regarding fluorine concentration mentioned earlier) simply by multiplying the data in Figure 10.4 by a factor of 60 and in Figure 10.5 by a factor of 7.4. These factors were obtained by calibrations with transuranic fluoride sources. The data in Figure 10.6 are independent of chemical composition. Similarly, the calibration curves can be made to represent different matrices by multiplying them by the appropriate experimentally determined constant listed in Table 10.4. Both chemical species and matrix material changes can be obtained by multiplying by the product of the conversion coefficients. For matrix materials, geometries, or chemical speciation different from those listed here, a little intuitive logic can be used to obtain a conversion coefficient that will yield "ballpark"

concentrations. More accurate results can be obtained with a few simple "cross calibration" experiments.

This technique has a practical detection limit of less than 10 nCi/g for most field situations. Greater sensitivity can be obtained by using ^3He or $^{10}\text{BF}_3$ proportional counters for monitoring the neutron flux, but these electronic systems will operate only in gamma radiation fields of ≤ 20 R/hr without sacrificing sensitivity, and are primarily sensitive to thermal neutrons. Therefore, neutron energy analysis is difficult, and hence isotopic or chemical composition cannot be determined. The gas proportional counters are more suitable, however, for real-time logging operations, and a logging system will be developed on these principles to complement the metal activation technique described here.

Although the data shown in Figures 10.4-10.6 indicate only minimal dependence on the moisture content of the system at $\leq 16\%$ H_2O , certain shallow land burial monitoring operations may be required in systems of potentially higher moisture content. Often the moisture level of these systems can be determined with a commercial neutron moisture probe. However, it may occasionally become necessary to measure the moisture in a system that cannot be monitored with a commercial neutron probe because of physical constraints or interfering gamma or neutron radiations. Neutron proportional counters cease to be reliable in gamma radiation environments exceeding about 20 R/hr. In the case of systems containing transuranic activities, neutrons generated either by (α ,n) reactions on light isotopes or by spontaneously fissioning isotopes create a "background" which, if uncorrected, results in erroneously high moisture readings. The following simple technique for determining the moisture content of any system, including those containing extreme

FIGURE 10.4.
Thermal Neutron Flux
Generation by Trans-
uranic Oxides Homo-
geneously Distribu-
ted in Sediments as
a Function of
Moisture Content

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FIGURE 10.5.
 ${}^{64}\text{Zn}(n,p){}^{64}\text{Cu}$ Reac-
tion Rate Generation
by Transuranic Ox-
ides Homogeneously
Distributed in Sedi-
ments as a Function
of Moisture Content

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FIGURE 10.6.
 ${}^{24}\text{Mg}(n,p){}^{24}\text{Na}$ Reac-
tion Rate Generation
by Transuranic Ox-
ides Homogeneously
Distributed in Sedi-
ments as a Function
of Moisture Content

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TABLE 10.4. Conversion Coefficients for Calibration Curves in Figures 10.4-10.6

To Convert:	To:	Multiply By:
Figure 10.4	Fluorides in sediments	60
Figure 10.5	Fluorides in sediments	7.4
Figures 10.4-10.6	Oxides in dry wastes	1.4
	Oxides in salt cake	1.2
	Oxides in pure sand	5-6

levels of gamma radiation or transuranic activities, has been developed to make possible the choice of appropriate calibration data for determining the transuranic content.

A small, fast neutron source, such as $^{238}\text{PuBe}$, $^{239}\text{PuBe}$, $^{241}\text{AmBe}$, or ^{252}Cf , is coupled to a metal form and exposed in the matrix to be analyzed. After removal from the system, the metal is analyzed for the thermal neutron-induced activation products generated in it. The neutron flux, which is proportional to the moisture content, is calculated from cross section data and standard equations of radioactive growth and decay.

In practice, a metal is chosen which is inexpensive, easily machinable, and which has a relatively high thermal neutron activation cross section that results in a radioactive product with decay characteristics which enhance its measurement sensitivity. Copper and indium are two such metals. Ordinarily, taping the fast neutron source to the metal is satisfactory. The neutron source and metal detector are exposed in the matrix for a time sufficient to generate an easily measurable quantity of activation products. This time period is dependent on the neutron source strength, the mass of metal, the moisture content of the system, and other parameters. Typical exposures with copper detectors and small PuBe sources are about 1 to 3 hr. Less time would be required with indium detectors. Following exposure, the source and detector are separated, and the activation products in the metal are determined by gamma-ray spectroscopy. Equal exposure and counting

periods are most efficient. The moisture content of the unknown matrix is obtained from appropriate calibration data.

Before calculating the thermal neutron flux, it is necessary to correct the data for extraneously induced activation products. First, the normal background level in the metal, a low level of activity generated by the cosmic-ray neutron flux, should be subtracted from the quantity of activation products measured. Secondly, in certain field conditions, particularly if transuranic elements are present, the neutron flux generated by spontaneous fission or (α, n) reactions may be sufficiently high to sustain a non-negligible activation product concentration in the metal detector. Finally, the fast neutron source will generate some activation products in the monitor in the absence of any moderating medium, which must also be subtracted. In theory, this baseline factor should be determined in outer space to avoid backscattering from surrounding materials. In practice, an exposure with the source/detector system suspended in the middle of a large room is adequate. This "air" background is a constant for any given source and detector combination, and for the PuBe sources on copper detectors used here, amounts to about 1% of the thermal neutron flux measured in a water environment and about 16% of that in completely dry sediments.

Typical calibration curves for Hanford sediments are shown in Figures 10.7 and 10.8 using $^{238}\text{PuBe}$ and $^{239}\text{PuBe}$ neutron sources

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FIGURE 10.7. Thermal Neutron Flux Generated by a 4.6 mg $^{238}\text{PuBe}$ Source in Sediments as a Function of Moisture Content

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FIGURE 10.8. Thermal Neutron Flux Generated by a 1.2 g $^{239}\text{PuBe}$ Source in Sediments as a Function of Moisture Content

and copper detectors. These curves have virtually identical shapes, and similar curves are obtained in other matrices or with other fast neutron sources. A single cross calibration is usually adequate to establish the calibration curve for a new matrix and/or a new neutron source.

The inherent accuracy of this technique for determining moisture is the same as that for commercial neutron probes. Errors are introduced by uncertainties in the calibration standards, background and baseline determinations, and measurements of the neutron activation products. Counting and

exposure times required to maintain a total uncertainty no greater than $\pm 10\%$ for copper detectors with a 4.6 mg $^{238}\text{PuBe}$ fast neutron source are given in Figure 10.9 for different matrices. The dose rate from this neutron source is 2 mR/hr at contact, and a much larger source could easily be used to reduce the time requirement.

Thermal neutron activation of a metal detector has several advantages over conventional methods for determining the moisture content of a system. First, the metal detectors can be fabricated in virtually any configuration that will facilitate access to

remote locations. Secondly, the method will operate in extreme gamma radiation environments. Finally, the technique can be used in systems containing transuranic elements by making measurements with and without the fast neutron source.

Two open literature publications based on this work, "A Technique for the In Situ Determination of Transuranic Elements in Relatively Inaccessible Locations" and "A Technique for In Situ Moisture Level Determinations in Relatively Inaccessible Matrices," by R. L. Brodzinski, have been prepared.

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FIGURE 10.9. Count and Exposure Time Requirements to Obtain Total Uncertainty $\leq 10\%$ for a 4.6 mg $^{238}\text{PuBe}$ Source on Copper Detectors in Sediments of Various Moisture Content

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11.0 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 of contaminants from disposal sites for low-level solid wastes.

SUMMARY

Laboratory tests of radionuclide transport in unsaturated soil columns were continued. Cobalt, technetium, tritium, strontium, and iodine were tested for mobility in Hanford sediments. The distribution coefficient of iodine was found to be a function of concentration. Batch distribution coefficient was found to be less accurate (>100 relative error) than column analysis for iodine and cobalt complexed with EDTA.

Physical models consisting of bench-scale 208-l steel drums were constructed and used to evaluate field radionuclide transport resulting from simulated precipitation. Downwell monitoring devices were designed, built, and tested on these models before their field use.

Construction of a field test site has been completed. This site is located adjacent to a retired radwaste burial site and is used to monitor atmospheric and soil conditions capable of inducing the transport of radionuclides from burial sites. Data from instruments installed within this site are being collected and analyzed.

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

The flow of water and radionuclides and sorption of radionuclides within partially

saturated geohydrologic media is an important consideration to radioactive waste burial. In order to quantify water flow and radionuclide migration from shallow land waste burial arid sites, tests to determine water flux, retardation, and distribution coefficients (K_d 's) are being conducted. K_d analysis of cobalt, tritium, iodine, technetium, and strontium in two different salt solutions have been analyzed and reported.^(1,2)

Unsaturated column tests with Hanford soil materials were conducted using ^{125}I as a pulsed tracer at several ion concentration levels. The data from the pulsed column studies indicate that the inhibition of tracer breakthrough is a function of the concentration of ^{125}I in the pulse and is also time-dependent. Figure 11.1 compares the amount of ^{125}I retained with time, after column flow started, with the amount of Co-EDTA and tritium retained in the same soil columns. Pulsed volumes were slightly different for each run (data point) for each tracer, but the comparisons indicate that for ^{125}I in all cases, under all treatments, significant amounts of ^{125}I were retained on the soil. In contrast, Co-EDTA and tritium were flushed through the column, and virtually 100% of the applied tracer was recovered (nearly 0% retained on the column). The amount of ^{125}I retained on the column

FIGURE 11.1. Isotope Retained in Unsaturated Columns of Soil B as a Function of Time

was influenced by tracer concentration and possibly by microbial inhibition. After 4 days the amount of ^{125}I retained in Soil B at 20 ppb + phenol, 20 ppb - no phenol, and <1 ppb - no phenol was 16, 24, and 44%, respectively (Table 11.1). The influence of concentration level suggested that further testing of iodine would be necessary to evaluate the influence of concentration on K_d . Batch K_d tests were run at several iodine levels for both Soil A and B materials. All tests were run in triplicate. The data indicated that increased tracer concentration produced significant decreases in the measured K_d 's. For Soil B the K_d values ranged from 2.8 at the lowest concentration (<1 ppb) to 0.08 at the highest concentration (100 ppb). There was a general trend for lower K_d values with the high salt concentration with Soil B. Soil A exhibited K_d 's not significantly different from those of Soil B (although the precision was considerably better at the <1 ppb level for ^{125}I).

Batch testing produced K_d values generally within $\pm 0.5 \text{ mg/l}$. At low absolute K_d (near zero) this precision produces high rela-

tive error (>100%). It is likely that batch K_d determinations cannot be used to resolve differences in transport of mobile tracers. Column studies yield greater precision for mobile tracer tests. However, the concentration level of the tracer is important, particularly for isotopes like iodine and perhaps other halogens.

PHYSICAL MODELING - G. W. Gee and K. O. Schwarzmiller

Physical models were used to conduct and evaluate accelerated testing of migration of radionuclides in soil columns. Data from the laboratory task of this project were used to design bench-scale columns tests in 208-l steel caissons. Soils of known unsaturated conductivity and distribution coefficients were placed in caissons with cobalt-EDTA and leached with water. The leachate was collected and radiochemically analyzed. Simultaneously the concentration of cobalt-EDTA in the caisson was monitored with a sodium iodide detector and a neutron moisture meter. Collectively the data was used to determine

TABLE 11.1. Batch K_d Data for Tritium and ^{125}I Under Specified Salt and pH Conditions. Equilibration time was 7 days.

Isotope	Solution ^(a)	Soil A		Soil B	
		K_d ml/g	pH	K_d ml/g	pH
Tritium	High salt	-0.103 ± 0.346	8.6	0.086 ± 0.260	8.1
	Low salt	-0.119 ± 0.708	8.9	0.351 ± 0.540	8.4
<u>Iodine</u>					
^{125}I (<1 ppb I^-)	High salt	0.921 ± 0.344	8.5	—	—
	Low salt	0.163 ± 0.486	8.9	—	—
^{125}I (<1 ppb I plus 1 Phenol)	High salt	—	—	2.482 ± 0.282	7.7
	Low salt	—	—	2.794 ± 0.213	8.2
^{125}I (20 ppb I^-)	High salt	—	—	0.782 ± 0.582	8.0
^{125}I (100 ppb I^-)	High salt	-0.201 ± 0.076	8.4	0.535 ± 0.432	8.0
	Low salt	0.675 ± 0.346	8.7	0.497 ± 0.231	8.4
^{125}I (100 ppb I^- plus ^{60}Co -EDTA)	High salt	—	—	0.077 ± 0.374	7.9
<u>Cobalt</u>					
^{60}Co -EDTA plus PPB I^-	High salt	—	—	3.647 ± 0.465	—

(a) High salt — 0.15 M NaNO_3 , 0.15 M KNO_3 , and 0.01 M $\text{Ca}(\text{NO}_3)_2$.

Low salt — 0.15 M NaNO_3 , 0.01 M KNO_3 , and 0.002 M $\text{Ca}(\text{NO}_3)_2$.

the transport of leaching solution and the radionuclide. Conducting analytical experiments on these physical models also provided evaluation and sophistication of techniques used to monitor, in situ, actively transported gamma-emitting radionuclides. This test was then used for experimental decision of field radionuclide migration tests which are currently being initiated.

FIELD MONITORING — M. D. Campbell, G. W. Gee, and S. J. Phillips

Characterizing and monitoring shallow land radioactive waste burial sites requires in

situ installation and operation of sensors capable of measuring radionuclide migration and environmental parameters. Construction of a field test site has been completed and instruments installed which can monitor mass and energy balance variables. These parameters control the rate and magnitude of water and radionuclide transport at radwaste burial sites. Figure 11.2 schematically illustrates the field site as it now exists. Figure 11.3 is a photograph of the ground surface after installation of the facility. One half of the site consists of one large buried caisson containing soil, two smaller

FIGURE 11.2. Schematic of Buried Waste Test Facility

FIGURE 11.3. Ground Surface After Installation

caissons containing soil and radionuclides (cobalt-EDTA and tritium), and one weighing lysimeter is located to the right of the illustration. This half of the site is used to monitor ambient conditions. The other half of the site consists of the same configuration except that it monitors the effect of increased precipitation. Increased precipitation is added to the site by a large irrigation system. By monitoring both sides of the site with similar sensors, comparisons of radionuclide transport under standard and accelerated conditions are made.

Instruments were recently added to the weighing lysimeter which receives increased precipitation. Figure 11.4 schematically illustrates the instruments located within

WIEGHING LYSIMETER NUMBER 2

FIGURE 11.4. Schematic of Instruments Within Lysimeter

the lysimeter. Tensiometers were installed to measure the matrix potential of the soil within the lysimeter. Filter candles were installed near the bottom of the lysimeter to control the moisture content of the soil. The negative pressure of these filter candles can be regulated to control the rate of migration of fluid through the lysimeter. Heat dissipation units were installed to monitor the thermal and soil water potential

within the lysimeter. Thermocouples were also included which monitor the soil temperature with depth.

Currently over 1000 data points are automatically collected on a daily basis and over 100 data points are manually collected on a weekly basis. The data are being compiled and analyzed to be used to provide an efficient monitoring system at arid burial sites.

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12.0 DETECTION AND CHARACTERIZATION OF MOBILE ORGANIC COMPLEXES OF FISSION PROJECTS

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 the storage of low-level waste in shallow land burial facilities.

SUMMARY

During this quarter experimental efforts were hampered by a manpower shortage, but a concentrated search was made of literature on TcO_4^- and its reaction (in lower oxidation states) with organic type ligands. The search was directed chiefly toward 1) preparation of Tc-organic complexes in the IV and V oxidation states, 2) separation of these oxidation states when both states are present, and 3) characterization of these Tc-organic complexes. Some of the Tc-organic complexes that will be examined are: citrate complexes where the IV, V and III oxidation states have been observed; diarsine complexes where the V oxidation state is unique to the reaction; EDTA and DTPA complexes; and possibly some thiocyanate complexes. Chromatographic techniques (gel permeation, ion exchange and electrophoresis) will be employed to separate mixed oxidation state products. NMR, ESR, and UV and IR spectroscopy, as well as electrophoresis, will be used in the characterization.

Experimental efforts will continue with the examination of niobium EDTA and DTPA complexes.

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

Experimental efforts were hampered this quarter by manpower curtailment; however, a more detailed literature search has been conducted. It focuses on techniques for preparing, separating, and characterizing technetium (IV and V) organic complexes. This search is part of an effort to better understand how the technetium organic complex, in a specific oxidation state, interacts with the soil.

Based on the recently extended literature search, the following technetium organic complexes will be examined:

1. Citrate complexes - Münze has reported the preparation of Tc(IV, V and III) complexes.⁽¹⁻³⁾ He has proposed that the Tc(IV) citrate complex can exist in either of two polymeric forms, depending on the Tc/citrate ratio. These polymeric forms are presented in Figure 12.1. When the Tc/citrate ratio is 1:1, the sole product is a brown monocationic high-molecular-weight polymer

a) $\left[\text{Tc}(\text{OH})_3 \text{cit} \right]_n^{2-}$ - HIGH MOLECULAR WT POLYMER

b) $\left[\text{Tc}(\text{O})\text{cit}_2 \right]_n^{6-}$

c) $\left[\text{Tc}(\text{OH})_2 \text{cit}_2 \right]^{6-}$

FIGURE 12.1. Proposed Structures for Polymeric and Monomeric Tc(IV) Citrate Complexes

As the Tc/citrate ratio decreases, a purple lower-molecular-weight polymeric dicitrate complex is also reported to be formed; however, when the Tc/citrate ratio is 1:100, only the lower-molecular-weight polymer is present as $[\text{Tc}(\text{OH})_2(\text{cit H}_2)_n]^{4-}$; this reacts with water to yield the monomeric (IV) dicitrate complex $[\text{Tc}(\text{OH})_2 \text{ cit}_2]^{6-}$.

Tc(V) dicitrate present as $[\text{TcO}_2 \text{ cit}_2]^{6-}$ is prepared when TcO_4 is reduced by Sn(II) in the presence of citrate.⁽²⁾ Unfortunately, the V oxidation state is not the sole product of the reduction; the IV oxidation state is also observed.

Münze⁽³⁾ has reported that a Tc(III) dicitrate complex is formed upon further reduction of the Tc(IV) dicitrate complex with Sn(II).

2. Tc(V) diarsine complex - Fergusson and Nyholm⁽⁴⁾ have prepared $[\text{Tc} \text{ diarsine Cl}_4] \text{ Cl}$ where diarsine = O^- phenylene bisdimethyl arsine

The V oxidation state is unique to the reaction.

3. EDTA and DTPA complexes - Work will continue in further examining Tc com-

plexes of these ligands. Although the IV oxidation state seems to be common for these types of complexes,⁽⁵⁾ the III oxidation state has also been observed for the DTPA complex.⁽⁶⁾ The V oxidation state has not been reported for these complexes. The possibility of preparing the Tc(V) complexes with these ligands will be examined.

4. Tc(IV,V) thiocyanate - $\text{Tc}(\text{SCN})_6$ (red complex) and $\text{Tc}(\text{SCN})_6^{2-}$ (yellow complex) have been prepared in solution by Crouthamel.⁽⁷⁾ More recent literature indicates that these species can be isolated as solids when mixed with quaternary ammonium salts such as $(\text{CH}_3)_4\text{NCl}$.^(8,9) This should facilitate both the isolation and characterization of the complexes in the individual oxidation states.

Methods such as NMR, ESR, UV and IR spectroscopy and electrophoresis will be utilized to characterize technetium in these complexes. Gel permeation chromatography and ion exchange will be used to separate multiple oxidation states.

Necessary chemical reagents have been ordered, and experimental work will commence shortly.

Niobium salts have been ordered so that efforts can continue in the preparation and examination of DTPA and EDTA type complexes.

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13.0 ELECTROPOLISHING FOR SURFACE
DECONTAMINATION OF METALS

R. P. Allen and H. W. Arrowsmith - Project Managers

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

SUMMARY

The effectiveness of both electropolishing and vibratory finishing as decontamination techniques for TRU-contaminated surfaces was further demonstrated by the decontamination of more than 500 ft² of plutonium-contaminated metallic waste to well below the 10 nCi/g limit. This work also verified the effectiveness of vibratory finishing as a pretreatment technique to prepare metal surfaces for final decontamination by electropolishing. Substantial savings in decontamination time and labor can be realized for material that has been pretreated by vibratory finishing as compared with material pretreated using chemical and mechanical methods.

In addition, the ability of vibratory finishing to decontaminate a variety of non-metallic materials to below the 10 nCi/g limit was demonstrated by the reduction of plutonium contamination to nondetectable levels for representative samples of Plexiglas®, Neoprene® gasket material, and Hypalon® glove box gloves. This means that essentially all major components of a typical plutonium glove box (metal structure, plastic panels, rubber gaskets, and gloves) can be converted into non-TRU waste by using vibratory finishing techniques.

Studies also were conducted to evaluate liquid honing as a possible pretreatment method. The high-pressure, liquid-abrasive spray was effective in cleaning and removing gross contamination from metal and rubber surfaces and also threaded areas and holes. However, containment of the dispersed contamination was a major problem.

Solution treatment studies are in progress to develop purification methods for the electrolyte and rinse/pretreatment solutions to minimize generation of secondary waste from the decontamination process. The results of reciprocating acid adsorption purification tests for phosphoric acid electrolytes containing dissolved stainless steel show that the iron and chromium can be removed and recovered as a metal-phosphate precipitate. A dual-effect evaporator system that will be used for purification/recycle studies of the rinse and pretreatment solutions was installed and cold tested, demonstrating its ability to process up to 60 gal of water per hour. A direct caustic neutralization procedure also was developed that converts the spent phosphoric acid waste into a neutralized solid suitable for onsite disposal.

Other program activities included 1) removal and transfer of 11 plutonium glove boxes from retrievable storage containers to

a temporary storage facility in the Hanford 231-Z Building to provide test material for the component disassembly/sectioning studies and 2) establishment of a subcontract with the Health Physics Instrumentation group at the Los Alamos Scientific Laboratory for assistance in developing the approaches, equipment and operating systems needed to ensure the criticality safety of the decontamination process and to permit the high-volume, high-sensitivity monitoring of the decontaminated material.

DECONTAMINATION STUDIES

The effectiveness of vibratory finishing and electropolishing as decontamination techniques for TRU-contaminated waste was further demonstrated by the successful decontamination of more than 500 ft² of plutonium-contaminated metallic waste to below the 10 nCi/g limit. The demonstration was divided into three parts to permit a direct comparison of processing parameters and effectiveness for vibratory finishing only, vibratory finishing followed by electropolishing, and electropolishing only. The latter test was modified to include chemical and mechanical pretreatment to remove tape, paint, glue, and other nonconductive material. The demonstration was conducted as a production-type operation, with emphasis on output and maintaining representative processing conditions.

Most of the test material used in the demonstration was typical plutonium-contaminated metallic waste (pipe, ducting, glove box pieces) generated by the decommissioning of the Hanford 231-Z plutonium facility. The material was sectioned into convenient sizes and shapes using mechanical cutting methods as described in a previous report.⁽¹⁾ The sectioning time was not

included in the processing time for the decontamination demonstration.

The vibratory finishing portion of the demonstration was conducted using a 4-ft³ vibratory finisher of the type illustrated schematically in Figure 13.1. The machine was enclosed in a walk-in glove box for containment. Ceramic media and a commercial latex stripper compound were used throughout the demonstration. A relatively hard ceramic burnishing medium was used initially because of its low wear rate characteristics. It soon became apparent that this medium was not providing sufficient cleaning capabilities. A fast-cutting but higher wear rate ceramic medium was tried. This medium provided excellent cleaning capabilities and was used during most of the demonstration.

The main problems encountered in this portion of the demonstration were inadequate rinsing of the material after processing, and handling the material in the glove box without recontaminating it. A very effective two-step rinse was developed consisting of an initial rinse using a recirculated compound from the vibratory finisher followed by a rinse with high-pressure, high-purity water. The recontamination problem was solved by using two baskets to transport material, one to introduce material into the vibratory finisher and one for the processed material. In addition, clean canvas gloves were worn over glove box gloves when removing material from the vibratory finisher. These canvas gloves were changed after every run.

The vibratory finisher reduced the contamination level of the test material to an average of 0.11 nCi/g, including 0.005 nCi/g smearable contamination. After perfecting the rinsing and handling techniques, levels of only 0.0004 nCi/g smearable were obtained. This level is at the detection limit of the Hanford field survey instruments. In

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FIGURE 13.1. Schematic Drawing of Vibratory Finishing System Used for Decontamination and Pretreatment Studies. The contamination removed by the abrasive action of the vibrating medium is flushed out of the tub by the solution spray and is collected in the sludge tank.

practice, much of the material had no detectable smearable contamination. Material with excessive smearable contamination was rerun.

Of the 315 ft² of material vibratory finished, 131 ft² was subsequently electropolished. The electropolished material was randomly selected. The 400-gal electropolishing system was used for the demonstration. Phosphoric acid was used for the electrolyte followed by a hot water rinse and a cold nitric acid rinse.

The racks used were constructed with a 1/2-in. by 2 in. copper bus bar, to which seven vise grips and copper contacts were attached. The material was clamped to the copper contact by means of the vise grip. Two racks were used, one for electropolishing and one for rinsing. This technique reduced the possibility of recontamination.

Racking presented the major problem during this part of the demonstration. The vise grip jaws often broke during electropolishing,

dropping material into the electropolishing tank. The addition of a third rack for drying would speed up the operation.

The vibratory-finished material was ideal for final decontamination by electropolishing. It could be easily handled and racked because of its low contamination level. In addition, electropolishing time was minimized by the material's having a clean, completely conductive surface. Figure 13.2, for example, illustrates the ability of vibratory finishing to remove rust and gross contamination even from the inside of pipe sections. The contamination that remained in the vibratory-finished material was concentrated in rough welds or in small gaps at joints.

The last portion of the demonstration was conducted using electropolishing to decontaminate material that had not been pretreated in

the vibratory finisher. Initial racking was slow and difficult because of the high contamination levels. The pieces required repeated electropolishing with scraping and application of paint stripper between runs. This resulted in longer electropolishing times and much longer handling time per unit of material.

Because of the poor results achieved by electropolishing material without pretreatment, a chemical pretreatment was developed and used during this part of the demonstration. The material was soaked in a commercial latex stripper at 150°F for 20 to 60 min, depending on the tenacity of the residue. It was then rinsed with a high-pressure water spray. This method successfully removed paint, tape, grease, and a very thick, oily, highly contaminated film from inside some of

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FIGURE 13.2. Comparison of As-Received Pipe and Section Pretreated Using Vibratory Finishing To Remove Rust and Gross Plutonium Contamination in Preparation for Final Decontamination by Electropolishing

the sectioned ducting. This pretreatment technique reduced contamination levels to as low as 0.24 nCi/g.

Table 13.1 summarizes and compares the results of the three-part demonstration. It should be noted that these results represent averages and not optimum values for the entire demonstration. The time requirements and final contamination levels both decreased as the demonstration progressed, reflecting the normal evolution of research and development type procedures into production-oriented material handling methods. Moreover, these results were generated using small, manually operated vibratory finishing and electropolishing systems and do not reflect the substantial increase in production rate and decrease in labor requirements that could be realized through system scaleup and automation.

The results of the demonstration do show that both vibratory finishing and electropolishing techniques are capable of decontaminating typical TRU-contaminated metallic waste to well below the 10 nCi/g limit and that large amounts of material can be decontaminated on a sustained basis. The results also show that vibratory finishing is a very effective pretreatment method to prepare

material for final decontamination by electropolishing. Lower contamination levels can be achieved at a substantial savings in time and labor as compared with material pretreated using chemical and mechanical methods.

PRETREATMENT STUDIES

Vibratory Finishing

Although vibratory finishing has previously been shown effective in decontaminating epoxy-coated surfaces,⁽¹⁾ further studies have demonstrated its effectiveness in decontaminating other TRU-contaminated nonmetallic materials to below the 10 nCi/g limit. This means that all of the major components of a typical plutonium glove box can be decontaminated using this technique (Figure 13.3).

Approximately 40 ft² of Plexiglas® taken from the plutonium-contaminated glove box panel and splash guard in the electropolishing facility was processed in the vibratory finisher in 4- by 18-in. pieces to allow smooth, easy operation. Contamination was reduced to nondetectable levels except in cracks and holes, where levels averaged 0.18 nCi/g. The Plexiglas® had a frosted, opaque appearance after processing.

TABLE 13.1. Comparison of Demonstration Results

	<u>Vibratory Finishing</u>	<u>Electropolishing With Vibratory Finishing</u>	<u>Electropolishing Without Vibratory Finishing</u>
Number of runs	19	21	21
Total area processed, ft ²	315	131	118
Processing time, min/run	65	12	36
Production rate, ft ² /hr	17	7	3
Labor, man-hr/ft ²	0.14	0.37	0.72
Final contamination level, nCi/g	0.11	0.0006 ^(a)	0.0014 ^(a)

a. Electropolishing can completely decontaminate metallic surfaces. The objective of this study was just to decontaminate material to well below the 10 nCi/g limit.

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FIGURE 13.3. Examples of Plutonium-Contaminated, Nonmetallic Glove Box Components Decontaminated to Below the 10 nCi/g Limit by Vibratory Finishing. These components include 1) the Plexiglas glove box panel, 2) the rubber gasket and plastic glove-port ring, and 3) the rubber gloves.

The Neoprene® gasket taken from the glove box panel was cut into 6-in. lengths and processed in the vibratory finisher. The contamination levels were reduced to nondetectable except in the notch of the gasket, where smearable contamination of about 0.2 nCi/g was detected.

A whole Hypalon® plutonium glove box glove was also processed in the vibratory finisher. The glove, which had been cut open, moved nicely with the media but tended to bunch up. After 1 hr of processing time, portions of the glove had nondetectable contamination while other portions showed little or no decontamination. A contaminated portion, 3-by-6-in., was cut from the glove and processed an additional hour. No bunching was observed, and contamination was reduced to nondetectable levels.

Liquid Honing

Liquid honing is another process being evaluated as part of our pretreatment studies. Liquid honing is used in the metal finishing industry to clean surfaces before electroplating, to remove burrs and machine marks, and to relieve stress concentrations. This process combines a liquid containing about 30 vol% abrasive particles with a stream of air at 90 psi. The abrasive and liquid mixture is then propelled by the air against the surface to be cleaned. During operation, the liquid and air are directed with a hand-held gun, which can be designed for specific applications. For example, a special gun can be used to facilitate cleaning of holes that have a large depth-to-diameter ratio. Metal thickness removed

during a typical decontamination cycle using liquid honing techniques equals about 0.1 mm. A typical liquid honing system is shown in operation in Figure 13.4.

We have tested liquid honing on a variety of nuclear reactor components that were contaminated with beta/gamma fission products. For example, the contamination level of a ball channel inspection tool constructed of mild steel with inflatable rubber sides was reduced from 900 to 80 mrem/hr after 5 min of processing. A reactor process cap was decontaminated from 100 to <1 mrem/hr after 3 min

of processing. In these examples, the honing technique not only cleaned exterior metal surfaces, but also decontaminated rubber surfaces as well as threaded areas and deep into bolt holes.

The disadvantage of liquid honing is that the blast system tends to disperse the contamination. Thus, although the liquid honer is useful for rapid decontamination of small parts, it would require a well-engineered containment system and a high degree of operator care for routine, high-volume decontamination or pretreatment applications.

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FIGURE 13.4. Operation of Liquid Honing System Used for Pretreatment and Decontamination Studies

FACILITIES TEST SYSTEMS AND SERVICES

Eleven plutonium-contaminated glove boxes were removed from retrievable storage containers and placed in a temporary storage facility (Figure 13.5) to provide test material for the sectioning, pretreatment and decontamination studies. These glove boxes were from the decommissioning of the Hanford 231-Z Building and originally had been placed in the 8 x 8 x 20-ft containers in preparation for 20-yr retrievable storage.

A consideration of the costs, operations, and waste generation associated with the retrievable storage and ultimate geologic disposal of plutonium-contaminated glove boxes illustrates the incentive for decontaminating this material to convert most of it to non-TRU waste suitable for shallow land burial. The transfer of the glove boxes emptied

three (two metal and one wood) of the large storage containers. The metal boxes, which cost \$16,000 each, were composed of 23 ft³ of metal and had a storage capacity of 1280 ft³. However, even with the most careful packaging, only the equivalent of 18 ft³ of glove box metal would fit into these storage boxes, yielding a maximum packing density of only 1.4% and a cost of nearly \$900/ft³ of metal stored. Furthermore, the storage container itself will become contaminated during the 20-yr storage process, which will more than double the amount of TRU-contaminated metal requiring geologic disposal. The wood storage boxes (no longer acceptable) are less expensive, but represent a potential ninefold increase in TRU waste volume.

Use of electropolishing and vibratory finishing methods to convert most of the

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FIGURE 13.5. Typical Plutonium-Contaminated Glove Boxes That Will Be Used as Test Material for Integrated Disassembly, Sectioning, Pretreatment, and Decontamination Studies

contaminated material to non-TRU waste eliminates the entire retrievable storage process with its attendant costs, hazards, and increased waste volume. Table 13.2 compares the steps required for treatment of TRU waste by decontamination with those required for retrievable storage followed by geologic disposal. It should be noted that disassembly/sectioning is required in both cases and that the transportation, sectioning and repacking operations for the deteriorated retrieved waste will be potentially more hazardous than similar prestorage operations.

CRITICALITY SAFETY/CONTAMINATION MEASUREMENT STUDIES

A subcontract has been established with the Health Physics Instrumentation group at the Los Alamos Scientific Laboratory for assistance in developing the approaches, equipment and operating systems needed to ensure

the criticality safety of the decontamination processes and to permit the high-volume, high-sensitivity monitoring of the decontaminated material. Emphasis for the initial studies has been on the selection of optimum detector geometry for low-level radiation measurements and on the development of a liquid assay system for plutonium-contaminated process effluents.

Optimum HpGe Detector Specifications

The characteristics of three different hyperpure germanium detectors (HpGe) have been studied to determine the best detector geometry for general low-level radiation measurements for application to electro-polishing. A closed-end coax (47.5 cm³) has relatively good efficiency for high-energy gamma rays ($E_\gamma > 1000$ keV), but the aluminum can surrounding the detector and other absorbing material between the can and

TABLE 13.2. Comparison of TRU Waste Treatment by Decontamination Versus Retrievable Storage/Geologic Disposal

<u>Retrievable Storage/Geologic Disposal</u>	<u>Decontamination To Produce Non-TRU Waste</u>
Remove contaminated component	Remove contaminated component
Load into storage box	Transport to decontamination facility
Transport storage box	Disassemble/section
Store/monitor for 20 yr	Pretreat/decontaminate
Exhume box	-----
Transport to repackaging facility	Non-TRU Waste - final disposal by convenient shallow-land burial
Unpackage deteriorated waste	
Disassemble/section waste	
Process waste	
Repackage for geologic disposal	← Prepare small amount of secondary waste for geologic disposal
Overpack for transport	
Transport to disposal site	
Final disposal	
<u>Amount of TRU Waste for Disposal</u>	<u>Amount of TRU Waste for Disposal</u>
At least double the initial amount	Small fraction of the initial amount

the crystal prevent low-energy photons ($E_\gamma < 60$ keV) from entering the crystal. This makes a coax detector undesirable for low-level radiation measurements. The other two detectors were planar HpGe detectors, each having a thin beryllium window in front of the crystal. (One had an area of 21 cm^2 and a thickness of 0.7 cm, and the other an area of 10 cm^2 and a thickness of 1.2 cm.) Both of these detectors have very similar intrinsic efficiencies for low-energy photons ($E_\gamma \leq 100$ keV). However, for higher energy gamma rays ($E_\gamma \approx 500$ keV), the thicker crystal has an intrinsic efficiency that is about a factor of 2 greater than the thinner crystal's. A good general-purpose HpGe detector for low-level radiation measurements would be a planar detector having a beryllium window and a thickness about 1.5 cm.

Low-Level Plutonium Solution Assay

Using the thicker of the two HpGe planar detectors, plutonium solutions were analyzed to obtain plutonium detectability limits. The maximum concentration plutonium solution had a concentration of 10.7 nCi/L (~ 2 MPC). No plutonium signal above background was seen for any of these solutions, so the detectability limit for plutonium in 100 sec at the 3σ level above background is >2 MPC in this configuration.

Additionally, uranium and thorium detectability limits for the thicker HpGe planar detector were determined using several uranium solutions and one uranium/thorium solution. Detectability limits for uranium and thorium, using the thicker HpGe planar detector (1000 sec, 3σ level above background), are shown in Table 13.3.

For very low-level plutonium solution assay, a thin NaI detector should be used. Several liquid assay systems capable of sub-MPC detection limits for public waters have been built at LASL.⁽²⁾ A lead shield and sample chamber (to hold 250-ml plastic flasks) for such a system have been procured. The other components are available and will be assembled into a system and tested to determine detection limits using representative samples of plutonium-containing spent electrolyte.

SOLUTION TREATMENT STUDIES

Electrolyte Purification Studies

Solution treatment studies are in progress to develop methods for purifying the electrolyte and the rinse/pretreatment solutions so as to minimize the generation of secondary waste in the decontamination process. The primary emphasis in these studies has been on identifying and developing safe and effective

TABLE 13.3. Detectability Limits for Uranium and Thorium Using an HpGe Planar Detector

Isotope	MPC, (a) $\mu\text{g/ml}$	Gamma Ray, keV	Detectability, $\mu\text{g/ml}$	MPC
^{235}U	14	136	0.28	0.02
^{238}U	120	63	20	0.17
^{232}Th	18	238	12	0.67

a. Public water, USAEC Manual Chapter No. 0524.

techniques for removing dissolved metal and contamination from the phosphoric acid electrolyte. Of the more than ten approaches evaluated,⁽³⁾ the most promising is an acid adsorption purification process in which the spent electrolyte is forced through a column containing a suitable ion exchange resin. The phosphoric acid is preferentially adsorbed (retarded), allowing the dissolved impurities to pass through the column. The purified acid is then recovered using water as the eluant.

A commercial acid purification system has been acquired and is presently undergoing cold testing to determine the ability of reciprocating acid adsorption techniques to remove dissolved metals and to produce a waste with a high metal-to-acid ratio to maximize acid recovery while minimizing waste volume. The three main parts of the acid purification unit are 1) the ion exchange bed, 2) the acid- and water-metering tanks, and 3) the control system for the unit. The ion exchange bed consists of two large spools, each having a cylindrical void (6 in. dia by 12 in. long) in the center. These spools, contain a very fine ion exchange resin. Watch glasses are located on the top and bottom of the bed so that the color and flow of the acid and water can be monitored during processing to determine the effect of the various parameters on the unit's operation. The acid- and water-metering tanks hold the acid to be processed and the water to be used to elute the acid from the resin. The volume of the solutions in the waste and product streams is governed by the position of electrodes in the metering tanks. The control system automatically sequences the unit through the adsorption and elution steps.

The effectiveness of acid adsorption as an electrolyte purification method has been evaluated for various operating conditions

using phosphoric acid electrolytes containing electrolytically-dissolved stainless steel. The acid and metal content of the initial feed solution and the resulting product and waste streams were determined using neutralization titration and x-ray fluorescence methods.

The purification tests conducted using normal system operating parameters (alternate short flows of electrolyte and water in opposite directions) produced an adequately purified product, but the metal-to-acid ratio for the waste stream was substantially lower (0.10) than the target ratio of 1.0. The operating cycle was therefore modified to permit recycle of the waste stream to determine whether the metal content of the recycled solution could be increased to a level representing an acceptable waste composition. However, the highest metal-to-acid ratio that could be attained with this mode of operation was 0.08, or even lower than for normal system operation. In addition, recycle of the waste stream resulted in excessive dilution of the process stream and also significantly increased the processing time.

The effect of unidirectional operation with alternate flows of electrolyte and water in the same direction also was evaluated. This mode of operation produced waste with a higher metal-to-acid ratio (0.21), but the product-to-waste volume ratios were not adequate for a practical purification process.

The best purification results were obtained by extending the duration of the reciprocal electrolyte and water flows and by extracting only that part of the waste stream representing a high metal-to-acid ratio. The variation of waste stream composition with waste volume is shown in Figure 13.6 for a representative acid adsorption test. The dissolved nickel emerged from the ion exchange

FIGURE 13.6. Metal/Acid Concentration Ratio as a Function of Waste Volume for Passage of Phosphoric Acid Containing Dissolved Stainless Steel Through Acid Adsorption Bed

bed first, followed by the iron and the chromium in the form of an amorphous precipitate with a molar metal-to-phosphorus ratio of about 1:2. The total metal-to-acid ratio for the waste stream increased from about 0.20 to a maximum of 0.28 and then dropped rapidly at the acid breakthrough point. The amount of metal removed and acid lost for this initial portion of the waste stream as compared with an equal volume of feed solution was 100% for the nickel, 70% for the iron, 60% for the chromium, and only 15% for the acid.

The iron-chromium precipitate obtained in these tests would be an excellent waste form for disposal if it could be reproducibly obtained in reasonable quantities. Although the precipitate forms in the resin bed, a substantial fraction apparently is flushed out by the low-acid solution. The remaining precipitate is redissolved and removed as

the phosphoric acid concentration reaches 150 g/L. These acid adsorption studies will continue, with emphasis on determining the effect of system parameters on the production and recovery of the precipitate and on the total metal-to-acid ratio of the waste stream.

Evaporator Installation and Operation

A dual-effect evaporator system (Figure 13.7) has been installed for purification and recycle studies of the pretreatment and electropolishing rinse solutions. This system is comprised of two independent units and has the versatility either to run one solution through two successive distillation cycles or to run two separate solutions through the process simultaneously. Water from the rinse tanks and any aqueous process effluents from the pretreatment facility, such as vibratory finishing liquids, will be

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FIGURE 13.7. Dual-Effect Vacuum Evaporator System Used for Purification and Recycle Studies of the Pretreatment and Rinse Solutions

pipled into feed tanks connected to the evaporator system. The evaporator will run this water through either one or two distillation cycles and into storage tanks, where it is monitored for residual contamination. If the liquid is still above release limits, the process can be repeated. The concentrated, highly contaminated "bottoms" resulting from this treatment will be removed and solidified for waste disposal.

Initial cold tests have shown that this evaporator system can distill up to 60 gal/hr. Feed and storage tanks are being installed, and criticality safety analyses are being completed. Testing of the system using contaminated liquids is expected to begin soon.

Spent Electrolyte Solidification

As a result of studies to determine the most effective means of converting spent phos-

phoric acid electrolyte into a neutralized solid suitable for onsite disposal, a direct caustic neutralization process has been selected and is now in use. In this process, 50 NaOH is added directly to the electrolyte, which causes a violent and instantaneous reaction, rapidly increasing the temperature from 25° to 105°C. After the pH reaches 9 to 10, addition of NaOH is stopped and the solution cools. By the time the mixture reaches ambient temperature, it has become a solid. This process produces about one barrel of solid per day and increases the waste volume by a factor of 2.1.

Two other alternative processes investigated were 1) adsorption of the electrolyte on an adsorbent clay followed by neutralization with 50 NaOH and 2) use of urea-formaldehyde to form a solid matrix to contain the electrolyte. The problems with the adsorption process were the difficulty in

mixing the electrolyte, caustic, and adsorbent together and the large increase in waste volume (a factor of 3.8). The urea-formaldehyde process was simple and effective and produced a barrel of solidified spent electrolyte per hour. However, since the elec-

trolyte was not neutralized prior to mixing, the acid could be easily leached away from the solid. In addition, since the matrix is organic, it could evolve radiolytic gases when containing an alpha producer.

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