Nuclear Waste Management Quarterly Progress Report April Through June 1978

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

November 1978

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NUCLEAR WASTE MANAGEMENT
QUARTERLY PROGRESS REPORT
APRIL THROUGH JUNE 1978

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

November 1978

Prepared for
the U.S. Department of Energy
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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 High-Level 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 January Through March 1977, PNL-2378-1.

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1.0 DECONTAMINATION AND DENSIFICATION OF CHOP-LEACH CLADDING RESIDUES

R. L. Dillon, R. S. Kemper and R. R. King

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 determine the feasibility of and to develop methods for removal of long half-life transuranics from the cladding residues and for consolidation of the zirconium and stainless steel residues. The study involves:

1. *selection and laboratory testing of methods for transuranic removal by*
 - a) *aqueous reagents*
 - b) *molten salt reagents*
 - c) *fluxing during melting*
2. *consolidation of the fuel element hulls by melting and casting Zircaloy, stainless steel, Inconel or alloys of the three*
3. *testing and evaluating the consolidated fuel hulls for long-term waste management*
4. *absorption and fixation of tritium into the waste ingots*
5. *consolidation of transuranics removed.*

SUMMARY

Pilot-scale equipment for chemical decontamination of cladding hulls has been assembled in a configuration simulating equipment placement for remotely operated hot cell decontamination work. Preliminary tests of hull flow through the prototype equipment were made. Hulls are decontaminated with HF/Ar in a gas reactor followed by an aqueous rinse. The decontamination prototype will be operated in conjunction with an Inductoslag ingot melting furnace in the same simulated hot cell configuration.

Melting tests of the Inductoslag melt densification furnace were continued in efforts to reduce ingot sidewall roughness encountered with

previous melts of Zircaloy-4. Modifications of the Inductoslag crucible and the melting procedures resulted in successful production of Zircaloy ingots with smooth sidewalls.

DECONTAMINATION PROCESS

A prototype system for decontaminating and densifying chop-leach fuel hulls is being assembled and tested in a building operated by PNL on the Hanford Reservation. Pilot-scale chemical decontamination equipment (~2 kg hulls/hr) and an Inductoslag melting furnace are set up on a simulated hot cell floor plan for eventual combined nonradioactive demonstrations.

The prototype decontamination equipment is being tested for proper

functioning. The basic decontamination unit, consisting of an HF/Ar gas reactor and an aqueous washer/rinser is shown in Figure 1.1. In a previous report this equipment has been illustrated with associated chemical storage tanks along with a schematic of the decontamination process itself.⁽¹⁾ Preliminary fuel hull trans-

port tests through the HF reactor and washer/rinser were made. The average volume of hulls discharged by one revolution of the screw feeder mechanism (detailed in Figure 1.1) is 725 ml, representing ~680 g of chopped fuel hulls. Tests are planned to further characterize the capabilities of the decontamination unit.

7806286-1

FIGURE 1.1. Fuel Hull Decontamination Unit

Control instrumentation for the decontamination unit was located outside the simulated hot cell wall, as were the gas cylinders supplying the process Ar and HF. A transformer was installed to supply power to the control cabinet and the heater elements of the HF reactor (detail of Figure 1.1). Inputs to a modified data logger and other instrumentation were defined and the necessary programming and electrical connections begun.

The scrubbed ventilation system of the building containing the decontamination prototype was modified to provide ventilation for the Inductoslag furnace and to remove any HF gas resulting from leaks in the decontamination prototype. Final connections are planned to make the extended ventilation system operable by the end of next reporting period.

DENSIFICATION PROCESS

Densification efforts this period concentrated on refining the procedures for melting simulated Zircaloy cladding residues in the Inductoslag melting furnace. The induction furnace is the densification portion of the prototype decontamination/densification system being set up for non-radioactive demonstration. The furnace has been pictured and described in previous reports.^(2,3)

Previous melting tests successfully produced Zircaloy ingots of acceptable quality except for roughness of the ingot sidewalls. The refinement of melting procedures this quarter was directed at improving the sidewall quality of Inductoslag ingots of

Zircaloy-4. The surface roughness, e.g., high surface area, makes flux removal difficult and reduces leaching resistance during long-term storage. The roughness is caused by metal freezing against the crucible wall without the benefit of a CaF_2 flux layer between the freezing metal and the crucible wall.

Table 1.1 summarizes the heats melted during this quarter. Heat numbers 13-17 involved variations in feed rate, power level, and molten pool position within the crucible. None of these variations had any apparent effect on improving the ingot sidewall roughness.

The crucible was removed and reshaped for less taper from top to bottom. The average taper (small diameter at the top) is now ~ 1.2 mm over ~ 20.4 cm (~ 0.046 in. over 8 in.). The Inductoslag crucible consists of 24 segments of water-cooled copper tubing, vertically aligned in parallel and coated with an insulating ceramic for separation and rigidity.⁽³⁾ Prior to the modification, the taper had been estimated by spacing of the crucible segments; careful measurement revealed that this procedure produced more taper than calculated because the width of the crucible segments is slightly larger at the bottom.

With the objective of creating better conditions for forming and holding a flux pool, the crucible and coil were altered. The crucible was re-coated with ceramic and installed. The induction coil was rewrapped with Varglass insulation and reinstalled with the top of the coil one turn above the crucible. This was done to allow a higher melting zone.

TABLE 1.1. Zircaloy Melting Heats in the Inductoslag Furnace

Heat Number	Melted Weight, kg	Melt Rate, kg/hr	Approximate Power, kW	Energy Use, kWh/kg	Hardness, BHN(a)	Remarks
13	24.88	62.2	110	1.8	183-192	Demonstration heat; no problems.
14	16.21	18.7	76-110	4-6	--	Varied kW and material feed rate for sidewall finish experiment; material feeder problems.
15	10.21	15.7	88	5.6	--	Feed chute altered for better control of feed rate; power level reduced to check effect on sidewall finish.
16	9.18	--	92	--	--	Low power with molten zone as low as possible in the crucible to check the effect on sidewall finish; worst surface finish to date.
17	10	13	90	6.9	181-189	Demonstration heat; 2.5-cm- and 5-cm-long cladding melted as low as possible in the crucible with low power level; rough ingot surface.
18	--	--	96	--	--	Crucible reshaped and coil raised 1.5 cm; objective to melt as high as possible in the crucible to form a flux pool; good flux pool formed; no metal feed.
19	10	40	100	2.5	--	Objective of melting ingot without losing flux pool was successfully met; 2.5-cm- and 5-cm-long cladding with end caps; smooth sidewall; thick flux layer on ingot.
20	20	43	108	2.5	181-187	20 kg of cladding and end caps melted at varying heights within the crucible; flux pool lost at lowest position but regained after rebuilding pool height; smooth sidewall; thick flux layer on ingot.

a. Brinell hardness number.

Ingot number 18 was made using only a Zircaloy starting stub (no feed material) to see if a flux pool could be formed and held. After success with ingot number 18, ingots numbered 19 and 20 were made using 10 kg and 20 kg, respectively, of mixed 2.5-cm and 5-cm lengths of Zircaloy cladding plus some solid Zircaloy end cap material. Both ingots had smooth sidewalls. On ingot number 20, during experiments with the molten zone's height in the crucible, a flux runout occurred during operation with the molten zone as low as possible in the crucible. The flux pool was immediately restored after the height of the molten zone was rebuilt with more metallic feed and flux. The effect on ingot surface quality of proper flux conditions during metal freezing is shown in Figures 1.2 and 1.3.

For making 20-kg Zircaloy-4 ingots with smooth sidewalls using the reshaped crucible, the melting practice is as follows:

1. Position a Zircaloy starting stub 7 cm from top of crucible.
2. Add 200 g of CaF_2 on top of the starting stub.
3. Add 800 g of CaF_2 to the flux feeder.
4. Mix 800 g of CaF_2 with the metal feed. (Because this results in a thick layer of flux on the ingot, it may be desirable to reduce this in future heats.)
5. Power on at 40-60 kW and hold for 5 min, or until the flux starts melting. Increase power to 100 kW and establish a molten pool. If a flux ring has not formed, add flux from feeder until one is established. Add metal feed and operate with the

7807074-13

FIGURE 1.2. Typical Rough Ingot Surface Caused by a Lack of CaF_2 Flux Layer During Metal Freezing (Zircaloy-4, Heat No. 12)

7807074-11

FIGURE 1.3. Typical Smooth Ingot Surface Resulting from Proper CaF_2 Flux Pool During Metal Freezing (Zircaloy-4, Heat No. 19)

molten pool as high in the crucible as the operator is comfortable with. Normal operating power will be between 100 and 120 kW, depending on whether or not there is a frozen metal ring around the crucible. After all metal has been added, power down slowly and shut off.

For heats 17 through 20 about half of the Zircaloy feed stock consisted of pieces 5 cm in length along with the

2.5-cm-long pieces. It appears that the longer pieces can be melted without difficulty.

Figures 1.4 and 1.5 are sections of ingots melted with a fast melting rate (62.2 kg/hr) and a slow melting rate (15.7 kg/hr) respectively. The finer grain size and shallower pool shown by ingots produced at a fast melting rate are probably indications of a lower molten metal temperature.

7807074-9

7807074-10

FIGURE 1.4. Zircaloy-4 Ingot Produced at a Fast Melting Rate, 62.2 kg/hr. Note the finer grain and shallower pool compared to Figure 1.5 (Heat No. 13).

7806716-1

7806716-3

FIGURE 1.5. Zircaloy-4 Ingot Produced at a Slower Melting Rate, 15.7 kg/hr. Note the coarser grain and deeper pool compared to Figure 1.4 (Heat No. 15).

REFERENCES

1. A. M. Platt, compiler, Nuclear Waste Management Quarterly Progress Report, January Through March 1978. PNL-2378-1, Pacific Northwest Laboratory, Richland, WA, August 1978.
2. A. M. Platt, compiler, Nuclear Waste Management Quarterly Progress Report, October Through December 1976. BNWL-2245, Battelle, Pacific Northwest Laboratories, Richland, WA, pp. 1.5-1.7, April 1977.
3. A. M. Platt, compiler, Nuclear Waste Management Quarterly Progress Report, April Through June 1977. BNWL-2377-2, Battelle, Pacific Northwest Laboratories, Richland, WA, pp. 1.3-1.4, November 1977.

2.0 MONITORING METHODS FOR PARTICULATE AND GASEOUS EFFLUENTS FROM WASTE SOLIDIFICATION PROCESSES

R. L. 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

During this reporting period, testing of out-of-cell sampling components' reliability under conditions expected during actual sampling was begun. Laboratory analytical techniques have been and are being formalized to optimize analytical procedures. An analytical x-ray fluorescence facility has been tested and calibrated. The direct inlet mass spectrometer has been modified to increase its analytical sensitivity.

X-RAY FLUORESCENCE FACILITY -

H. Tenny

An x-ray fluorescence analytical capability has been developed to complement nuclear decay measurements for the analysis of low-level calcined particulate effluent. This facility as developed can utilize either a microfocus x-ray generator or a radioactive isotope as the primary source of fluorescent excitation. An evacuable sample chamber having a 12-position carousel has been built for use with either type of excitation source. Sample fluorescence is detected with a lithium-drifted sili-

con detector. The data generated by this detector are routed to a PDP-8 computer, where they are stored and subsequently analyzed.

This fluorescent analytical system has been calibrated using a series of synthetic calcine samples containing known atom ratios of selected elements. Using jet mill technology, these standard samples were dispersed as submicron particles (PNL-2377-2) and were collected on filters under actual sampling conditions. Results from these calibration experiments indicated a need for greater analytical sensitivity for several important elements. Efforts to achieve a higher system sensitivity by use of a greater primary excitation flux and/or a more efficient detection system will be pursued during the last quarter of this fiscal year.

DIRECT INLET MASS SPECTROMETRY -

D. L. Styris

To achieve a greater ion collection efficiency and a concomitant gain in analytical sensitivity, the mass analyzer vacuum housing of the direct inlet mass spectrometer has been altered to accept a modified

2.2

cross axis analyzer. This modification will allow acceptance of particles impinging perpendicular to the analyzer axis. Optimization of particle angle of incidence with respect to the thermal ionization filament contained within the analyzer will be empirically determined.

Development of the direct inlet mass spectrometer will cease during the last quarter of FY-1978 upon completion of the construction phase. Further testing and development of this instrument during FY-1979 will be contingent upon sponsor interest.

SAMPLER TESTING AND QUALITY CONTROL - R. W. Goles and D. C. Hamilton

With completion of the design and construction of the vitrification off-gas sampling network, the sampling components have been extensively tested and calibrated. Maximum loading capacities of several species-specific sorbing agents have been and are being determined under diverse sampling conditions. Also laboratory chemical yields associated with the recovery of adsorbed samples from various trapping beds are concurrently

being established. Catalytic efficiencies and specificities are also being examined as a function of temperature, bed depth, and face velocity.

Compatibility of integrating batch mode samplers with the corrosive nature of the off-gas sampling stream has been assessed. In some instances, material substitutions were found necessary. In other instances, no adequate alternative corrosion-resistant sorption material could be found. Consequently, efforts are now under way to selectively eliminate the corrosive components from a portion of the sampled process off-gas stream.

CALIBRATION - R. W. Goles

Laboratory analytical techniques have been and are being formalized to develop optimized procedures for handling the integrating batch mode samples resulting from the hot solidification runs. Methods have also been started for calibrating detector systems for individual isotopes. Activity in these areas will continue through the fourth quarter of this fiscal year.

3.0 TRU WASTE IMMOBILIZATION PROGRAM

C. R. Palmer - Project Manager

The objectives of this program are to determine the degree of immobilization that may be necessary for the acceptable disposal of transuranic waste residues, and to develop process technologies to provide such immobilization.

SUMMARY

The program plan, completed and transmitted to the Department of Energy's Richland office, defines five tasks intended to address immobilization of several transuranium-contaminated wastes. HLW immobilization technology will be applied to the wastes to the maximum extent possible.

Several ongoing programs (of DOE, NRC, EPA and private sponsorship) were identified for review and evaluation. This review will provide a continuing means of guidance for the immobilization studies to assure compatibility between criteria development and waste form development.

A multicontractor meeting was held at Los Alamos Scientific Laboratory (LASL) to discuss TRU waste form development guidelines and measurement methods to characterize waste forms with respect to the guidelines.

PROGRAM ORGANIZATION

The current program is defined by five tasks, listed and briefly described below:

Task 1 - Program Management

This task includes administration, coordination, and maintenance of technical liaison with other related DOE laboratories to assure compatibility of programs.

Task 2 - Waste Containment Analysis

This task is composed of two major activities. The first is an in-depth review and assessment of ongoing environmental/safety analysis and criteria development programs. The purpose of this review is two-fold: 1) to provide continuing input to the immobilization tasks regarding implications of these programs for waste form performance requirements and 2) to attempt an objective technical assessment of the state of criteria development based on the current understanding of the behavior of nuclides in the geologic environment. This activity has been started.

The second activity of this task is referred to as support for near-field repository analyses. The

objective of such analyses is to evaluate the relative effectiveness of near-field confinement system components (e.g., local geology within ~20 ft, engineered barriers such as the waste form, canister, and back-fill material) in further restricting the movement of the transuranium radionuclides. This program will provide supporting data, such as actinide leaching in various environments, to nuclide migration studies and dose calculations.

Task 3 - Source Term Definition

This task will provide for a systematic identification and characterization of transuranic wastes and will provide a basis for prioritizing them in the experimental investigations. Some possible waste categories which can be differentiated are listed below:

- residues from volume reduction of combustible wastes (e.g. incinerator ash and acid digestion residues)
- Pu-contaminated sludges and miscellaneous wastes resulting from scrap recovery operations
- TRU-contaminated metals with induced activity
- Zircaloy and other alloys difficult to electropolish
- miscellaneous metallic wastes which could be decontaminated but would not be for cost-effectiveness or other reasons
- metallic salts, resins, concentrated electrolyte from electropolishing operations

- ZrO_2 and other secondary wastes from hull decontamination operations
- UF_6 plant wastes such as fluorinator fines.

Task 4 - Waste Form Development

This task will involve identifying alternative immobilization technologies for specific TRU waste types, selecting a candidate technology (or technologies) for investigation, formulating and screening waste forms through preliminary nonradioactive experiments, and finally carrying the most appropriate waste form through an extensive development and characterization program. It is important early in this task to specify the functional criteria upon which development will proceed. In the absence of explicit requirements, these criteria will be established in consensus with other laboratories so as to maintain consistent approach. In addition to product performance, process compatibility will be an important consideration. Waste forms will be emphasized which are compatible with current process technologies already developed largely in support of HLW immobilization programs.

This task will address the immobilization of incineration residues and electropolishing secondary wastes this fiscal year. Much work has already been completed for incinerator residues using borosilicate glass and concrete formulations. Other waste form candidates include phosphate glasses, sintered ceramics, and polymeric materials.

Task 5 - Process Development and Demonstration

This task will provide large-scale demonstrations of processing concepts indicated from waste form development results. These demonstrations will identify any equipment or process-conditions difficulties which might arise so that they can be dealt with appropriately. A further purpose of this task will be the generation of large-scale waste products for detailed characterization and correlation to laboratory results.

WASTE CONTAINMENT ANALYSIS

Several ongoing studies have been identified which will be the subject of review and evaluation for implica-

tions to TRU waste immobilization programs. Table 3.1 lists these programs.

SOURCE TERM DEFINITION

An incinerator ash composition has been defined which will be used in immobilization studies. The current Rocky Flats Plant (RFP) composition, it results from fluidized bed incineration of four types of waste: combustible alpha waste, degraded tributyl phosphate, HEPA filters, and organic resins. The residues from the incinerator will be blended with intermediate-level waste (primarily diatomite and mineral resins) to form the feed stream to an immobilization process. Table 3.2 shows the composition of this stream.

Table 3.1. Some Programs Related to Criteria Development for Transuranic Wastes

<u>Program Description</u>	<u>Organization</u>	<u>Contact</u>
Evaluation of handling and disposing of solid low-level nuclear fuel wastes	NUS Corporation	P. M. Garrett
WIPP TRU experimental studies	Sandia et al.	M. A. Moelecke
TRU waste handling studies	EG&G	M. McCormick
ONWI	BCL	R. E. Heineman
Preparation of environmental criteria	EPA	W. F. Holcomb
Performance criteria for solidified nuclear waste forms	LLL	J. J. Cohen
Determination of a waste classification system	Ford, Bacon and Davis Utah, Inc.	P. Macbeth
TRU waste management studies	LASL	T. K. Keenan
Waste management safety assessment program	PNL	W. K. Winegardner
Criteria for packaging and transport of radioactive wastes	ORNL	L. B. Shappert
Transportation safety studies	PNL	L. D. Williams
Radiolytic gas generation studies	RHO	A. L. Pajunen
Decommissioning assessment	PNL	E. S. Murphy
Non-HLW waste program	HEDL	G. L. Richardson
Spent fuel geologic disposal safety studies	PNL	M. O. Cloninger

TABLE 3.2. Reference Blended TRU Waste from RFP Fluidized Bed Incinerator(a)

Chemical Compound	wt%
NaCl	2.6
Na ₂ CO ₃	15.5
Cr ₂ O ₃	5.6
Al ₂ O ₃	24.1
SiO ₂	36.0
Na ₂ SO ₄	2.7
C	3.3
Na ₃ PO ₄	2.1
MgO	3.4
Fe ₂ O ₃	0.5
CaO	2.2
Na ₂ O	0.7
H ₂ O	1.4

a. D. L. Ziegler et al., Status Report: Waste Incineration and Fixation, RFP-2655, November 25, 1977.

Compositions have been obtained for the incinerator ash from controlled-air incineration of individual waste components at LASL. A design waste composition for a representative mixture of these components is being formulated for use in developing a disc-pelletized sintered waste form.

WASTE FORM DEVELOPMENT

A multicontractor meeting was held at LASL to discuss TRU waste form de-

velopment guidelines and measurement methods for characterization of waste forms with respect to the guidelines. Consensus has not been achieved, but potentially important candidate parameters have been listed, as shown below, for further consideration:

Gas Generation

- Radiolysis
- Organic content (potential for bacterial degradation)
- Thermal stability
- Chemical stability

Dispersibility

- Leaching behavior
- Particulates
 - Frangibility
 - Crush strength
 - Waste form physical properties (monolithic, marbles, etc.)
- Organic content
- Free water content
- Product degradation
 - Thermal
 - Chemical
 - Radiological
- Combustibility

Quality Assurance

- Ability to verify quality

Presently, a standard leach test is being developed, and other tests are being evaluated which can be used in all laboratories.

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 temperature and 2) entrapment of the krypton in solids during ion sputtering.

SUMMARY

Sputtered amorphous alloys have been shown to trap krypton at concentrations exceeding 10 at.%. Several readily available alloy materials have been identified as having potential to sputter in the amorphous state. Some of these are to be tested for trapping krypton. Release rates of krypton from an amorphous alloy ($\text{Fe}_{0.78}\text{Zr}_{0.20}\text{Me}_{0.02}$) have been measured. The data suggest two mechanisms of release, one at low temperature and another at high temperature. A sputtering apparatus with twice the sputtering area is currently being tested to evaluate potential problems in scaling up the process.

KRYPTON ENTRAPMENT DURING SPUTTERING -
M. A. Bayne, E. D. McClanahan,
G. L. Tingey, E. N. Greenwell, and
R. W. Moss

Earlier work demonstrated the potential for trapping fairly large quantities of krypton during sputtering to form krypton-loaded metal alloys. Several tasks remain in developing the process for economical use in containing the ^{85}Kr generated in nuclear power reactors and defense wastes.

During the past quarter we have focused our attention on three general areas: 1) develop and select a suitable matrix material for krypton storage, 2) measure the rate of release from the sputtered samples as a function of temperature, and 3) develop an apparatus capable of handling the quantity of krypton which may be generated from nuclear wastes. The following describes the results attained during the past quarter.

Matrix Material Development

Initially the krypton was loaded in several crystalline metals. In these materials krypton loadings of about 4 at.% were achieved when a pulsed negative bias of about 2000 V was applied to the substrate. We later observed that significantly higher krypton loadings could be achieved if alloys were used which would yield sputtered amorphous material. A krypton loading of over 10% was achieved in an amorphous 85% iron, 13% yttrium alloy, and loadings approaching 10% were achieved using an alloy of about 25% iron, 75% zirconium.⁽¹⁾

During this quarter a thorough search of the literature was conducted which suggests that several other easily obtainable alloys have the potential of yielding amorphous solids. Furthermore, the glassy to crystalline transition temperature is highly dependent upon composition, and changes in crystallization temperature of 100 to 150°C can occur with small changes in composition. Therefore, optimizing of gas retention in the matrix may require careful control of alloy composition. Final selection of the matrix material involves consideration of thermal and mechanical properties. At present, essentially no data have been published on the properties of amorphous metals. Thus research in this area will be required when the material is more well defined.

Krypton Release

Our early work on gas release has focused chiefly on measuring the total krypton content by releasing it at high temperature and determining the krypton pressure. Only very preliminary data on release rate as a function of temperature were obtained. During this quarter we have turned our attention to determining release rate as a function of temperature. Samples of sputter-deposited $\text{Fe}_{0.78}\text{Zr}_{0.20}\text{Me}_{0.02}$ * containing from 3 to 8 wt% krypton were heated at temperatures from 200 to 1300°C and the gases collected, measured, and ana-

lyzed. From these data we determined the release rate as a function of temperature. Data from one of the samples is shown in Figure 4.1, where the log of the release rates is plotted as a function of reciprocal temperature. This type of plot should yield a straight line if the release were a simple diffusion mechanism. In this case, the data appear to fall reasonably well on two straight lines, indicating two different mechanisms of release, one for high-temperature release and another for low-temperature release. The low-temperature release rates are difficult to establish accurately because of the low pressure of krypton generated within a reasonable time period. Despite this, the data appear to be reasonably reproducible and, thus, lead to concern about a larger low-temperature release than would be predicted from extrapolation of the high-temperature curve. The mechanism of the release of krypton at low temperature is unknown, and without further studies any suggestion as to its source would be only speculation.

Data from other sputter-deposited samples of the same alloy composition but with varying krypton loadings tend to agree well with Figure 4.1. In one sample tested, the sputtered deposit was stripped from the substrate. These data also agreed well at the higher temperatures but showed release rates a factor of two to ten higher at temperatures from 300 to 500°C.

The possible impact of a somewhat higher release rate at lower temperatures will be evaluated in subsequent

* 78% iron, 20% zirconium, 2% minor impurity

FIGURE 4.1. Krypton Release Rate from Sputter-Deposited $Fe_{0.78}Zr_{0.20}Me_{0.02}$ Containing 9.0 cm^3 of $Kr(STP)/g$ (3.3 wt%)

reports. Moreover, study is needed to learn whether all the krypton could be released at low temperature or whether only a portion of the gas is trapped in a way that could lead to the low-temperature release.

Apparatus Development

It is of interest to determine how large a sputtering apparatus is desirable for trapping the krypton generated from nuclear fuels in an actual plant. It is estimated that

a process that could trap krypton at a rate of $45 \text{ cm}^3 \text{ Kr}(STP)/\text{min}$ is required to handle Idaho National Engineering Laboratory-type waste if the process were to run continuously. Therefore, equipment capable of trapping 60 to $90 \text{ cm}^3 \text{ Kr}(STP)/\text{min}$ would allow time for assembly-disassembly, maintenance, etc. To date we have achieved a trapping yield of $16 \text{ cm}^3 \text{ Kr}(STP)/\text{min}$ in our laboratory-scale apparatus. Therefore, we have a goal to increase the size of our unit by a factor of four to six. This quarter

a machine twice as large as the laboratory apparatus was tested and showed increased efficiency due to reduced end effects. This increased efficiency indicates that a sputtering machine four times as large as the laboratory apparatus (4x) would trap krypton at a rate of $80 \text{ cm}^3(\text{STP})/\text{min}$.

Some operational problems encountered during initial testing of the 2x equipment have given us insight into requirements for further scale-up. The two major problems were that the plasma would not reignite after an arc and the ion current density was not uniform from the top to the bottom of the sputtering chamber. Changing the electron deflector-shield geometry and going back to the dual anode mode of operation corrected the first problem.

The second problem, that of plasma uniformity, is more subtle in that several parameters affect the current distribution. The main ones are pressure, geometry, and plasma density. For each system, the geometry is determined so that plasma uniformity can be optimized by adjusting the pressure and current. In general, lower pressure and higher current yield more uniform plasma current densities. The 2x apparatus lends itself to easy adjustment of these parameters since

the target is segmented and adjustments can be made continuously until the ratio of target currents approaches one. However, we are limited in the minimum pressure achievable without affecting plasma stability and in the maximum plasma current achievable without exceeding the power supply and arc limiter specifications. Experiments on optimizing parameters for the 2x chamber are in progress. When complete, they should provide the information necessary to predict the success of the 4x scale-up.

Also being tested on a 2x scale is the large-capacity target arc-limiter. It works at low powers, but when higher powers were attempted, an rf field was generated. The circuitry is being modified.

Work on the closed-loop recirculating vacuum system is continuing. Initial tests were started in June. Testing is on schedule, and it is expected that before October 1, 1978 a sputter deposition will be performed using the system.

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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 iodine-129 and carbon-14 released from the treatment of irradiated fuels.

SUMMARY

Additional tests on iodide-iodate conversion were made using ozone, cerium (IV), and boiling concentrated HNO_3 . Ozone in alkaline solutions gave rapid conversion with no iodine loss. Excessive iodine volatilization occurred with the other methods, as previously observed.

Preliminary analyses of the leachant data on metal iodates in Portland Type III cement have been carried out. Seventeen factors considered significant in affecting leaching were chosen for study. Early results indicate that temperature and CO_2 concentration in the leachant are among the more important variables.

A system for loading metal-exchanged zeolites with iodine was constructed. Preliminary runs indicated modifications are needed.

LEACHABILITY STUDIES - K. D. Wiemers

In Phase II of the cement leaching study, seventeen variables thought to influence the leach rate of iodate from cement were screened. Cement composition, fixation material interactions, and leachate composition were investigated using the leaching procedure established in Phase I.⁽¹⁾ The screening test results are expected

to aid in both the selection of the best fixation form and the predictability of leach rates under various environmental conditions.

The factors chosen for screening were selected on the basis of their suspected effect on the leach rate. The number of factors was limited by the practicality of leachate changes, analysis, and data handling.

Table 5.1 lists the selected factors and their ranges. The factors listed in Table 5.1 are described below.

1. Water/cement wt ratio - The theoretical amount of water required for complete hydration of Portland Type III cement is equivalent to a w/c ratio of 0.3 by wt. Double this ratio was required for the lower level to ensure proper mixing and ease of transfer from mixer to mold. The upper level value of 1.0 was restricted by the curing time.
2. Curing time - The IAEA standard leach method⁽²⁾ recommends 28 days of curing in a humid environment. The lower and upper levels for this factor lie ~3 weeks on either side of this period. It should be noted that 28 days is the standard curing time for Portland Type I cement. According to ASTM specifications⁽³⁾

TABLE 5.1. Factors Selected for Screening

Factor	Minimum and Maximum Statistical Levels
Cement Composition	
Water/cement wt ratio	0.6, 1.0
Curing time, days	7, 42
AlCl ₃ additive, wt%	0, 1
Bentonite additive, wt%	0, 1
Butyl stearate additive, wt%	0, 0.9
Sodium silicate coating	0, applied
Commercial dressing	0, applied
Leachate Composition	
Temperature, °C	20, 70
pH, initial	4, 10
[Ca ⁺²], M	0, 0.01
[SO ₄ ⁻²], M	0, 0.03
[CO ₂], M	0, 0.04
Fixation Material Interaction	
[IO ₃], mmole/g cement	0.137, 0.686
[Ag ⁺], mmole/g cement	0, 0.014
[Pb ⁺² or Sr ⁺²], "excess," mmole/g cement	0, 0.343
[Ba ⁺²], mmole/g cement	0, 0.056
Iodate solubility, solubility in water [I]	8.7×10^{-3} , 8.6×10^{-5}

- Portland Type I reaches its maximum compressive strength in 28 days. The maximum compressive strength for Portland Type III is reached in 3 days.
3. AlCl₃ additive - This is an integral waterproofing agent for cements. It belongs to the group of active pore-filling substances, its activity being the formation of calcium chloraluminate. AlCl₃ also accelerates setting, the rate of which is dependent upon its concentration and the composition of the cement.⁽⁴⁾ For this study a concentration of 1 wt% AlCl₃/cement was chosen to provide a water-

proofing action with minimal effect on the setting rate.

4. Bentonite additive - This is an integral waterproofing agent belonging to the class of inert pore-filler compounds. It is a residual clay whose main mineral constituent is either montmorillonite or beidellite. It is strongly thixotropic, has a high base exchange capacity, and is used to increase the plasticity of clays.⁽⁵⁾
5. Butyl stearate - This is an integral waterproofing agent belonging to the class of active water-repellent materials. The transmission of capillary water

- is inhibited although diffusion of water vapor still occurs. Up to 1 wt% butyl stearate/cement can be used without frothing.⁽⁴⁾
6. Sodium silicate coating - This material is capable of hydrolyzing the surface of cement, forming a protective, gelatinous silica film.⁽⁵⁾ It also acts as an active pore-filling material by reacting with Ca^{+2} to form calcium silicates.⁽⁴⁾
 7. Commercial dressing - "Concentrated Heavy Industrial Concrete Dressing" by Dylon Industries, Cleveland, Ohio, was applied according to manufacturer's instructions.
 8. Temperature - The selected levels for this factor are those which might be encountered at shallow-land burial sites (20°C) and at burial sites with high-level waste (70°C).
 9. pH - Values for the most extreme environmental conditions⁽⁶⁾ were selected.
 10. $[\text{Ca}^{+2}]$ - The concentration of calcium was selected on the basis of that normally found in seawater, ~400 ppm. Concentrations of calcium in normal potable groundwater generally range between 10 and 100 ppm. Complex interactions can exist between calcium and carbonates, sulfates, and chlorides.⁽⁶⁾
 11. $[\text{SO}_4^{-2}]$ - The concentration of sulfate was selected on the basis of that normally found in seawater, ~3000 ppm. Concentrations of sulfate in nature range from 0.2 to 100,000 ppm.⁽⁶⁾
 12. $[\text{CO}_2]$ - The concentration of CO_2 selected was based on its solubility in distilled water at room temperature, ~2000 ppm. Groundwater normally contains between 10 and 800 ppm HCO_3^- . Depending upon the pH, the CO_2 may exist in solution as CO_3^{-2} (pH >8.2), HCO_3^- (8.2 > pH >4.5) H_2CO_3 (pH >4.5).⁽⁶⁾
 13. $[\text{IO}_3^-]$ - The levels were selected based on previous studies.⁽⁷⁾ The mmole/g cement given in Table 5.1 is equivalent to 3 and 15 wt% $\text{Sr}(\text{IO}_3)_2$.
 14. $[\text{Ag}^+]$ - A minimal amount of silver may provide a sink for iodate "escaping" from the slightly more soluble, but less expensive, fixation form. The chosen concentration for Ag^+ was a factor of 10 lower than the lowest concentration of iodate added.
 15. $[\text{Pb}^{+2}]$ or $[\text{Sr}^{+2}]$ - An excess of cation common to the fixation material may inhibit the fixation material's dissolving in the free water of the cement. The chosen concentration was a factor of 10 greater than the lowest concentration of cation added with the iodate.
 16. $[\text{Ba}^{+2}]$ - The addition of barium may eliminate the exchange between the iodate fixation compounds and sulfate present in the cement by precipitation of BaSO_4 . The maximum allowable wt% of SO_3 in Portland Type III cement containing greater than 8% $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ is 4.5%.⁽³⁾ Twice the amount of barium required to precipitate this was added.

17. Solubility - To determine the role of the fixation material's solubility on the leaching mechanism, two iodate compounds of different solubilities were selected, $\text{Pb}(\text{IO}_3)_2$ and $\text{Sr}(\text{IO}_3)_2$. Their solubilities in water in terms of $[\text{I}]$ are 8.6×10^{-5} and 8.7×10^{-3} , respectively.

To screen these factors a Plackett Burman design⁽⁸⁾ was employed. This design contained a 27×28 matrix. The 27 factors included the 17 listed above and 10 unassigned factors. The latter were used for estimation of experimental error. Each of the 28 trials consisted of a unique set of factors as defined in the design. Statistical evaluation of the data from the 28 trials provided an estimate of the effect each factor had on the measured quantity.

The experimental procedure consisted of the following steps:

1. The specimen was prepared with the appropriate cement composition for each trial. Portland Type III cement was used in each case. The fixation compound was either $\text{Pb}(\text{IO}_3)_2$ or $\text{Sr}(\text{IO}_3)_2$.
2. Curing took place in a humid environment for the proper time period.
3. The specimens were removed from their molds and the ends sliced to approach ideal cylindrical geometries. The average dimensions of the specimen were 2.5 cm dia x 3.5 cm height.
4. The correct leachate composition was prepared for each trial. The specimens were suspended in their respective leachate and placed on a shaker. A thermoregulated shaker bath was used for the high-temperature trials.
5. The leachate volume and frequency of change are given in Table 5.2. The study ended after 30 days.
6. Analysis for the iodate ion in the leachate was carried out by reacting an acidified aliquot of the leachate with excess KI and determining the I_3^- ion spectrophotometrically. The quantity of material leached was expressed as the cumulative fraction material leached times the volume to surface ratio,

$$L = \left(\frac{\sum a_n}{A_o} \right) \left(\frac{V}{S} \right), \text{ cm}$$
 where
 - L = leach rate
 - a_n = iodate lost during leach period, t_n
 - A_o = initial iodate present in specimen
 - V = volume of specimen, cm^3
 - S = exposed surface area, cm^2 .
7. To decrease the time required for statistical handling of data, a programmable calculator was employed.

To date, samples from only the first two leachate changes have been completely analyzed and statistically evaluated. At a 95% confidence level the major effects were from temperature and CO_2 concentration for both leach periods. Further analysis of

TABLE 5.2. Leachate Change Frequency and Volume

Leaching Period t_n , days	Volume, ml
0.1	400
0.1	400
0.7	550
0.1	400
0.1	400
0.1	400
0.7	550
0.3	400
0.7	550
0.3 ^(a)	400
0.7	550
0.3	400
0.7	550
0.3	400
0.7	550
0.3	400
0.7	550
0.3	400
0.66	550

a. The remaining sequence of frequency and corresponding leachate volume was continued until completion of the study.

of Phase II data is necessary to more fully comprehend the chemistry of iodate leaching from cement and to evaluate the effectiveness of the Plackett Burman Screening Design in application to complex cement leaching systems.

IODINE TRAPPING - K. D. Weimers and R. D. Scheele

Extensive testing of different metal zeolites for trapping of I_2 has been carried out at the Idaho National Engineering Laboratory.^(9,10) This

included potential recycle of the beds by regeneration with hydrogen. Several aspects of this study are being continued here, in particular the behavior of methyl iodide and different stripping techniques.

The apparatus as now constructed is schematically represented in Figure 5.1. The water vapor generator consists of four water bubblers in series. A U-tube containing solid iodine acts as an I_2 generator. Both generators are placed in independently thermoregulated water baths. Methyl iodide is introduced similarly to the main air stream. Air flow through the generators is combined in a heated manifold. Additional ports are available in the manifold for NO and NO₂. A U-tube packed with glass beads preheats the gas to the reaction vessel temperature. After passing through the thermoregulated, quartz reaction vessel, a sample is collected into a caustic scrubber by means of a known split off ratio from the main exhaust stream. A condenser was placed prior to the main exhaust flow meter to eliminate water condensing in the flow meter. The caustic solution was analyzed for [I] using the iodide specific ion electrode.

Using this apparatus two runs were made using silver-exchange mordenite, both commercially and locally prepared. The test results and experimental conditions are given in Table 5.3. The lower than expected decontamination factor for the commercial material may be due to the flow rate and/or the column length. Tests of this material and of commercial silver-exchanged faujausite at 15 m/min face velocity

FIGURE 5.1. I_2 Loading ApparatusTABLE 5.3. I_2 Loading Conditions and Results

Experimental Conditions	Absorbent	
	Ag Mordenite, Commercial	Ag Mordenite, Local
Column dimensions	2.5 cm x 5.0 cm	2.5 cm x 5.0 cm
Face velocity	5 m/min	15 m/min
% H_2O	7	7
[I], effluent	2 g/m ³	2 g/m ³
Pretreatment	12 hr at 15 m/min face velocity and 7% H_2O	Same
DF at loading of 12 mg I/g Agm		>10 ³
at loading of 25 mg I/g Agm	50	59

and a column length of 15 cm are scheduled. These are to ascertain that the I_2 loading system confirms results previously reported, thus ensuring reproducibility.

IODIDE TO IODATE CONVERSION -

R. D. Scheele

Various possibilities for oxidation of iodide to iodate were discussed in the previous quarterly report.⁽¹⁾ Chlorine was the only oxidant which quantitatively converted

iodide to iodate without loss of iodine by volatilization.

Further examination of the alternatives suggested that modifications in apparatus or experimental conditions should be considered. Ozone, cerium (IV), and hot concentrated nitric acid were each re-examined.

Previous work using ozone as an oxidant resulted in iodine loss through the formation of a white solid in the vapor phase.⁽¹⁾ The reaction vessel was modified to greatly increase the contact time of the ozone with the

solution. Using 0.1 M KI solutions, iodine was still volatilized from acid solution but not from 0.05 M NaOH. Approximately 3% ozone in air was used as the oxidant. A possible mechanism involves the two-electron oxidation, reaction 1, followed by disproportionation of the hypoiodate, reaction 2, which is very rapid in alkaline solution.

However, the color of the basic iodide solution after contact with ozone shows that some free iodine is formed, possibly by reaction 3, which is followed by reactions 4 and 2.

In either case, hydroxide ion is necessary.

For the cerium tests, low-concentration KI solution, 0.025 M, was added slowly to the bottom of a refluxing saturated ceric sulfate solution. Unfortunately, iodine formed

and volatilized as it had in previous experiments at higher iodide concentrations. Kahn and Wahl⁽¹¹⁾ had had success converting microquantities of iodide to iodate. Therefore, we had hoped that working at very low concentrations of iodide would eliminate the iodine volatilization problem.

An experiment similar to the last one described was performed using refluxing concentrated 15.6M HNO₃ and 0.1M KI feed solution. Immediate volatilization of I₂ occurred.

Based on the results of these and previous experiments, ozone and chlorine appear to be the only suitable chemical oxidants for iodide. Both have disadvantages, however. Chlorine and the byproducts from its reaction with iodide are not compatible with commonly used plant materials. The ozone reaction must be carried out in a basic solution, which introduces an alkali such as sodium into the waste stream.

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6.0 INTERNATIONAL PROGRAM COORDINATION

K. M. Harmon - Project Manager

Promote waste management technology exchange between the United States and other nations through the establishment of an international technology information center at PNL.

SUMMARY

Collection, review, and summarizing
of significant documents continued.

A computerized reference retrieval
system was developed for the program,
and input of data was started.

7.0 WASTE MANAGEMENT SYSTEM STUDIES

J. V. Robinson - Program 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 permanent storage data base for seismic data has been designed, and the three computer programs to work with the data base have been completed. A trip was made to NOAA Headquarters in Boulder, Colorado, to meet the staff at NOAA and the Cooperative Institute for Research in Environmental Sciences (CIRES) and the USGS staff at Golden, Colorado. These three groups are working primarily on earthquake data bases, earthquake prediction, and earthquake risk.

The digitizing of coastlines, lakes, and rivers for the region from 116°W to 126°W and from 45°N to 49°N was completed. Improvements were made to the stereo plotting program (MAP3D) to increase its generality and flexibility; it can now read both formats of geographic files used by the other mapping programs.

An effort was begun to evaluate the potential applicability of kriging to site selection for geologic storage of high-level radioactive wastes. Kriging is a statistical method for estimating functions that describe spatially

distributed phenomena (e.g., ground-water elevation) from very sparse data. The first step in the evaluation process is to characterize representative data sets using kriging techniques. This was completed during this quarter using contours for Hanford water elevations. The kriging contours proved similar. Work was begun on the second step, evaluating the impact of a sparse data set on the kriging estimates using depth-to-basalt measurements.

The first comment draft of the knowledge/attitudes of Washington State residents was split into two report areas and was partially rewritten. The report on print media coverage of nuclear power and nuclear waste management was finalized. The data collection aspect of the analysis of DOE's communication process was completed. Analysis of TV coverage was continued, and most of the nuclear power news stories were content-analyzed this quarter.

Representing five different areas of the country, over 200 responses to the risk perception/risk evaluation questionnaire have been received. The data evaluation is in its final stages.

DATA BASE DEVELOPMENT FOR NUCLEAR
WASTE MANAGEMENT - H. P. Foote and
T. N. Bishop

This work is aimed at providing data and methods to quantitatively address technical factors such as seismic stability that are a concern in licensing and safety analysis procedures for waste repositories.

Present work is developing the data base and computerized capability to manipulate the data for practical applications.

Seismic Data Base

During this quarter a permanent storage data base for seismic data was designed, in a common format, and the three computer programs to work with it were completed. All data is stored on a disk instead of tapes so that information on earthquakes can be accessed or modified easily.

The three computer programs are:

- NEWQK1 Reads input data (cards or tape) and writes them on a disk in common format. In the common format, there are 60 parameters which use 85 integer words. The data are stored using File-Q, three earthquakes per 256-word block.
- QEDIT1 (a) Lists desired earthquakes (either the 18 key parameters or all 60 parameters).
(b) Edits the permanently stored data.

QBIN Creates our working rapid access files by reading the 18 key parameters from the permanent File-Q file and writing them on a binary file.

This permanent storage data base will provide the flexibility and completeness needed for future studies.

A trip was made to the National Oceanic and Atmospheric Administration headquarters in Boulder, Colorado, to visit the staff at NOAA and CIRES (Cooperative Institute for Research in Environmental Sciences) in Boulder and the U.S. Geological Survey (USGS) staff at Golden, Colorado. These three groups are working primarily on earthquake data bases, earthquake prediction, and earthquake risk. Common problems were discussed, and we presented our mapping and data base capabilities. We acquired a card deck of Chinese earthquake data dating from 1177 B.C., and hopefully more data will be exchanged in the future.

Work in the next quarter will concentrate on constructing a seismic risk map for the Pacific Northwest.

Mapping and Geographic Data Base

During this quarter we completed the digitizing of coastlines, lakes, and rivers from the USGS 1:250,000 scale maps for the region from 116°W to 126°W and from 45°N to 49°N. Figure 7.1 is a plot of all of the digitized features for this region. The

FIGURE 7.1. Plot of Digitized River, Lake, and Coastline Data for Washington State

features are digitized at a uniform spacing of 0.02 in. on the original maps. This interval is fine enough to preserve essentially all the accuracy present in the maps. A hierarchy of detail is established when the features are digitized. They are assigned to classes and ranks according to the type of feature and its importance. For example, a small stream would be in the general class of rivers with its rank set to 3, designating a stream. Structuring the data this way allows maps to be plotted containing the desired features at the level of detail required. The map files may then be considered with other digital files to form the final plot.

Figure 7.2 is a plot of the current state of digitized files for Oregon. The coastlines and lakes are complete. Work on the rivers and streams will continue in the next quarter.

Improvements have been made to the stereo plotting program (MAP3D) to increase its generality and flexibility. It can now read both formats of geographic files used by the other mapping programs. The procedures required to generate a stereo pair have been considerably simplified. It is now necessary only to specify either the left or right view, and the computer will work out the actual three-dimensional coordinates and angles for the oblique projection portions of the program. The program has been tested on a wide range of plotting problems and is now considered operational. We have recently finished a set of stereo pairs of the microseismic activity in the Hanford area. Several of the

satellite data processing programs have been converted to use the PDP-11/55 computer and its associated 80M byte disk. These programs now run about twice as fast as on the PDP-11/45. Since these programs typically take several hours of computer time, the improved speed represents significant savings.

KRIGING - P. Doctor

Kriging is a statistical method for estimating functions that describe spatially-distributed phenomena such as groundwater elevation and depth to basalt. The objective of this effort is to evaluate the applicability of kriging to site selection of geologic repositories for the permanent storage of high-level radioactive waste.

A potential repository must be evaluated from very sparse data. Core samples, which provide the most reliable information, are intrusive and costly; thus, it is desirable to minimize the number of cores taken. Kriging can contribute in two ways. First, kriging produces contours (having an associated measure of uncertainty) of the geologic formation of a potential site. This characterizes more completely than other contouring methods do. Secondly, given the existing data, kriging can be used to optimize the selection of additional intrusive sampling locations. This feature provides a rationale for selecting sample locations and could cut data acquisition costs significantly.

The most efficient way to evaluate kriging is by experimenting with

7.6

the techniques on representative data sets. The Hanford Wells data base proved to be the most accessible within the projected study time constraints. Water elevation tends to be a fairly smooth spatially distributed phenomenon, and since the Hanford Wells water elevation data set is fairly extensive, the September 1973 and January 1975 data were used to gain familiarity with the kriging techniques. The depth-to-basalt measurements from the well data base seem more characteristic of the type of data used to evaluate potential sites.

The kriging computations were performed using BLUEPACK, a computer package developed by the Paris School of Mines and installed at the DOE-Las Vegas computing facility.

The study evaluation process is perceived to be a two-stage procedure. The first step is to characterize the data sets using kriging techniques. The second is to observe the behavior of the technique as the number of data points decreases, thereby simulating an actual site-evaluation data set.

During the quarter the first step was completed. The kriging contours calculated for the water elevations are similar to the Hanford Wells data. The basalt and water elevation data show the same overall structure. This includes a linear trend over distance, the same form of variance structure, and roughly the same range over which the data are correlated. The water elevation data appear to be smoother than the basalt measurements, but

this may be due in part to the smaller (by half) size of the basalt data set.

Work was begun on the second step, evaluating the impact of a sparse data set on the kriging estimates using the basalt measurements.

NUCLEAR WASTE COMMUNICATIONS - S. M. Nealey, HARC

The first comment draft of the survey of Washington State residents was split into two report areas and was partially rewritten during this quarter. A report entitled Nuclear Knowledge and Nuclear Attitudes: Is Ignorance Bliss? has been written and has received study center clearance. This report discussed from which sources people have received their information about nuclear power, from which sources they would like to receive further information, and what areas of the nuclear fuel cycle people would like to learn more about. Additionally, the report discusses how much and what types of information people possess about nuclear power and how this knowledge relates to their attitude about continued nuclear power development.

A second report, entitled The Relationship of Human Values and Attitudes to the Nuclear Power Conflict, has been started and should be completed early next quarter. It discusses how human values, basic energy attitudes, and attitudes about specific nuclear power issues combine to determine one's attitude about the continued development of nuclear power. It was found that certain values, especially a

comfortable life, a world at peace, a world of beauty, family security, freedom, and national security were basic determinants of one's nuclear power attitude.

However, basic energy attitudes were also found to add explanatory insight beyond the values explanation. More specifically, attitudes about the relationship between electricity production and the economy, about the ability of conservation to forego increased electricity production in the future, and about the ability of new energy technologies to supply a large amount of electricity in the next 20 years are also important in determining attitudes about nuclear power. The survey revealed that some respondents who are against building nuclear power plants at this time still think that nuclear power plants should be developed and that the U.S. may need nuclear power in the future. This seems largely to be due to the belief (held by both pronuclear and antinuclear respondents) that the U.S. is going to have a serious energy shortage within the next 25 years. Finally, attitudes about specific nuclear power issues--primarily regarding power plant safety and nuclear wastes and secondarily regarding nuclear power pollution and reprocessing--were also of importance in determining attitude.

The report Analysis of Print Media Coverage of Nuclear Power Issues was finalized. A comparative analysis of print media coverage of coal stories to supplement this report was started. The content analysis rating form for coal stories has been completed, the sample has been chosen, and the content analysis has begun.

The data collection aspect of the analysis of DOE's communication process was completed during this quarter. Information on the DOE information dissemination network, on the types of information being disseminated, and on the types of information that potential users would like to receive from DOE has been collected. A report on these findings will be prepared during the next quarter. In general, it appears that very little information has been disseminated to the public regarding nuclear power, and almost no information about nuclear waste management is available.

Analysis of television news coverage of nuclear power, coal, and solar stories progressed rapidly at the end of this quarter. The content analysis form for nuclear stories was completed, and most of the nuclear power news stories have been content analyzed. All nuclear power videotapes have been received from the Vanderbilt Library, although only two out of nine coal videotapes have been received. The content analysis rating form is in first-draft stage. The content analysis of all three energy technology news stories should be completed next quarter.

The revisions of the November 1977 draft Public Policy Issues in Nuclear Waste Management were completed. Effort has continued to develop a questionnaire which could be administered to nuclear waste technologists. This questionnaire would elicit judgments regarding the importance and content characteristics of a subset of the issues explored in the larger analysis.

PUBLIC PERCEPTION AND EVALUATION OF RISKS - J. A. Hébert and M. K. Lindell, HARC

Data analysis of the combined risk perception/risk evaluation questionnaire was nearing completion during this quarter. Completed questionnaires have been received from over 200 respondents in five areas of the country. In keeping with the sampling plan, these respondents range from highly pronuclear to strongly antinuclear. Seventeen business, professional, technical, labor, and interest groups are represented in the sample. These groups have been aggregated into six clusters.

Analysis of the data showed that three social issues listed in the questionnaire were rated as significantly more important than the others. In order of importance these were energy shortage, environmental pollution and inflation. Although all respondents considered energy shortage to be a very important social issue, they disagreed significantly about the importance of environmental pollution.

Disagreement about the overall importance of environmental pollution could also be found in specific attitude items elsewhere in the questionnaire. These items largely deal with measures the respondents thought should be taken to reduce pollution from various sources. Although respondents generally agreed that coal and oil have disadvantages, there was little consensus that this implied that there would be a need for more nuclear plants. Those groups that

did not feel a need for more nuclear plants also endorsed the idea that antipollution technologies for coal and oil are more effective and less costly than the technology needed to control nuclear waste.

As was expected, the questions on nuclear waste tended to provoke the most extreme responses. Pronuclear respondents strongly agreed that nuclear wastes are no greater hazard than the pollutants from coal-fired plants or other modern hazards. Antinuclear respondents strongly disagreed. Two items addressed the need to avoid increasing reliance on certain power sources until pollution problems are solved. One item specifically referred to coal; the other referred to nuclear. Both items received moderate levels of agreement from the sample as a whole. The antinuclear groups strongly agreed that increased reliance on both coal and nuclear needed to be avoided until pollution problems are solved. They more strongly favored avoiding nuclear than coal. The pronuclear groups strongly disagreed that either coal or nuclear needed to be avoided. But they more strongly opposed the idea of avoiding nuclear power than of avoiding increased reliance on coal. In the context of other items in the questionnaire, these results suggest that differences between pro- and antinuclear respondents are more general than their beliefs and attitudes toward nuclear power. Much, though not all, of the difference can be attributed to more general beliefs and attitudes toward environmental pollution.

Analysis of the questions most closely related to the issues associated with nuclear waste repositories shows that the clusters of respondents differed substantially on some questions and very little on others. Questions in this section were designed to measure specific beliefs about the need for and the efficacy of three potential characteristics of a repository: site control, information transfer and site monitoring. Additional items concerned overall responses to the general concept of a repository. Highest consensus was found on items concerned with the need for site monitoring, site control and information transfer. Respondents generally agreed that these features are needed for a waste repository. Responses to items addressing the efficacy of these factors showed more disparity. Responses to questions about site control indicate that some respondents are neutral on this issue. All the clusters fall within the neutral range on the question about information transfer. On the issue of monitoring, respondent groups range from neutral to strong endorsement on the possibility that technological monitoring can

be maintained over hundreds of years. They appear less optimistic that monitoring will ensure that hazardous conditions will be corrected.

A similar range of responses was found for items addressing the safety of geologic storage and the confidence in technical experts' ability to select and construct a facility that is safe enough.

Concerns about repository safety were also evidenced in a section of the questionnaire in which respondents were asked the minimum distance they were willing to live or work from each of a number of energy-related facilities. No significant differences appeared among clusters in the distances reported for natural gas, coal and oil burning power plants, oil refinery and liquefied natural gas storage area. Significant differences, however, were found for insecticide factory, nuclear power plant and nuclear waste repository. The most pronuclear group reported a mean minimum distance of 40 miles from the repository. The most antinuclear group wanted a nuclear waste repository to be no closer than 350 miles.

8.0 WASTE MANAGEMENT SAFETY STUDIES

W. K. Winegardner - Project Manager

Evaluate the safety of alternative waste management schemes for viable nuclear fuel cycles up to the final disposal step; develop the methodology necessary to permit the safety assessment; identify portions of waste management systems which could benefit by safety design emphasis.

SUMMARY

Evaluation of the once-through fuel cycle waste management operations was started. Work was begun on methods for providing insights concerning trade-offs between management by dispersion/dilution and by accumulation/containment.

ONCE-THROUGH FUEL CYCLE ASSESSMENT -
P. J. Pelto

The system description of the once-through fuel cycle waste management operations and the proposed analysis methods summarized in the last quarterly report⁽¹⁾ form the basis for the evaluation which began during this quarter. A specific reference system is being evaluated that consists of one pressurized water reactor and one 3000-MT away-from-reactor storage basin and their respective waste streams and management processes. Parallel subtasks have been established for the evaluation of each of these systems. Information gaps in the system description are being identified and filled in where possible.

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

Work was begun on methods for providing insights concerning trade-offs between management by dispersion/dilution and by accumulation/containment. Assessment of noble gas management techniques is being used as the basis for this work. More than 20 radioisotopes of the noble gases xenon and krypton are produced as fission products within reactor fuel. A small percentage of fuel elements develop minute leaks during irradiation and handling, releasing some of the gases to the reactor radwaste management system. Because of their short radiological half-lives, the majority of these gases decay within the reactor system. Krypton-85 and xenon-133 are the only radioactive noble gases released to the atmosphere by routine reactor operation in significant quantities. However, most of the fission product ⁸⁵Kr is released from the fuel to the environment during fuel shearing and dissolution within the coprocessing facility.

Krypton-85 deserves special attention because of the difficulty of its control and its essentially nonreactive and mobile nature in the atmosphere. Although all the ^{85}Kr has been intentionally released to the atmosphere in the past, collection of about 86% of the ^{85}Kr and long-term storage (100 years) will be required by federal regulations after 1982.

The properties and origin of ^{85}Kr have been identified and its production in light water reactor fuel reviewed. This information will be used in the radiation dose calculation methodology. Alternative processes for recovering ^{85}Kr in a LWR coprocessing facility have been studied. Cryogenic distillation and fluorocarbon absorption appear commercially feasible. Fractional release values taken from the literature for the ^{85}Kr discharges to the atmosphere will be

incorporated into the comparison of radiation dose values. Shielding designs for the reference process are under review. From this review it is expected that occupational doses can be calculated from the operation and maintenance characteristics of the system.

Krypton-85 should be immobilized before storage. Alternative immobilization techniques have been identified and briefly described. A reference immobilization technique will be selected and used in predicting radiation doses to occupationally exposed individuals and members of the world population.

REFERENCE

1. A. M. Platt, compiler, Nuclear Waste Management Quarterly Progress Report January Through March 1978. PNL-2378-1, Pacific Northwest Laboratory, Richland, WA, August 1978.

9.0 WASTE ISOLATION SAFETY ASSESSMENT PROGRAM

H. C. Burkholder - Project Manager

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

- 1. develop the generic methods needed to assess the long-term safety of geologic isolation repositories*
- 2. obtain the generic and site-specific data necessary to apply the methods*
- 3. demonstrate the use of the methods for a specific site*
- 4. apply the methods to make safety assessments for sites of the National Waste Terminal Storage Program*
- 5. analyze societal acceptance issues and develop methods of communicating assessment results which enhance the rational resolution of those issues.*

SUMMARY

Work during the quarter continued the development of long-term safety assessment methods and the generic data base. Work was initiated to gather the data needed for a site-specific application of the methods. Several reports were issued, and a number of others are being cleared.

RELEASE SCENARIO ANALYSIS -

J. Greenborg and J. A. Stottlemire

The geologic consultants team continued work to characterize the potentially disruptive phenomena at nuclear waste repositories. Work also continued to develop computer software for repository simulation. A workshop for the geologic consultants team was held June 12 and 13 at the Battelle Seattle Research Center.

WASTE FORM RELEASE RATE DATA -

D. J. Bradley and R. P. Turcotte

The leaching studies continued for unclad spent fuel and glass waste forms doped with technetium, plutonium, americium, curium, and neptunium isotopes. The analysis of solutions from these experiments has been delayed due to a shortage in analytical personnel, equipment, and laboratory space. The characterization of the doped glass waste form samples is complete; the characterization of the unclad spent fuel samples is 50% complete.

Leaching studies for doped glass waste forms under flowing conditions were initiated. The test matrix will include three flow rates, three solutions, and two temperatures. Preparations were made to make electrical conductivity, pH, and Eh measurements on the leachate from these experiments in addition to counting radioactivity.

Preparations to acquire quantities of Rocky Flats incinerator ash for incorporation into transuranic waste forms were started. Leaching specimen formulations for incorporation of this ash into Portland cement, vinyl esterstyrene, urea-formaldehyde, and bitumen are being developed. Specimens with a wide range of ash content have been produced with each solidification agent in order to determine the maximum ash content that can be incorporated without adversely affecting waste-form integrity. A leaching system was designed that allows the IAEA/ISO leach test to be performed remotely with a minimum of sample handling.

RELEASE CONSEQUENCE ANALYSIS -

J. R. Raymond and J. K. Soldat

Work continued to interface and test the hydrologic and contaminant transport, and water-dose and air-dose models. All code conversions have been completed. A data management and model input system for release consequence analysis was designed. Draft documents describing all models and the data management system were completed.

Testing of the PATHS computer code was completed and preliminary work was done to assess the practicality of implementing a three-dimensional PATHS-type computer code. Sensitivity analysis and verification work continued with the DAVIS FE code. Good agreement has been obtained between modeling calculations and field measurements. The GETOUT and MMT were successfully cross-checked with one another.

TRANSPORT DATA - R. J. Serne

Characterizations of the surface area (B.E.T. and ethylene glycol), cation exchange capacities, bulk chemical analysis, and mineralogy of the "standard" rock materials (granite, shale, limestone, and basalt) were completed. Sorption experiments for strontium, cesium, technetium, plutonium and americium in "standard" groundwaters are under way by most of the subcontractors and have been completed by some.

Batch sorption measurements for strontium, technetium, iodine, cesium, neptunium, and americium have been completed on 12 minerals and 4 simulated groundwaters in both the sorption and desorption directions. These data are being correlated with the system properties and experimental parameter values.

Experiments were completed in determining oxidation states of plutonium in solutions in contact with PuO_2 and $\text{Pu}(\text{OH})_4$. Speciation determinations showed Pu(V) to be the predominant soluble species under oxidizing conditions.

A draft document has been completed that applies basic thermodynamic data to determine solution activities and mineral stabilities.

The high-pressure intact core sorption measurement apparatus has been fabricated and tested. The apparatus along with its auxiliary equipment is being assembled inside a laboratory hood so that radioactive experiments can be performed.

SOCIETAL ACCEPTANCE - A. H. Schilling

The revised version of a report on the management of social and economic impacts anticipated with a nuclear waste repository was completed. Two

additional reports on state and local regulation relevant to waste management and on compensation for the adverse effects of nuclear waste management projects are being revised.

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 trans-uranics at sensitivity levels which will provide useful information for the proper operation of a shallow land burial site.

SUMMARY

A large ^{90}Sr source has been obtained which should facilitate determination of bremsstrahlung and activation analysis detection limits. A conceptual design for a downwell tritiated water analyzer has been examined, and modifications are being considered to increase its versatility. A liquid scintillator solution with superior properties for analysis of tritiated water has been found, and further evaluations are in progress. Calibration of passive neutron detection techniques for quantitative analysis of plutonium oxides and fluorides in semi-dry soil has been completed, and continuation of the methodology at higher soil moisture levels is under way. A versatile well logging photon spectrometer has been designed for application in ^{90}Sr and transuranic well logging operations.

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

Some initial experiments on neutron activation analysis of ^{90}Sr have been completed. Results were inconclusive due to the small sample size, and a

larger ^{90}Sr source has been obtained. Studies on the determination of ^{90}Sr by measurement of the bremsstrahlung radiation and by thermal and fast neutron activation analysis will continue, utilizing this larger source.

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

Two different techniques are currently being evaluated for tritium analyses. Logging systems which will utilize either liquid scintillation spectroscopy or gas proportional spectrometry are being given primary consideration. Different scintillator solutions are being studied for optimum efficiency, sensitivity, and stability parameters with regard to the direct analysis of water samples. Gas proportional counting is being considered for analysis of tritium gas, tritiated water vapor, and tritiated water which has been converted to a gas sample. After these two techniques are optimized, more exotic techniques such as mass spectrometry and laser excitation analysis will be evaluated, and any improvements in sensitivity or detection limit will result in a rather stringent cost benefit analysis before incorporation of the new method.

DEVELOPMENT OF LOGGING SYSTEMS CAPABLE
OF MEASURING ACTINIDES -

R. L. Brodzinski

A versatile well logging photon spectrometer has been designed which can be utilized for the analysis of actinide gamma radiation, for the measurement of ^{90}Sr bremsstrahlung radiation, or in conjunction with a neutron source for in situ activation analysis of ^{90}Sr or transuranics. Attempts are being made to secure partial funding from other sources for the acquisition of this system.

A $^{239}\text{PuBe}$ source and a $^{238}\text{PuBe}$ source have been acquired for development of a technique to determine the soil moisture content in a burial ground. To determine transuranic element concentrations by any technique requiring the measurement of neutrons, it is necessary to know the effective moisture content of the matrix being analyzed, and commercial

moisture measuring devices have limited utility in high gamma-ray fields. These PuBe sources will allow moisture level determinations to be made even in gamma-ray environments of megarads per hour.

A $^{238}\text{PuO}_2$ source is being obtained as a calibration standard for both photon and neutron measurement techniques and may be used, along with the above PuBe sources, for studies involving activation analysis of transuranics in a burial ground.

Calibration of passive neutron detection techniques for PuO_2 and PuF_4 have been completed in semi-dry soil. These experiments will be continued at higher moisture levels to facilitate the eventual determination of unknown transuranics in areas of high gamma radiation and the cross calibration of active neutron monitoring methods for well logging in shallow land burial grounds.

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 waste.

SUMMARY

Analyses of parameters controlling the transport of radionuclides through partially saturated sediments are in progress. Distribution coefficients (Kd) have been determined for I, Se and Co in six synthetic groundwater solutions. Also, Kd values for Tc, Sr, Cs, I and Co have been determined in two additional salt solutions and found to correlate well with observed breakthrough in saturated soil columns. Unsaturated flow studies with several radioisotopes have begun. Observations with chloride tracers indicate that a considerable portion of the unsaturated column water is immobile and does not contribute to the solute transfer. Nonisothermal fluxes are shown to contribute to flow only under very dry conditions. In draining soils the contribution of thermal induced flow is insignificant. A field site and test facility has been established to monitor water and radionuclide transport. A wide range of flow situations can be simulated with the physical model that has been constructed.*

*For the background of this overall program and its specific contributing tasks, see PNL-2377-4, an earlier report in this series.

LABORATORY ANALYSIS - R. J. Serne,
G. W. Gee, and A. C. Campbell

Chemistry

Batch Kd's and unsaturated column effluent data were obtained and compared. Distribution coefficients for ^{125}I , ^{75}Se , ^{60}Co and $^{60}\text{Co-EDTA}$ were determined in selected sediments taken from the 300 North Burial Ground area. Sediment characteristics have been described in previous quarterly reports but are listed for reference in Table 11.1. Synthetic groundwater solutions used for contacting sediments are listed in Table 11.2. The distribution coefficients for I, Se, Co, and Co-EDTA were determined in triplicate after seven days of contact. Results are presented in Table 11.3.

Soil B was tested with two additional salt solutions. Their compositions were 0.15 M NaNO_3 , 0.01 M KNO_3 , and 0.002 M $\text{Ca}(\text{NO}_3)_2$ for the low salt and 0.15 M NaNO_3 , 0.15 M KNO_3 and 0.01 M $\text{Ca}(\text{NO}_3)_2$ for the high salt solutions, respectively. The high salt solution generally yielded the lowest Kd values. The data also illustrate that complexing agents such as EDTA can dramatically affect the

TABLE 11.1. Soil B Descriptive Parameters

1. Soil texture	sand, 87%; silt, 9.3%; clay, 3.7%
2. Particle density	2.85 g/cm ³
3. Sample bulk density	1.70 g/cm ³
4. Column diameter	5.4 cm, i.d.
5. Flow rate (saturated column)	0.51 cm/hr

TABLE 11.2. Composition of Solutions Contacting Sediments

	Na	K	Ca	Mg	HCO ₃	CO ₃	SO ₄	Cl	NO ₃
	ppm								
Solution	Soil A								
1	113	1.2	15	3.6	80	10	200	8	2
2	17	0.6	9	1.8	31	0	39	2	0.5
3	550	6.2	49	12.6	232	50	950	34	13
4	138	1.3	30	5.1	-	-	-	271	-
5	26	0.4	11	2.1	-	-	-	57	-
6	760	6.7	126	18.3	-	-	-	1485	-
	Soil B								
1	5.8	3.7	4.2	3.4	32	8	7	0.5	6
2	1.0	1.1	4.1	1.3	16	0	4.5	<0.5	1
3	23	17	6.4	11.3	80	24	36.5	0.8	32
4	7.4	1.2	38	5.6	-	-	-	99	-
5	1.8	0.6	8	1.3	-	-	-	21	-
6	46	6.2	185	22.6	-	-	-	474	-

TABLE 11.3. Batch Distribution Coefficients (Kd) for Soil B

Radionuclide	Seven Day Values, ml/g $\pm$ standard deviation							
	^{95m} Tc	⁸⁵ Sr	¹³⁷ Cs	⁷⁵ Se	¹²⁵ I	¹²⁵ I-EDTA	⁶⁰ Co	⁶⁰ Co-EDTA
Solution								
1	-	-	-	27 $\pm$ 2	7 $\pm$ 2	-	4570 $\pm$ 650	1.0 $\pm$ 0.2
2	-	-	-	26 $\pm$ 2	8 $\pm$ 1	-	2750 $\pm$ 200	1.2 $\pm$ 1
3	-	-	-	16 $\pm$ 3	11 $\pm$ 3	-	3670 $\pm$ 160	1.4 $\pm$ 0.3
4	-	-	-	38 $\pm$ 12	15 $\pm$ 5	-	11070 $\pm$ 6480	-
5	-	-	-	40 $\pm$ 2	10 $\pm$ 4	-	2735 $\pm$ 490	-
6	-	-	-	72 $\pm$ 10	4 $\pm$ 2	-	4090 $\pm$ 620	-
Low salt	$\sim$ 0	6 $\pm$ 1	268 $\pm$ 4	-	18 $\pm$ 22	4 $\pm$ 3	-	0.1 $\pm$ 1
High salt	$\sim$ 0	1 $\pm$ 0.2	25 $\pm$ 1	-	4 $\pm$ 6	$\sim$ 0 $\pm$ 3	-	0.9 $\pm$ 1

mobility and retention of radionuclides. The uncomplexed cobalt had K_d values of 1000, indicating very strong sorption and extremely low mobility. In contrast, the complexed cobalt exhibited very low sorption, indicating high mobility. Complexing agents present in low-level effluent stored in burial grounds will play a large role in determining the magnitude of nuclide transport at these sites.

Column studies with B soil continued. A 96-ml spiked high salt solution was added at 10 pore volumes to a B soil column with a saturated pore volume, V_0 , equal to 47 ml. Figure 11.1 shows the breakthrough curves for ^{95m}Tc , ^{85}Sr and ^{137}Cs through the soil column. The relative sorption of these three nuclides is illustrated by the retardation of strontium and cesium.

In contrast to previous observations with the low salt solution, breakthrough was observed for both strontium and cesium. However, the retardation compared well qualitatively with the observed K_d 's (0, 1, and 25) for technetium, strontium, and cesium, respectively.

A partially saturated column experiment was begun. Design of the equipment necessary to analyze unsaturated flow parameters followed closely methods described by Gaudet et al. (1977) and van Genuchten and Wierenga (1977). The equipment used is shown in Figure 11.2. The leaching solution is applied with a modified syringe pump to the top of the column. The bottom of the column is maintained at a constant suction by a vacuum chamber regulated at the desired vacuum. The maximum vacuum applied is controlled by the bubbling

FIGURE 11.1. Movement of ^{95m}Tc , ^{85}Sr , and ^{137}Cs Through Column B5

FIGURE 11.2. Apparatus for Measuring Solute and Radionuclide Movement in Unsaturated Soil Columns

pressure of a sintered metal plate located in the bottom of the soil column. Maximum suction with the sintered plate is >65 mbars. Samples are collected in an automatic fraction collector. A multichannel analyzer is used for counting gamma-emitting nuclides in the effluent. The number of pore volumes displaced through the soil is calculated by dividing the volume of effluent by the volumetric water capacity of the soil column. This water capacity is defined as the total amount of water (in milliliters) remaining in the soil column after the column has reached steady state. Generally 2 to 3 days are required to establish steady flow in sand columns when the percent saturation is less than 50%. This is due in part to the low flow rates. Some preliminary re-

sults (Figure 11.3) show the breakthrough curve for $^{39}\text{Cl}^-$ when the column was wetted to 43% saturation with the low salt solution. The data indicate that part of the soil solution is stagnant and does not participate in the flow process. The equation that can be used to describe noninteracting and nonlinear solute movement is:

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D_{ap} \frac{\partial^2 C_m}{\partial z^2} - v \theta_m \frac{\partial C_m}{\partial z}$$

where θ , C , and D_{ap} are volumetric water content, solute concentrations, and apparent dispersion coefficients, respectively, and where the subscripts m and im refer to the mobile and immobile or stagnant phases of soil water and $v = q/\theta_m$ is the mobile pore water velocity. For a semi-infinite column

FIGURE 11.3. Relative Salt Concentrations in Effluent of Partially Saturated Soil B Column. Curve is drawn for two runs with 0.01 M Cl^- pulse. Point at $C/C_0 = 0.5$ and 1.0 pore volume is theoretical breakthrough point for saturated column.

and pulse, input of solute the boundary and initial conditions can be written:

$$\lim_{z \rightarrow 0} \left(vC_m - D_{ap} \frac{\partial C_m}{\partial z} \right) = vC_0 \quad 0 < t < t_1$$

$$= 0 \quad t > t_1$$

lim

$$z \rightarrow \infty \quad C_m(z, t) = 0$$

$$C_m(z, 0) = C_{im}(z, 0) = 0$$

where C_0 is the concentration of the influent (g/cm^3). Analytical solutions to this equation have been obtained by van Genuchten and Wierenga (1976); however, numerical methods have proved to be entirely satisfactory (Gaudet et al., 1977). To simulate the observed salt concentration

distributions, values for D_{ap} , the fraction of mobile water $f = \theta_m/\theta$, and the diffusional mass transfer coefficient, α , must be known. Since these are not measured directly, a curve-fitting routine must be applied to the data, using experimental results. Data from Gaudet et al. (1977) for sand suggest that f (the fraction of mobile water) is lower than 0.6 when the water saturation drops below 50%. This implies that more than 40% of the water volume in partially saturated sand is stagnant and does not participate in solute transfer. In Figure 11.2 the flow rate, q , is 6.4 cm/day, the pore water velocity q/θ is 37.0 cm/day, and the velocity

of the mobile water fraction is estimated to be 67.3 cm/day. The data show that breakthrough occurs earlier than predicted for a saturated column which is transporting a noninteracting solute. It should be noted that the flux rate $q = 6.35$ cm/day for this partially (43%) saturated column is over 200 times smaller than the flux rate at saturation ($q = 1440$ cm/day); hence the exit time for 1 pore volume of unsaturated effluent at 43% saturation content is correspondingly retarded even though the solute comes through the column sooner than expected. These data are in agreement with previous findings of Gaudet et al. (1977) and van Genuchten and Wierenga (1977) and suggest that the model of mobile and immobile water in unsaturated soils is appropriate and that the immobile or stagnant water can be a substantial fraction of the total water present.

Physics

Matrix Potential Measurements.

Testing of sensors for measuring capillary pressure continued. A three-point (0, -0.1, -1000 bar) calibration was used to test 18 heat dissipation-type sensors for repeatability of measurement. Eight of these sensors were tested over a period of two months and demonstrated adequate calibration stability (coefficient of variation <5%). Part of the difficulty in obtaining repeatable calibration stems from the requirement of having a suitable porous material that can drain adequately and still maintain some stability. Several of the

calibrated sensors will be used in the field monitoring program. Development of a more stable sensor will continue and also modification of the heat dissipation probe size so that the unit can be used in near-surface soil applications. This will provide for measuring steep and rapidly changing water potential and water content gradients near the soil surface.

Nonisothermal Flow. Measurements are currently being made on evaporating soil columns to assess the enhancement of vapor transfer in soil due to coupled heat flow. Vapor flow enhancement is significant near the surface of drying porous material under thermal gradients but can be shown to be insignificant at greater depths in shallow land burial sites where the thermal driving force is only the geothermal gradient. The equations used to express thermally induced flow can be written as:

$$J_w = K(d\phi/dz) - \beta L(T)(dT/dz)$$

for unsaturated, nonfrozen soil conditions where:

- J_w = total water flux due to liquid and vapor transfer
- K = liquid conductivity
- $d\phi/dz$ = water potential gradient
- β = enhancement factor - combines effect of porous material and thermal gradient interactions on water vapor transfer
- dT/dz = thermal gradient
- $L(T)$ = temperature dependence factor for water vapor.

From literature values of water vapor temperature dependence, $L(T)$ can be expressed as: $L(T) = 0.0732 \exp$

($0.0547T$) when T is expressed in $^{\circ}\text{C}$. For a wide range of soils, the value of β has been found experimentally to vary from 1 to 2 and seldom exceeds 1.5. Data from our laboratory on sandy sediments indicate that β may be <1 under some circumstances. Table 11.4 shows computed water flow data in deep sediments above the water table that have known or estimated water transport coefficients.

Table 11.4 data indicate that the total water flow is only slightly affected at water contents $\geq 0.055 \text{ cm}^3/\text{cm}^3$ when the geothermal gradient is acting as a driving force. In this case the net flux is downward as a result of the dominant, gravity gradient. For a $\beta = 2$ the net downward flux of water is reduced $<3\%$. At the next lower water content value (0.040) there is a greater relative influence of the thermal flux. The net downward flux is reduced by as much as 30%, but even at this low water content the drainage component of flow due to

gravity still dominates. Gravity flow dominates even at -16 bars water potential for the B soil (Table 11.4). The conclusion from these calculations are:

1. Thermally induced water flow is insignificant at the normal, drained water content values in deep sediments.
2. When water contents drop below drained water content values due to plant root extraction or some other drying means, thermally enhanced vapor flow may tend to dominate the slow process; however, flow rates at these water contents are so low that transport upward due to vapor would seldom exceed 0.06 mm/yr (this rate is 4×10^{-4} times the estimated annual evaporation).
3. Larger thermal gradients would produce greater thermal flows, but significantly larger gradients exist only in the top 2 m of the soil profile.

TABLE 11.4. Thermal Flow Estimates at Shallow Land Burial Sites on Hanford Reservation

Water Potential, -bars	Water Content, cm^3/cm^3	K , (a) mm/yr	$d\phi/dz$, cm/cm	β	dT/dz , (b) $^{\circ}\text{C/cm} \times 10^{-4}$	J_w , (c) mm/yr
0.7	0.055	1.21	-1.0	1.0	4.6	1.18
0.7	0.055	1.21	-1.0	1.5	4.6	1.17
0.7	0.055	1.21	-1.0	2.0	4.6	1.15
4.1	0.040	0.205	-1.0	1.0	4.6	0.175
4.1	0.040	0.205	-1.0	1.5	4.6	0.165
4.1	0.040	0.205	-1.0	2.0	4.6	0.145
16.0	0.035	0.074	-1.0	1.0	4.6	0.044
16.0	0.035	0.074	-1.0	1.5	4.6	0.034
16.0	0.035	0.074	-1.0	2.0	4.6	0.014

a. Estimated from soil water characteristics of B Soil (see Table 11.1).

b. Geothermal gradient.

c. $J_w = K d\phi/dz - \beta L(T) dT/dz$.

There is still some uncertainty regarding thermally induced water flow influences on evaporation at the soil surface. In nearly all modeling efforts to date, isothermal or very simple thermal flow models have been used to predict evaporation from bare surfaces. Additional work will be required to estimate evaporation from a wide range of surface treatments and evaporation demand (atmospheric) conditions to better assess the utility of present models.

FIELD MONITORING AND DATA EVALUATION

A field site (buried waste test facility, BWTF) was selected adjacent to the 300 North Burial Grounds (SW 1/4 section Sec 21, T 11 N, R 27 E). The site was selected to study water and radionuclide transport under field conditions. In order to confine the radionuclide transport, seven caissons were installed to depths of 7.6 m (25 ft) at BWTF.

Figures 11.4 and 11.5 show the plan and elevation schematic diagrams of the field laboratory installation. Figure 11.6 shows the installation in progress, and Figure 11.7 shows the completed study site after caissons were backfilled with well-mixed, screened sand and a small weighing lysimeter (1.5 x 1.5 x 1.5 m) was installed. Neutron moisture probe access tubes were installed during backfilling and are located in all caissons. Figure 11.8 shows the neutron probe monitoring in progress.

A portable power generator and an irrigation pipeline and water reserve tank have been installed adjacent to the site for applying additional water to half of the caissons. The irrigation system is not yet complete, however.

Installation of calibrated sensors at the field site is in progress. Data has been collected on temperature, water content, and evaporation from the weighing lysimeter since June 1.

FIGURE 11.4. Field Installation Plan View

FIGURE 11.5. Field Installation Elevation View

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FIGURE 11.6. Caisson Installation for Field Laboratory in Progress

78D762-2

FIGURE 11.7. Completed Field Installation. Instrument caisson is below railing and hatch lid. Arrows show positions.

FIGURE 11.8. Monitoring of Soil Water by Neutron Probe in Lysimeters at Field Installation

Electrical resistance, thermocouple psychrometers and temperature sensors have been placed in the weighing lysimeter, and similar units are being placed in the other lysimeters. Data for water content in large lysimeters are being collected. The weighing lysimeter sensitivity has been shown to be slightly less than previously reported due to the response of the lysimeter to wind gusts. As a result, the weighing lysimeter sensitivity is approximately ± 0.03 cm water equivalent (± 2 lb weight change). This sensitivity can be improved by using an electronic damping circuit to stabilize the output signal.

The lack of AC power at the field site presently restricts the collection of evaporation data to daily and

weekly measurements. Since bare soil evaporation rates are normally low, this restriction should present no major problems. Mid-June evaporation rates from dry soil were observed to be less than 0.3 mm/day. Another measurement difficulty is the transport of sediment both away from and onto the lysimeter during high winds. A surface leveling device was installed after daily weight measurements were found to be affected by this wind transport action. The leveling device provides for accurate realignment and positioning of the zero depth periodically.

Wind direction, humidity, and precipitation are all presently being recorded on data logging equipment.

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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

Two open literature papers and one meeting abstract have been prepared. These papers present results from the study of zirconium and technetium organic complexes in soil media.

During this quarter, effort was concentrated on the study of organic complexes of technetium. Procedures for the synthesis and isolation of DTPA, EDTA, and citrate complexes of Tc(IV) and Tc(V) were worked out using gel permeation and ion exchange chromatography. The resulting complexes were used in soil K_d determinations in saturated soil systems. The stability of $\text{TcO}_2 \cdot \text{OH}_2$ to oxidation in soil media to TcO_4^- was examined. It was confirmed that $\text{TcO}_2 \cdot \text{OH}_2$ becomes soluble after short exposures to aerobic soil media, presumably being re-oxidized to TcO_4^- . Tc(IV) organic complexes have been found to exhibit very low K_d 's, thus increasing the mobility of Tc(IV) in saturated soil media. By contrast, a Tc(V) species [Tc(V) oxodicitrate] was strongly absorbed by soil and may provide a model for microbial fixation of technetium in soil.

IDENTIFICATION OF NUCLIDES AND COMPLEXING AGENTS - D. J. Wiggins and J. A. Franz

This task involves continual refinement of our existing data on complexes and nuclides. This has been continued throughout the study.

STUDY OF MOBILITY CHARACTERISTICS OF ORGANIC COMPLEXES - D. J. Wiggins and J. A. Franz

Procedures were adopted this quarter for the synthesis and isolation of technetium-organic complexes. Technetium VII as a pertechnetate (TcO_4^-) can be reduced in steps by mild reducing agents to Tc(V) and Tc(IV). The rate of reduction in the VII $\rightarrow$ V step (a) proceeds very rapidly, followed by a slower V $\rightarrow$ IV step (b):

The intermediate Tc(V) species of step (a) may thus be trapped if an excess of organic chelating agent is present coupled with the use of 1.0 equivalent of reducing agent, or the

reduction may be allowed to proceed through step (b) with 1.5 equivalents of reducing agents in the presence of an organic chelating agent to produce Tc(IV) organic complexes.^(1,2) A less effective method for producing Tc(IV) complexes is to treat TcO_4^- in 12 M HCl solutions with an organic complexant such as EDTA or DTPA.⁽³⁾ Both of these procedures were used to produce DTPA and citrate complexes of Tc(IV) and Tc(V). The complexes were isolated by use of chromatography on Sephadex G25m[®] columns (7 x 61 mm). The Sephadex column was fed aqueous eluent from a liquid chromatography pump. An automated fraction collector was used to collect the eluent from

the Sephadex column, which was then analyzed by scintillation counting. Figure 12.1 shows the separation of Tc(IV)-DTPA from unreacted TcO_4^- , and Figures 12.2 and 12.3 show the isolation of Tc(IV) and Tc(V) citrate complexes.

By these procedures samples of Tc(IV)-DTPA, Tc(V)-oxodicitrate and Tc(IV) dioxodicitrate were isolated and characterized by ultraviolet spectroscopy. Samples of 10 ml of 10^{-6} M Tc(IV) and Tc(V) citrate complexes were shaken with 5 g Hanford soil for 1 hr. K_d values were 0.026 for Tc(IV) O_2 citrate $_2^{6-}$, and 204 for Tc(V)-oxodicitrate. By comparison, TcO_4^- gave a K_d of 0.04.

FIGURE 12.1. Elution Curve of Technetium-DTPA Solution. Peak A represents 25% of the technetium as Tc-DTPA. Peak B represents 75% of the technetium as uncomplexed TcO_4^- .

FIGURE 12.2. Elution Curve of Technetium-citrate Solution. The peak represents 100% of the technetium as Tc(IV)-citrate.

FIGURE 12.3. Elution Curve of Technetium-citrate Solution. The peak represents 57% of the technetium as Tc(V)-citrate.

These results indicate that the Tc(IV) organic complex exhibited no absorption by the Hanford soil, similar to TcO_4^- . The Tc(V) complex was nearly quantitatively absorbed by Hanford soil. Technetium is known to be absorbed by microbial or enzymatic action in soil.⁽⁴⁾ Both organic complexes were stable to air oxidation and hydrolysis for 60 days.

To examine the stability of (insoluble) uncomplexed Tc(IV) to aerobic conversion to TcO_4^- , samples of TcO_4^- were reduced with Sn(II) (1.5 eq) to TcO_2 in the presence of Hanford soil. The procedure for K_d determination revealed a " K_d " value of 0.33, indicating substantial air

oxidation to TcO_4^- . The results of this work clearly show that citrate complexes stabilize the lower oxidation states IV and V of technetium and act to enhance the mobility of Tc(IV) in anaerobic soil systems. To our knowledge this is the first examination of the interaction of technetium-organic species with soils.

Work now in progress includes the further examination of EDTA and DTPA complexes of technetium. Materials are now on hand for the preparation of quadridentate niobium complexes, and work will begin on this as well as efforts under way to examine nickel-EDTA behavior in Hanford soils.

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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 as a large-scale decontamination technique for radioactive metal surfaces. Major program activities include 1) the establishment and operation of a demonstration decontamination facility and 2) laboratory studies to understand and optimize the decontamination process.

SUMMARY

Decontamination studies have continued, using sectioned glove box material and glove box wastes from Rocky Flats, a stainless steel power reactor check valve contaminated with ^{60}Co , and a cesium-contaminated foot clamp from a core-drilling apparatus. A nibbler device was used effectively to section the glove box material at a rate of 1 ft/min.

Evaluation studies of silicon-surface-barrier alpha detector systems have shown that a 2000-mm² detector can measure contamination levels as low as 5 dis/min distributed over a 5-cm² area. They can also measure Pu concentrations as low as 0.25 mg Pu/g of phosphoric acid.

The public information meeting held April 18-19 provided information to over 150 registrants on electropolishing as a method of decontaminating radioactive metal surfaces. The program included a film summarizing the progress of the decontamination program, distribution of a report giving a comprehensive review and explanation of the technology, and a tour of the electropolishing facilities.

DECONTAMINATION STUDIES

Stainless steel power reactor check valve parts were successfully decontaminated in our electropolishing facility. Exposed to primary coolant for 8 years, these valves were heavily coated with corrosion products--primarily ^{60}Co --and had radiation readings as high as 800 mrem/hr (Figure 13.1). The parts were electropolished in a phosphoric-sulfuric acid electrolyte using a temporary plastic tank to avoid cross-contamination with transuranics from the regular electropolishing tank. After electropolishing, the stainless steel parts were releasable, except for one component that had contamination incorporated in a weld (Figure 13.2).

Some difficulty was encountered in decontaminating a B-Cr-Ni part due to the formation of a corrosion film in the phosphoric-sulfuric acid electrolyte. This problem was controlled by using a phosphoric-hydrochloric acid electrolyte. Further studies are needed to develop an electrolyte that will effectively electropolish B-Cr-Ni alloys.

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FIGURE 13.1. Power Reactor Stainless Steel Check Valve Component Coated with Corrosion Products and Contaminated with ^{60}Co

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FIGURE 13.2. Power Reactor Stainless Steel Check Valve Components After Electropolishing in Phosphoric-Sulfuric Acid Electrolyte

Over 9000 lb of plutonium-contaminated glove box materials and glove box wastes were received from Rocky Flats Plant, Colorado for decontamination. The recently installed glove box line in the pretreatment facility is being used to section and prepare this material for decontamination in the 400-gal electropolishing facility. Decontamination studies on the prepared material are now under way.

A foot clamp component of a core drilling apparatus was decontaminated using vibratory finishing and special electropolishing techniques. This mild steel foot clamp, consisting of two identical blocks, 4 x 4 x 2 in., with a grooved semicircular depression on one side, was heavily corroded and contaminated with cesium. Pretreatment in the vibratory finisher using a fast-cutting ceramic medium removed the corrosion layer from all surfaces except in the grooves in the depression and reduced the contamination level from 400 to 24 mrad/hr. Subsequent electropolishing, using a phosphoric chromic acid electrolyte and a cathode constructed from 1/4-in. copper tubing that fit into the depression, further reduced the contamination level to less than 6 mrad/hr, which permitted reuse of the foot clamp.

PRETREATMENT STUDIES

Work with the vibratory finisher is continuing. A new, fast-cutting ceramic medium has been undergoing tests to establish its optimum operating frequency to maximize surface layer removal while minimizing wear of

the medium. This medium has a wear rate three times faster than other media tested, but has effectively removed epoxy paint. A sludge settling tank to remove spent abrasive and other surface material from the cleaning solution pumped through the vibratory finisher has arrived and been installed.

A nibbler device (Figure 13.3) has been used effectively to section glove box components in the pretreatment facility. This device, which uses a punch and die action, cuts through metal 160 mil thick at the rate of 1 ft/min. Although further studies are planned, preliminary indications are that this method of sectioning does not result in entrained contamination on the cut surfaces.

CONTAMINATION MEASUREMENT STUDIES

Two silicon-surface-barrier alpha detector systems are being evaluated. Their advantages are:

- a very low background counting rate (<10 counts/day)
- nearly 100% sensitivity for alpha particles
- a variety of detector sizes and shapes to permit monitoring of complex geometries.

One of these detector systems is a self-contained, high-sensitivity monitoring system consisting of two separate detectors with vacuum chambers and counting equipment. The other is a portable system for field monitoring with detectors that range in diameter from 0.3 to 5 cm (Figure 13.4).

Low-level measurement studies indicate that the 5-cm-dia (2000 mm² area)

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FIGURE 13.3. Nibbler Device Used to Section 160-mil-thick Stainless Steel Glovebox Components at 1 ft/min

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FIGURE 13.4. Silicon-Surface-Barrier Alpha Detector System with Detectors Ranging in Diameter from 0.3 to 5 cm

detector can measure contamination levels as low as 5 dis/min distributed over a 5-cm² area in less than 8 min. The surface-barrier detectors have also been used to measure the plutonium content of the electrolyte. Concentrations as low as 0.25 mg plutonium per liter of phosphoric acid can be detected.

PUBLIC INFORMATION MEETING

A public information meeting was held April 18-19 to provide information on electropolishing as a method of removing radioactive contamination from metal surfaces. Topics discussed included an in-depth review of electropolishing as a decontamination technique, examples of electropolishing decontamination projects at Hanford, and the plans for DOE-sponsored development of the technology. Representatives of government and industry also discussed commercial electropolishing technology and decontamination needs and potential applications of electropolishing in the nuclear industry. The PNL presentation included an 18-min film summarizing the progress of the decontamination program. Also, a 60-page report providing a comprehensive review and explanation of the technology was distributed.⁽¹⁾

A tour of the electropolishing facilities at the Hanford 231-Z Building (Figure 13.5) was attended by 116 of the 158 registrants, and 65 attended the Working Group Meeting for DOE Applications. Topics discussed at the Working Group Meeting included:

- design of electropolishing systems for decontamination applications
- in situ techniques and portable systems for decommissioning and decontamination applications
- decontamination of canisters and shipping casks
- power reactor applications
- measurement techniques and release criteria for disposition of cleaned material
- criticality safety considerations for fissile contaminants.*

*Additional information on electropolishing as a decontamination technique is available in AFCT/TFCT/ISFS Program - Technical Progress Report for the Period April 1 - June 30, 1978, compiled by O. F. Hill, Pacific Northwest Laboratory.

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FIGURE 13.5. Electropolishing Meeting Attendees Touring the 231-Z Building. Some large items decontaminated by electropolishing are displayed.

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