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**Nuclear Waste Management
Quarterly Progress Report
April through June 1977**

A. M. Platt

November 1977

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Battelle
Pacific Northwest Laboratories

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NUCLEAR WASTE MANAGEMENT
QUARTERLY PROGRESS REPORT
APRIL THROUGH JUNE 1977

Compiled by

A. M. Platt
Nuclear Waste Technology Program

November 1977

BATTELLE
Pacific Northwest Laboratories
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 Battelle, Pacific Northwest Laboratories. These programs are funded by the Waste Management, Production and Reprocessing Division of ERDA. The Commercial Radioactive Waste Fixation 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, BNWL-2290. This report is now published under a series number. During the remainder of 1977 it will be BNWL-2377-3 and BNWL-2377-4.

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1.0 DECONTAMINATION AND DENSIFICATION OF CHOP-LEACH CLADDING RESIDUES

R. L. Dillon and R. S. Kemper - Project Managers

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

The first decontamination run of leached BWR fuel hulls has been completed in the miniscale equipment. Complete removal of the oxide scale was achieved with an average weight loss of about 3 g/dm².

The detailed design of the HF reactor and aqueous reactor portion of the prototype fuel hull decontamination facility is complete. The layout of the chemical decontamination equipment is shown as planned for nonradioactive demonstration and later hot cell operation.

The Inductoslag ingot melting furnace to be used in hot cell densifica-

tion of chop-leach hulls is being installed for nonradioactive demonstration. Zircaloy melting experiments, with an Inductoslag melting furnace run by the U.S. Bureau of Mines, are summarized here. The work described includes methods for attaching the completed Zircaloy ingot to the ingot withdrawal mechanism. It also includes melting rate tests for Zircaloy-4 and Zircaloy-4/Inconel mixtures.

PNL work evaluating press compaction as a possible method of densifying chop-leach cladding residues is summarized.

DECONTAMINATION PROCESS

The treatment of surface oxidized Zircaloy with an anhydrous HF-Ar mixture at 600°C followed by a dilute, aqueous, organic acid solution has proved effective in the removal of the surface oxide and surface contamination without excessive removal of the metal. A miniscale process was set up in a shielded facility and has been operated with unirradiated Zircaloy testing to develop and improve the remote operation of the process. The flow schematic, equipment, and process have been previously described.⁽¹⁾

Several pieces of irradiated BWR cladding have recently been treated to determine the effect of irradiation on the behavior of the cladding during decontamination. The irradiated pieces of BWR cladding were leached, after mechanical fuel removal, in 95°C 8M HNO₃ for two 4-hr periods followed by a short, hot, nitric acid rinse. This leach removed most of the leachable fuel from the Zircaloy surface, 0.4 mg/dm² of ¹³⁷Cs from the inside surface and 7 μ/dm² ⁶⁰Co from the outside surface. Leached pieces of cladding about 10 cm long were found to read between 300 and 1200 mR/hr on a closed window CP at contact. Three pieces of leached tubing 3.3 cm long were cut by remote shears from a tube section which read 0.7 R/hr with a CP (closed window, contact). These three pieces were combined with nine nonirradiated oxidized tubing pieces and treated in HF-Ar gas mixture at 600°C for 1 hr. The

cooled pieces were then treated in 0.4M ammonium oxalate - 0.16M ammonium citrate - 0.1M ammonium fluoride - 0.3M hydrogen peroxide solution at 95°C for 30 min, rinsed in H₂O for 5 min, and the process repeated with clean solutions.

The resulting specimens and solutions showed that:

- Surface oxides were completely removed from irradiated and nonirradiated pieces.
- Nonirradiated pieces picked up a few percent of the β-γ contamination on their surfaces.
- Irradiated and nonirradiated samples lost 3.1 and 2.8 g/dm² respectively during the entire process.
- Some fine undissolved solids are present in the wash solutions; these can mostly be dissolved in concentrated HF made slightly oxidizing with HNO₃.

The detailed design was completed for the HF reactor and aqueous washer portion of the prototype fuel hull decontamination facility. The drawings were sent to the Materials Resource and Process Metallurgy Section at Battelle-Columbus for an engineering review. This portion of the facility is now out for fabrication bids. Design effort is now concentrating on the chemical make-up and spent liquid holding tanks and the associated piping, pumps, and instrumentation. Figure 1.1 shows the planned layout of the hull decontamination equipment as it will be placed in the 306W Building for nonradioactive demonstration and later in the 324 Building D hot cell.

FIGURE 1.1. Planned Layout of Chemical Decontamination and Densification Equipment in the 306 Building Mockup of the 324 Building D Hot Cell

DENSIFICATION PROCESS

The Inductoslag melting furnace⁽²⁾ has been delivered and set up in the D cell mockup area located in the 306W Building. Figure 1.1 shows the layout of the furnace and associated equipment. Figure 1.2 is an east-facing photograph of the area without the cell walls in place. Installation of the furnace is under way. The 2-ft-high stand on which the furnace rests simulates the difference in floor heights between the D cell floor and the floor of the D cell control and manipulator area in the 324 Building.

The Inductoslag melting furnace will require about 110 gal/min of cooling water to remove the maximum of 200 kW of heat it will dissipate. To keep the quantity of water introduced into the highly contaminated 324 D hot cell to a minimum, a recirculated water cooling system was designed. Delivery of the packaged cooling system is expected in August. The system will be installed next to the mock-up cell in the 306W Building as shown in Figure 1.1.

Melting experiments with an Inductoslag melting furnace continue under a contract with the U.S. Bureau of Mines in Albany, Oregon. Experiments

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FIGURE 1.2. Inductoslag Melting Furnace in the 306W Building
Nonradioactive Demonstration of "D" Cell Equipment

during the last quarter were directed toward 1) improving the melting rate of Zircaloy-4/Inconel 718 alloys and 2) developing a gripping method for ingot withdrawal.

It has been shown that mixtures of Zircaloy with Inconel and stainless steel melt slowly in the Inductoslag furnace, ~ 6 kg/hr, compared with ~ 20 kg/hr for pure Zircaloy.⁽³⁾ Calculations show that if the stainless steel end fittings were removed from the waste fuel hulls, the remaining mixture would be composed of about 99.5 wt% Zircaloy - 0.5 wt% Inconel for BWR cladding residues and 96 wt% Zircaloy - 4 wt% Inconel for PWR cladding residues. Therefore alloy compositions for melting rate studies were chosen at 0.5, 3.0 and 4.0 wt% Inconel with the balance of Zircaloy-4. Reject Inconel 750 plenum

springs were procured from a spring manufacturer for use as the Inconel in the alloys. The Zircaloy-4 consisted of 3.04 kg of chopped, reject cladding tubing and 1.5 kg of simulated end cap material. Pure calcium fluoride was used as flux.

The results of these melt rate studies are shown in Table 1.1. All three compositions melted at rates between 21 and 27 kg/hr, comparing favorably with heat Nos. 660 and 661, which were pure Zircaloy-4 melted at 23 and 27 kg/hr. Figure 1.3 shows an etched cross section of heat No. 662, Zircaloy-4 (4 wt% Inconel), melted at 25 kg/hr. Previous work⁽³⁾ showed that the Zircaloy-4 (4 wt% Inconel) alloy had a melt rate of only 4.7 kg/hr when a CaF_2 - MgF_2 eutectic flux was used. Observations at that time were that the ingot after melting had no

TABLE 1.1. Inductoslag Melting Experiments

Heat No.	Composition	Melt Rate, kg/hr	Melt Charge Starting Pad Configuration	Remarks
637	Zr-4; 3 wt% Inconel	--	Dovetail with "Z" strips + mixture of end caps and tubing	Aborted: insufficient inductive coupling to start melt. "Z" strips fused to melt stock for a good grip.
638	Zr-4; 3 wt% Inconel	21	Dovetail with "Z" strips + solid block of Zr-4, 2.8 cm thick	Withdrawal pad separated from ingot and then gripped, allowing continued withdrawal.
639A	Zr-4; 4 wt% Inconel	27	Dovetail with "Z" strips + solid block of Zr-4	Melt progressed without incident: dovetail grip ok for withdrawal.
639B	Zr-4; 4 wt% Inconel	19	Melt started on top of Heat 639A	Inconel springs loose in the charge rather than encased. Withdrawal difficulty encountered because of lack of bonding between Heats 639A and 639B. This accounts for the lower melt rate. Withdrawal movement due to gravity, some difficulty in removing ingot from the dovetail.
640	Zr-4; 0.5 wt% Inconel	27	Dovetail with "Z" strips + 40 grams of tubing with two 1-in. thick x 3 in. dia compacts of tubing on top	Gripping and withdrawal with dovetail was excellent. Fused but unmelted pieces of cladding were on the ingot bottom. Some difficulty in removing ingot from dovetail.
641	Zr-4; 0.5 wt% Inconel	--	16 pieces of cladding placed in and around the dovetail with two solid pieces (1903 g)	Aborted after losing contact with the withdrawal pad. Flux ran down and around the dovetail and did not have the strength for withdrawal.
642	Zr-4; 0.5 wt% Inconel	23	Preshaped Zr-4 starting block slipped into dovetail	Simulated end caps removed from melt stock to check their effect on melt rate--no real effect.
659	Zr-4; 4 wt% Inconel	16	3/8-in. steel stud; Heat 639B starting block (4.457 kg) + 875 g Zr-4 + 75 g Inconel springs	Aborted after 15 min because ingot pulled apart below junction of starting stub and metal added during melting
660	Pure Zr-4	23	3/8-in. Zr-4 stud + Zr-4 block	For pure Zr-4 stock for refabrication development and BNW personnel training. Melted by PNL personnel on USBM equipment.
661	Pure Zr-4	27	3/8-in. Zr-4 stud + Zr-4 block	For pure Zr-4 stock for refabrication development and BNW personnel training. Melted by PNL personnel on USBM equipment.
662	Zr-4; 4 wt% Inconel	25	3/8-in. steel stud + Zr-4, 4 wt% Inconel starting block (3.3 kg) + 1.037 kg of Zr-4, 4 wt% Inconel alloy	Melt progressed without incident. Simulated end caps removed from melt stock

FIGURE 1.3. Etched Cross Section of a Zircaloy-4 (4 wt% Inconel) Inductoslag Ingot Melted at 25 kg/hr - Heat No. 662

visible slag on the ingot side wall. Subsequent tests melting these alloys with the pure CaF_2 flux showed a thin uniform layer of flux on the ingot side wall, which provided a layer of insulation between the ingot and the water-cooled crucible. This layer was similar to but thinner than the flux layer found on the pure Zircaloy ingots. The tapering at the top indicated that the upper part of the ingot melted with a thicker slag layer (Figure 1.3). The metal at the top of the ingot, the last to solidify after feeding has stopped, is apparently free of unmelted Zircaloy.

Heat No. 662 was melted without the simulated end caps and demonstrates that end cap material in the

charge does not influence the melting rate. The Inconel springs were encased in the cladding tube sections as they might be obtained from the dissolver. Heat No. 639B was made with loose springs in the charge and showed no appreciable effect on melting rate.

Prior to this series of melting experiments, feeding tests were run to determine if charge separation occurred in the feed hopper during melting. These tests showed that the encased springs did not separate; however, the simulated end cap material did separate considerably, sinking toward the feed hopper bottom.

Withdrawal gripping experiments were continued using the modified dovetail design⁽⁴⁾ and a new small-diameter stud design.

Heat Nos. 637, 638, 639A, and 640 (see Table 1.1) were made using "Z" strips of Zircaloy sheet on the dovetail as shown in Figure 1.4. The results of those heats showed that: 1) bonding and successful withdrawal can be achieved if there is enough solid or compacted material placed on top of the "Z" strips to obtain an inductive coupling and start a molten pool, and 2) without the "Z" strips flux will flow around the dovetail and form a connection too weak for withdrawal (Heat No. 641).

An alternative mechanism for ingot withdrawal consists of a stud screwed into the water-cooled base as shown in Figure 1.5. This method requires a starting technique that consists of 1) melting small increments of solids; 2) allowing the mass to cool;

FIGURE 1.4. Z-Shaped Inserts for Gripping the Inductoslag Ingot

FIGURE 1.5. Threaded Stud Method of Gripping for Withdrawal

3) lowering the pad after cooling; and 4) repeating the procedure until about 10 to 13 cm of ingot length has been melted. Melting can then proceed normally.

It appears that either gripping method can be made to work, providing a charge with sufficiently high density is present to start a molten

pool. The choice of the ingot gripping method will depend on the ease of remote operation and the overall melting cycle time. The dovetail design allows the finished ingot to be knocked off the dovetail on the water-cooled starting pad, while the stud design will require the ingot to be unscrewed from the starting pad. The best method of operation will be determined in the 306W Building non-radioactive demonstration of the equipment that will be used in the D hot cell of the 324 Building.

Heat Nos. 639B and 659 were the Zircaloy-4 (4 wt% Inconel) alloy started on solid blocks of the same alloy. These ingots pulled apart at the junction between the starting blocks and the metal added. The reasons for this are not clear at this time. It is possible that a low melting eutectic mush was formed, causing a weak zone in the ingot. This phenomenon is being investigated further.

Heat Nos. 660 and 661 were pure Zircaloy-4 cladding tube melts made for refabrication development stock. These were melted by Pacific Northwest Laboratories personnel during training on the U.S. Bureau of Mines Inductoslag melting equipment.

Previous work^(1,5) described the Inductoslag casting of Zircaloy-4 pipe "tee" sections using molds of baked zircon sand and sodium silicate binder. Another molding process, the evaporative molding technique, was investigated this quarter using the Inductoslag melting process. This technique uses low-density foam polystyrene patterns having a refractory

wash coating. For casting, the patterns are surrounded with several inches of dry sand. When metal is poured, the polystyrene evaporates, forming the mold cavity.

Five evaporative castings of a wedge shape ($\sim 2.5 \times 3.75 \times 7.5$ cm) were made using titanium. These were poured under three conditions: full vacuum, one-third atmosphere, and one-fifth atmosphere. The casting made at full vacuum and one of the castings made at one-fifth atmosphere were acceptable. The remaining three castings were rejected because of shrink voids and gas pockets.

Investigations of other molding techniques for the Inductoslag melts of Zircaloy-4 are continuing. MISCO, a division of Howmet, Inc., MI, has a patented investment shell molding technique called "Monograp Mold." This process uses a wax pattern with built-up outer layers of carbonaceous shell. It is currently used for making titanium castings and will be investigated for making Zircaloy-4 castings.

In other contract work this quarter, press compaction received a limited evaluation as a method of densifying chop-leach cladding residues. Although press compactations of zirconium and zirconium alloys are routinely made in industry on relatively clean, oxide-free material, very little information is available on the compaction of zirconium materials that have an oxide coating and brittleness typical of goal-exposed PWR cladding hulls emerging from the chop-leach process. Using press

compaction equipment at the U.S. Bureau of Mines in Albany, Oregon, several compacts were made from unirradiated Zircaloy-4 PWR cladding (2.5-cm lengths) with oxygen levels ranging from a clean, nonoxidized condition to a very brittle, highly oxidized condition (Table 1.2).

The tubing was steam autoclaved in 91-cm lengths and sheared into 2.5-cm lengths for compacting. The compaction tests were performed in a

cylinder 10 cm in diameter, using 750 g of hulls (starting height of 10 cm) for each run. A slow rate of compaction was used to allow the recording of the press ram pressure and displacement.

A plot of percent volume reduction versus unit compaction pressure is shown in Figure 1.6 from test data. The plot shows that more than 90% of the volume reduction is accomplished with a unit pressure of 15,000 psi, although the compacts were pressed to 45,000 psi before being ejected from the die. Some cladding lengths flaked from the compact surfaces while being ejected from the die and during a subsequent 60-cm drop test, but the compacts remained reasonably intact. This was true for all four groups of material.

TABLE 1.2. Oxygen Levels for Cladding Hulls Used in Press Compaction Tests

Designation	O ₂ Level
Clean (as manufactured)	1200 ppm
Low O ₂	34 to 80 mg/dm ² gain
Medium O ₂	50 to 112 mg/dm ² gain
High O ₂	3 to 870 mg/dm ² gain

FIGURE 1.6. Volume Reduction Achieved by Press Compaction of Clean and Oxidized Unirradiated PWR Cladding Hulls

A small residue of fines was generated in compactions of the low and medium oxidized material with a con-

siderable quantity of fines being produced with the highly oxidized material.

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

R. L. Gordon - Project Manager

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

SUMMARY

A particle generation and dispersion apparatus was designed and assembled for use on the laboratory mock-up system. Initial testing of the apparatus was done. Design and planning activities were conducted in support of radionuclide sampling and analysis. The subcontract with Science Applications, Inc., was completed.

LABORATORY MOCK-UP SYSTEM -

H. G. Rieck, Jr.

A major component of the laboratory mock-up system for measuring trapping efficiency of selected filters for submicrometer particles is a particle generation and dispersion apparatus. The approach chosen for application on this program uses the micronizer principle. Figure 2.1 is a schematic diagram of this apparatus.

The particle disperser utilizes six jets of air to move a mass of particles around a circular cavity. Centrifugal force keeps the particles tumbling along the outer wall of the cavity. This action causes fracturing of the particles by contact with the cavity wall and other particles.

SECTION A-A

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FIGURE 2.1. Schematic Diagram of Particle Disperser for the Laboratory Mock-Up System

As a particle becomes smaller, centrifugal force on the particle decreases to the point where it becomes airborne in the radial movement of the jet air toward the center. The particle then moves from the grinding zone into the settling chamber.

Six hypodermic needles, 26-gage, are inserted through the wall of a lucite tube 2-1/2 in. OD x 2 in. ID x 1/2 in. high. The needles are

inserted through holes drilled slightly undersize at 41° with the radius at the point of insertion. The ends of the needles are flush with the inside wall of the cavity. The 1/2 in. section of the tubing is the grinding cavity and is welded to an 8 x 8 x 3/8 in. thick lucite plate equipped with three leveling screws. Three 4-40 screws are located through the bottom plate in the cavity section to adjust the height of inserts in the cavity bottom. Distance between the cavity bottom and the needles can be adjusted for optimum grinding action. The shape of the cavity bottom can also be altered by changing inserts.

The settling chamber is a lucite tube 1 1/2 in. OD x 1 1/4 in. ID x 24 in. long, equipped with a flange at the lower end. The flange is recessed to fit down over the cavity and is held in place by six 6-32 screws bolted to the bottom plate. The bottom of the settling chamber contains a lucite insert 2 in. long with a tapered hole 3/4 in. ID at the bottom and 1 1/4 in. ID at the top. This insert is a transition between the cavity outlet and the settling chamber.

The parameters which affect the ultimate particle size generation have not been fully evaluated. The speed of particle movement around the cavity is controlled by the velocity of the six air jets. Particle sizes are classified in the settling chamber by the vertical air velocity. A particle will be moved out of the chamber if the Stoke's settling velocity is less than the vertical

air velocity in the settling chamber. The vertical air velocity is governed by the volume output of the air jets and the cross section area of the settling chamber.

The particle sample is introduced into the grinding cavity by removing the settling chamber. After reassembly, air pressure is applied to the jets and proper flow is adjusted by use of a rotameter. Typical total air flow through the six jets is 1 l/min.

The material to be used for particulate trapping efficiency measurements on candidate filter materials is irradiated calcine from WSEP run PW7-a. Thirty 1-g ampoules of that material were irradiated in the Washington State University TRIGA reactor for use in planned experiments. Radionuclide counting will be used to compare the amount trapped on the test filter to that collected in a HEPA filter, assumed to be 100% efficient.

RADIONUCLIDE SAMPLING AND ANALYSIS - F. P. Brauer

Specifications were prepared and orders placed for purchase of tritium stack monitoring equipment.

A conceptual design was established for gaseous radionuclide sampling of the 324 Building process off-gases during nuclear waste vitrification experiments. Separation of particles, HT, HTO, organic tritium, $^{14}\text{CO}_2$, CO, organic ^{14}C , $^{129}\text{I}_2$, organic ^{129}I and gaseous ^{106}Ru is feasible. Detailed equipment design is required.

Preliminary plans were initiated for preoperational environmental sample collection and analysis. Measurements of potential effluent radionuclides in the environment will be conducted prior to the demonstration run to establish baseline values.

Multichannel analysis equipment required for development and testing of radioactive effluent monitoring detectors and methods was delivered, tested, and placed in operation. The equipment will be used for both laboratory and in-plant (324 Building) measurements. The equipment is being interfaced to a PDP-11 minicomputer to expedite data handling and analysis.

The extent of involvement of this program with monitoring requirements for alternative waste disposition processes has not yet been determined. However, in preparation for possible

expansion of the technical activities of the program, plans were made for preliminary measurements at an irradiated nuclear fuel storage site. No data on the composition of gaseous effluents from such facilities are available. Primary consideration was given to measurements of ^3H , ^{14}C , ^{85}Kr , ^{99}Tc , $^{134,135,137}\text{Cs}$, and ^{129}I .

SCIENCE APPLICATIONS, INC., CONTRACT

The final report for the Science Applications, Inc., subcontract, "Critical Assessment of Methods for Treating Airborne Effluents from High Level Waste Solidification Processes," was received. The project was satisfactorily completed. The report has been reviewed by Pacific Northwest Laboratory personnel and will soon be submitted for final clearance prior to publication and distribution.

3.0 TRU WASTE FIXATION STUDIES

J. H. Jarrett - Program Manager

The objectives of this program are to: 1) develop candidate criteria for the immobilization of TRU wastes; 2) provide technological bases needed to support the adoption of those criteria; 3) evaluate waste forms from current commercial and ERDA TRU waste programs relative to the recommended criteria; and 4) develop improved waste management systems and final waste forms if necessary.

SUMMARY

The thrust of this program for the remainder of FY-1977 has been directed toward a further understanding of the scope of TRU waste management and related studies throughout the U.S. and a resulting indication of needed approaches in the areas of criteria and TRU waste form development.

Waste form characterization and development work is continuing at an expanded level. A contract is in place with Brookhaven Labs regarding concrete waste form characterization work.

CRITERIA DEVELOPMENT - M. O. Cloninger

Investigations regarding TRU waste management programs in the U.S. have identified five major R&D areas supported by ERDA, EPA, and NRC:

1. Criteria Development
 - Commercial TRU Program (ERDA)
 - WIPP Acceptance Criteria (ERDA)
 - Environmental Protection Criteria (EPA)
 - HLW Criteria Development (NRC)

2. Waste Classification System Development

- Based on final disposition needs

3. Waste Volume Reduction Technology and Fixation Products Development

4. Transportation Studies

- Risk Assessment
- Logistics and Economics

5. OWI Program

- Directed towards HLW, but considers TRU.

These program areas are related either by common subject matter or methodology used.

Ongoing work includes organizing developmental efforts for the timely generation of generic TRU waste management criteria that are widely reviewed and accepted.

WASTE FORM CHARACTERIZATION -

W. A. Ross and E. T. Sherman

Several TRU ash residues have been found which represent a broad variety of compositions. Tables 3.1 through 3.3 list the compositions for the Rocky Flats plutonium recycle TRU ash, the HEDL Acid Digester TRU ash and the Mound Laboratories Cyclone Incinerator TRU ash, respectively. The BNW

TABLE 3.1. Rocky Flats Plutonium
Recycle TRU Ash

Oxide	wt% Oxide
Al ₂ O ₃	5.00
BaO	0.80
B ₂ O ₃	2.27
CaO	4.93
Cr ₂ O ₃	3.20
CuO	0.87
Fe ₂ O ₃	7.93
PbO	0.73
MgO	3.93
MnO	0.13
NiO	0.67
P ₂ O ₅	0.80
K ₂ O	0.67
PuO ₂ (substitute UO ₂)	3.53
SiO ₂	61.00
Na ₂ O	1.20
Ta ₂ O ₅ (substitute V ₂ O ₅)	0.87
SnO	0.20
TiO ₂	2.93
C(a)	0.0

a. Carbon can be burned off at 800°C.

TABLE 3.2. HEDL Acid Digester TRU
Ash

Component	wt%
SiO ₂	29.00
CaO	24.00
MgO	15.00
Al ₂ O ₃	12.00
TiO ₂	5.50
ZnO	3.00
Fe ₂ O ₃	1.25
S	10.75

TABLE 3.3. Mound Cyclone Incinerator
TRU Ash

	Ash 11A ²	Ash 10A ²	Ash 12A ²
SiO ₂	35.08	14.33	31.44
Al ₂ O ₃	37.60	41.57	23.24
CaO	7.14	8.40	1.82
Fe ₂ O ₃	5.72	14.30	4.29
MgO	9.95	3.32	3.32
Cr ₂ O ₃	2.92	9.62	2.92
TiO ₂	6.67	15.01	5.00
MoO ₃	0.045	---	0.03
NiO	0.636	1.27	1.27
ZnO	3.73	4.98	1.24
CuO	0.125	---	0.25
B ₂ O ₃	0.032	---	
SnO	0.057	1.02	
Na ₂ O		0.67	
MnO		0.65	

ash composition was described in the previous quarterly report of this series. These TRU ashes have been simulated, and vitrification efforts are under way on each.

Most work to date has been done on the BNW ash. Melt 77-153 (26.4 wt% SiO₂, 12 wt% B₂O₃, 9.6 wt% Na₂O, 6 wt% K₂O, 6 wt% Fe₂O₃, 40 wt% Ash) is the best glass made from this particular ash. The melt has low leachability [pH 9 (19 hr), 0.18 wt% loss; pH 4 (19 hr), 0.54 wt% loss; Soxhlet (24 hr), 1.09 wt% loss], and its viscosity is below 200 poise at 1090°C. The ceramic melter, which operates at 1100°C, requires that the melt be below 200 poise.

The Rocky Flats ash forms a glass readily due to a high SiO₂ content. The melts to date are quite fluid

(<100 poise) at 1050°C, dark and homogeneous, and most have low leach rates in pH 9 and pH 4 solutions. The leach rates are 0.09 wt% loss and 0.20 wt% loss, respectively for 1 g, -40 to +60 mesh samples leached for 19 hr at 25°C. Soxhlet leach rates are running somewhat high at 2.2 wt% loss over a 24-hr period. Details of these types of experiments have been previously reported in a formal report.⁽¹⁾

The acid digester ash contains almost 11 wt% sulfur, which may be a problem. The sulfur combines with either the sodium (from the frit) or

the calcium (from the waste) to form a thin, clear liquid melt on top of the glass. When cooled, the sulfate phase is a white, relatively insoluble mass of crystals. Carbon is now being tested as a reducing agent to prevent the sulfate from forming.

Ongoing work includes glass forming and characterization using the Mound incinerator ash.

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4.0 KRYPTON SOLIDIFICATION

G. L. Tingey - Project Manager

The objective of this program is to determine the feasibility of alternative techniques for storing krypton in a solid matrix. Two techniques are currently being investigated: dissolution in a glass matrix and entrapment in solids during high-rate sputtering.

SUMMARY

Krypton solubilities have been determined for several glass types at pressures of 193 MPa (1905 atm). The solubility of krypton in these glasses is significantly less than required for a viable storage technique for radioactive krypton even though the gas dissolved is retained to temperatures of 400 to 700°C. Previous data indicate that gas solubilities increase rapidly with increasing void volume. This phenomenon will be evaluated by measuring the krypton solubility in low density glasses.

A krypton loading of about 11 at% has been achieved in an amorphous metal alloy of about 87% Fe/13% Y. The krypton content is over twice that which we have achieved in the crystalline metals examined to date. The high krypton trapping efficiency is attributed to the larger void spaces in the amorphous metal deposits. Krypton release rates from this sample are found to be very low below 600°C, and the amorphous metal thus appears to be very suitable for storage of radioactive krypton.

DISSOLUTION OF KRYPTON IN GLASS -

G. L. Tingey and G. B. Mellinger

During the present quarter, high-pressure krypton loading of various samples was performed by Allied Chemical Company at the Idaho Nuclear Engineering Laboratory (INEL). Samples were subjected to a pressure of about 193 MPa (1905 atm) of krypton for periods of 1 and 24 hr. The weight increase of these samples was measured at INEL and the krypton contents, calculated from the weight increase, are shown in Table 4.1. Also

TABLE 4.1. High-Pressure Krypton Loading (samples loaded at 510°C; 197 MPa; 24 hr)

Sample	Krypton Loading [cm^3 (STP) Kr/g glass]	
	Based on Weight Gain	Based on Gas Chromatography
7930 Vycor	6.25	4.45
Silica Gel #62	3.12	1.43
Silica Gel #81	2.38	0.581 ^(a)
Silica Gel #12	0.13	0.052
7913 96% SiO_2	1.06	0.866
7940 Fused SiO_2	0.91	0.283
Quartz Fibe.	5.51	0.315

a. Outgassing measurements only made to a temperature of 495°C due to equipment malfunction.

shown are krypton contents determined from gas release measurements conducted in our laboratory. The difference between the weight gain and the krypton released is not completely accounted for. Small quantities of H_2 , CO , and CH_4 were released, but the mass from these gases is far too small to account for the difference. In the gas release measurements, the evolved gas was passed through a trap maintained at $195^\circ K$. At this temperature, H_2O and other low-vapor-pressure compounds would be condensed. The presence of significant quantities of such species could account for the additional weight gain. It does not appear that significant quantities of krypton should remain at the maximum release temperature, but if this occurred it could also account for the difference. For our analysis we have used the krypton released as the correct measure of krypton content, rather than the one calculated from weight gain during the loading process.

The fused SiO_2 (7940) and the quartz fibers are basically the same material, but with different diffusion paths. The similar krypton loadings for these two samples indicate that diffusion is rapid enough to approach saturation in both samples. The solubility of krypton in these samples follows the pattern of decreasing solubility with increasing molecular weight observed by Perkins and Begeal⁽¹⁾ for helium, neon, and argon. These solubilities, extrapolated to 193 MPa are as follows:

He = $17 \text{ cm}^3 \text{ (STP)/cm}^3 \text{ of } SiO_2^{(1)}$
 Ne = $16 \text{ cm}^3 \text{ (STP)/cm}^3 \text{ of } SiO_2^{(1)}$
 Ar = $7.6 \text{ cm}^3 \text{ (STP)/cm}^3 \text{ of } SiO_2^{(1)}$
 Kr = $0.66 \text{ cm}^3 \text{ (STP)/cm}^3 \text{ of } SiO_2$
 (this work)

Figures 4.1-4.3 show the krypton released from the samples as a function of temperature. All samples underwent a linear heating of $200^\circ C/hr$ from 25 to $1000-1100^\circ C$. The temperature was then held constant at the latter value to ensure that all krypton was released.

The silica gels and Vycor powder showed the maximum release at temperatures of 300 to $550^\circ C$. The 96% SiO_2 , fused SiO_2 , and quartz fiber showed maximum release rates at temperatures of 400 to $750^\circ C$. The higher temperature release of the latter materials

FIGURE 4.1. Total Krypton Release as a Function of Temperature

FIGURE 4.2. Total Krypton Release as a Function of Temperature

is probably due to their lower surface to volume ratio. The reason for the very significant differences in krypton loading of the various silica gels and Thirsty Vycor powder may be related to differences in their surface area or pore diameter. These parameters, taken from manufacturers' data, are shown below:

	Grade 12	Grade 81	Grade 62	Vycor
Surface area, m ² /g	750	600	340	250
Pore volume, cm ³ /g	0.4	0.7	1.1	0.16
Average pore diameter, Å	22	60	140	400

FIGURE 4.3. Total Krypton Release as a Function of Temperature

In the case of the silica gels the increase in pore volume also follows the trend of increasing krypton loading. However, the Thirsty Vycor does not fit this pattern.

The differences in the solubility of krypton found for the various glasses are probably due to fundamental structural differences among the various samples, or to incomplete saturation of the glasses. For example, large differences are found between the krypton content of the 96% SiO₂ and of the Vycor samples. Both are the same material but differ in surface area and pore volume. The

lower loading of the 96% SiO₂ may be due either to incomplete saturation of this glass or to inherent differences in solubility because of a difference in pore volume.

The krypton loadings of all the samples are disappointingly low. Based on krypton release measurements of samples loaded at 1 atm, reported in the April 1977 quarterly report, loadings on the order of 40 cm³ of Kr (STP)/cm³ of glass should have been achieved. That this level was not reached confirms the previously identified probability that surface adsorbed krypton may have contributed significantly to the total krypton released.

For storage of radioactive krypton in glass to be feasible, solubilities must be increased. Glasses with low inherent density have been found to have increased gas solubility compared with more dense glasses. This is due to a larger void volume as a result of a more open structure. Glasses of this type will be obtained and tested in an attempt to achieve higher krypton loadings. In addition, experiments will be conducted in which krypton is bubbled through molten glass. This technique may result in a low-density glass with larger amounts of krypton dissolved or trapped in pores. Measurements on these samples will be used to determine krypton loading and the temperature dependence of the krypton release.

KRYPTON ENTRAPMENT DURING SPUTTERING - E. D. McClanahan and M. A. Bayne

One objective of the work for FY-1977 was to prepare a body containing about 10 at% krypton gas. This goal was reached and exceeded this quarter with the preparation of an iron alloy of atomic composition Fe₇₆Y₁₂Kr₁₁Xe₁. The deposit also contains low-level impurities which were present in the steel target and yttrium casting. The deposition parameters are given in Table 4.2. X-ray diffraction data indicate that the deposit is "non-crystalline." Detailed radial distribution analyses are required to distinguish between microcrystalline and amorphous structures, and this analysis has not been conducted. The macroscopic fracture surface is similar to a normal glassy fracture surface, giving evidence for the amorphous state. The deposit weighed 126 g and contained 5204 cm³ at STP of inert gas. The measured density of the deposit is 6.30 ± 0.03 g/cm³, which is 87% of the density of a crystalline alloy of 13 at% Y - 87 at% Fe not containing gas and assuming a linear mixing rule. This is close to the density of physically generated models of dense random packed (drp) hard spheres, which is about 86% of that of crystalline close-packed (cc-p) structures.⁽²⁾

The electrical resistivity of a portion of the deposit containing very small gas concentrations (<1 at%) was

TABLE 4.2. Deposition Parameters, GT-25

Plasma voltage: 40 volts
 Plasma current: 36 amps
 Target voltage: 2450 volts
 Average target current density:
 5.6 mamp/cm²
 Substrate voltage: 242 volts
 Average substrate current density:
 4 mamp/cm²
 Gas: Kr-9.5% Xe
 Gas throughput: 1.1 cm³/min at STP
 Gas usage rate: 7.2 cm³/min at STP
 System pressure: 0.53 Pa (4.0 x
 10⁻³ Torr)

measured at room temperature, and a value of 303 $\mu\Omega\text{-cm}$ was obtained. This indicates that the electron mean-free-path is about one atomic diameter, suggesting the noncrystalline state. Using this value and the Wiedemann-Franz law,⁽³⁾ a value of the thermal conductivity of $2.4 \times 10^{-2} \text{ W/cm}\cdot^\circ\text{K}$ is predicted. This result will be verified when a sam-

ple is deposited thick enough to measure the thermal conductivity. A single gas release was measured on a free-standing chip from the deposit, and release rates were very low--below 500°C.

Table 4.3 is a compilation of maximum gas loadings for several of the metals tested to date. The large increase in content exhibited in the iron-yttrium noncrystalline alloy is a major advancement towards use of this technique for storing radioactive krypton because even without a completely optimized experiment, the power efficiency of the system has been improved by 330%. This was made possible by a lower substrate power requirement, due to the lower ion energy required for efficient gas trapping, as illustrated in Figure 4.4. In this figure, the Kr⁺-Fe curve is typical of crystalline metals except for the drop at the higher ion energies. This drop may be caused by exceeding the saturation threshold of the sputter-deposited metal and excessive

TABLE 4.3. Inert Gas Incorporation Status

Material	Deposition Rate, nm/sec	Gas Incorporation Rate, cm ³ /min at STP	Deposit Gas Content, cm ³ /g	Minimum Gas Release Temperature, °C
Nickel-krypton	6.05	4.0	16.9	600
Aluminum-krypton	5.0	2.3	30.1	300
Steel-krypton	2.65	1.74	19.8	570
Titanium-krypton	4.1	1.6	17	Not measured
Steel-yttrium-krypton-xenon	6.7	7.2	41.1	500

FIGURE 4.4. Trapping Efficiency Versus Ion Energy

resputtering in addition to the effect of secondary electron emission on the measurement of the ion current. The $\text{Kr}^+ / 9.5\% \text{Xe}^+ - \text{Fe} / 13\% \text{Y}$ curve is typical for noncrystalline solids. The primary difference is that in crystalline materials, the only realistic mechanism of gas atom incorporation is substitution because the krypton

atoms are so much larger than available interstitial locations whereas in amorphous materials, interstitial sites large enough to accommodate krypton atoms become available.⁽²⁾

A practical difference between these two curves is the method of accelerating the krypton ions toward the substrate. For high ion energies (>300 eV) required for crystalline metal, a pulsed-bias technique is mandatory with the present geometry to maintain a net deposition at the substrate. This effectively reduces the gas usage rate proportionately with the amount of "off-time" required in the cycle to maintain a net deposition. However, below ion energies of 300 eV, one can easily maintain a net deposition at the substrate without pulsing the substrate; thus a less complicated electrical system in the substrate circuit is required.

A xenon-krypton mixture was used in the current run to test the effect of xenon which may be present in the krypton from a radioactive gas separation process. Analysis of the gas during the sputtering run showed that xenon is trapped at a higher rate than krypton but does not adversely affect the process in any detectable way.

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5.0 CARBON-14 AND IODINE-129 FIXATION

L. L. Burger - Project Manager

The objectives of this program are to evaluate the various options for solidification or fixation of ^{129}I and ^{14}C collected from off-gas streams.

SUMMARY

A parametric study of electrolytic oxidation and removal of $\text{Hg}(\text{IO}_3)_2$ from mercury scrubbing solutions indicated that the process is efficient and can be carried out with negligible iodine volatilization.

Studies of copper and bismuth compounds for fixation of HI have been carried out. Both are promising. The use of bismuth, BiI_3 formation, avoids the reoxidation problem present in the case of copper.

A preliminary evaluation of the problems associated with long-term storage of irradiated fuel elements has been made, and some needed data noted.

REMOVAL OF IODINE FROM MERCURY SCRUB SOLUTIONS - R. D. Scheele

Iodine disproportionates in the mercuric nitrate scrub solution to form I^- and IO_3^- . A convenient method of separating the iodine is to precipitate $\text{Hg}(\text{IO}_3)_2$ by electrolytic oxidation of I^- . A parametric study has been under way to characterize this oxidation. The effects of temperature, 10 to 50°C, nitric acid

concentration, 1 to 11M, and current density, 0.1 to 1 amp/cm², on iodine behavior during electrolysis were studied. The cell contained about 100 ml of solution. The 2.9 cm-dia Pt electrodes were not isolated from each other.

Iodine-131 was used as a tracer. The percent precipitated at the end of a run was determined by dissolving the mercuric iodate precipitate in dilute hydrochloric acid. The percent volatilized was determined by the material balance between the initial solution and the final solution and solids. Samples of stirred solution were taken at selected time intervals during the run and centrifuged. The supernate was then counted and a material balance performed to obtain the total amounts volatilized and precipitated.

The results of our study indicate that by careful selection of operating parameters mercuric iodate can be successfully precipitated from a mercuric nitrate-nitric acid iodine scrub solution with high-current efficiency, up to 76% at 80% conversion, with little iodine loss by volatilization.

Preliminary examination of the results for the full range of the

study indicates that increased current density and temperature decrease the current efficiency and increase volatilization. Nitric acid concentration reduces volatilization and in general has a positive effect on current efficiency. Volatilization and current efficiency are not strictly independent parameters. The effect of current density is quite different at different nitric acid concentrations. At low acidities the current density effect is greater than the nitric acid effect; however, at high current densities the reverse is true. At high current densities and/or high nitric acid concentrations, nitric acid will be reduced at the cathode as described by Ellingham.⁽¹⁾ In our diaphragm-less cell, the nitric acid reduction products can be reoxidized at the anode or can react with the iodine oxidation products. Either occurrence will reduce the current efficiency for iodide oxidation. On the other hand, a high nitric acid concentration inhibits iodine volatilization by redissolving the mercury reduced at the cathode, thus preventing depletion of mercuric nitrate in the scrub solution. In all runs with high nitric acid, no iodine was seen in the vapor phase, on the glassware, nor in the sodium hydroxide scrub solution. At low current densities and low acidity, we do not have formation of parasitic reduction products, and the rate of iodine oxidation is close to the rate of iodine migration to the anode.

FIXATION AND STORAGE MEDIA -

L. L. Burger, W. J. Silker, and
R. D. Scheele

A previous report⁽²⁾ listed properties of various metal iodides, iodates, and oxides, and general factors to be considered in choosing compounds for fixation of iodine and carbon. Several iodides and iodates were seen to be acceptable. The present studies are concerned largely with bismuth and copper compounds and directed towards HI fixation, e.g., the regeneration stream from silver zeolite beds.

Removal by copper is based on the very rapid reactions:

Introduction of SO_2 into the gas stream completed the reaction by reducing I_2 to I^- . In the absence of sulfite, I_2 begins to carry over. With SO_2 present, decontamination factors of greater than 10^3 were obtained with a laboratory scrubber containing 1M CuSO_4 and a hydrogen stream containing 4 to 100 mg HI/min.

Bismuth solutions were employed to avoid the reoxidation problem noted above. BiI_3 forms a fine, dense, black precipitate. It is difficult to filter on first formation, but easy to centrifuge. Excess I^- forms higher soluble complexes--as is the case with most heavy metal iodides--but experiments with tracer HI in H_2 indicate that removal of iodine is complete even at large excesses of I^- . Addition of bismuth precipitates the

excess iodine. A possible complication is that BiI_3 removed from some solutions holds excess I_2 which is volatilized on heating. BiI_3 prepared from bismuth metal, and iodine is thermally stable but has appreciable volatility at higher temperatures. Separate tests made with a Bi_2O_3 slurry in water indicate that this also is an efficient iodine scrubbing medium.

Present work is concerned with TGA-DSC analysis of pertinent materials associated with these removal schemes.

STORAGE OF UNREPROCESSED FUEL - L. L. Burger

An alternative to reprocessing of spent fuel is controlled storage of unprocessed fuel elements. The concept examined here involves storage of three to nine fuel assemblies in a controlled atmosphere container, e.g., a sealed vessel filled with helium. This storage would be employed only after an appropriate cooling time in water following reactor discharge. Thus the dry controlled storage becomes a second step to the conventional well-established water basin storage. Table 5.1 shows the typical thermal output of a UO_2 fuel as a function of time based on ORIGEN tables. A 3-year period may be a minimum time for underwater storage prior to dry storage. After this time it is proposed that the assemblies be removed and stored in closed canisters which are to be air-cooled.

TABLE 5.1. Characteristics of LWR Irradiated Fuel, 30,000 MWd/MTU(a)

	Discharge	3 yr	10 yr	100 yr
Total thermal power, W	2.07E4	3.07E3	1.09E3	1.14E2
Total curies, γ	4.41E6	6.95E5	3.15E5	3.45E4
^3H , curies	6.92E2	5.85E2	3.94E2	2.47E0
^{14}C , curies(b)	5.5E-1	+	Same	+
^{129}I , curies	3.74E-2	+	Same	+
^{85}Kr , curies	1.10E4	9.10E3	5.81E3	1.80E1

a. Quantities per MTU. Curies can be converted to grams with the following specific activities:
 $^3\text{H} = 1\text{E4}$, $^{14}\text{C} = 4.5$, $^{129}\text{I} = 1.6\text{E-4}$, $^{85}\text{Kr} = 4\text{E2}$.
 b. Based on 25 ppm N in UO_2 .

A fuel storage canister may contain about four PWR assemblies or about nine BWR assemblies for a total uranium content of about 1800 kg. Using this as a reference unit, the canister would contain at 3 years' cooling time: 1.2M Ci γ activity including 1.0E3 Ci ^3H , 9.9E-1 ^{14}C , 6.7E-2 ^{129}I , and 1.6E4 Ci of ^{85}Kr . The total heat output would be 5.5 kW. This is to be dissipated internally with the aid of helium filling of the canister and externally by natural draft convection in the storage vaults.

The present concern is to evaluate the possibility of release of volatile radionuclides from the stored fuel and to determine methods of fixing or getting these nuclides within a storage canister.

If the fuel pins are unaltered, the sole source of volatile radionuclides would be pinholes or fractures in the cladding. However, the fuel pins may be deliberately punctured to release fission gases and/or helium fill gas. This operation requires an off-gas treating facility at the packaging

site similar to that considered for shearing operations at a fuel reprocessing plant.

Considerable migration of volatile fission products occurs during reactor operation. Tritium migrates out of the UO_2 and is fixed in the cladding, the amount increasing with increasing temperature.⁽³⁾ The amount in the gas phase is extremely small. Iodine also migrates along the temperature gradient and is found at the fuel-cladding interface. However, its movement and deposition appears to be associated with other elements, e.g., with cesium rather than in elemental form.⁽⁴⁾ Very little transport to the plenum is seen. Other experiments using getters in the fuel pins indicated that the pressure of free iodine during reactor operation was extremely low.⁽⁵⁾

No information is available on ^{14}C release. However, calculations have been made on the availability of oxygen, and it is shown that there is sufficient oxygen to combine with all the active metals plus some fraction of metals such as molybdenum.⁽⁶⁾ Since both CO and CO_2 are more stable than MoO_2 above 1000°K , it is expected that both CO and CO_2 should be present in the fuel pin gas. The predominant fission product gases released within the fuel rod are krypton and xenon.

Following puncture of the fuel pins and pumping out of the gas, the amount of fission gas release should be small and a function of the temperature of the fuel. This release varies from almost zero at ambient

conditions to virtually complete release near 2000°C .^(7,8)

Oxidation of the UO_2 releases trapped gas. Further, the accompanying expansion may rupture the cladding, leading to even faster and more complete release. This oxidation could occur if the punctured fuel pins are exposed to oxidizing gas.

Oxidation is slow at ambient temperatures, but studies have shown that oxidation to U_3O_8 will occur at temperatures as low as 300°C .⁽⁹⁾ A small amount of oxidation could be tolerated, and the exceptional stability of CsI restricts the movement of iodine. However, it must be noted that at the temperature of storage, perhaps 100 to 400°C , thermodynamic equilibrium cannot be assumed, and release mechanisms such as radiolysis need to be investigated.

Several questions then remain, some of which require experimental study. What temperatures will be attained by the stored UO_2 and what nuclides are released in the low temperature region 100 to 500°C as a function of time? What chemical species are present? What is the contribution of gamma radiation to gas release? What is the effect of the addition of small amounts of oxygen to the canister? It must be emphasized that these and similar questions are to be examined in the light of a 5 to 50-year storage time--in which relatively slow reactions may be quite significant.

Further work will attempt to provide information in this area and to determine whether specific getters may be required.

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6. J. Bazin et al., "Behavior and Physico-Chemical State of Fission Products in Fuel Elements for Pressurized Water Reactors." Bull. Inform. Sci. Tech., 196:55-71, 1974, NRC-TR-1.
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8. D. Davies et al., The Emission of Volatile Fission Products from Uranium Dioxide. AERE-R 4342, Atomic Energy Research Establishment, Harwell, England, 1963.
9. D. G. Boase and T. T. Vandergraff, "The Canadian Spent Fuel Storage Canister: Some Material Aspects." Nuclear Technology, 32:60, 1977.

6.0 INTERNATIONAL PROGRAM COORDINATION

K. M. Harmon - Project Manager

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

SUMMARY

Collection and review of significant documents continued. Waste management program summaries were

prepared for Brazil, France, Sweden, and Switzerland. Assembly of information for the "Directories" and "Bilateral Agreements" sections of the files was continued.

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7.0 WASTE MANAGEMENT SYSTEM STUDIES

J. W. Bartlett - 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 assure effective communication with the public.

SUMMARY

Work in this program is allocated to three major sectors of effort:

1) development of methods for evaluating waste management systems, 2) comparative assessment of alternative systems, and 3) development of information and concepts for public interfaces.

During the report period, progress in development of evaluation methods included restructuring of the GETOUT code to make it easier to use; development of a two-dimensional model to predict the hydraulic head distribution in unsaturated porous media; and start of work to adapt the CORAS system to provide a data base for waste management. Work to develop a seismic data base was also started.

Work on assessment of prospects for long-term pool storage of spent fuel continued by compiling and analyzing data gathered during the previous quarter and drafting the report.

In the public interfaces sector, information from official sources was analyzed and a method for discussing relationships among issues was developed. Development of the knowledge-interest questionnaire was completed,

and development of the risk perception survey instrument continued.

INTERFACE OF THE "GETOUT" MODEL WITH THE PDP-11/45 SYSTEM - J. F. Washburn

Investigation of GETOUT telecommunication data to the INFONET system shows that the transfer rate is low. The total time for data transfer for one run could be on the order of an hour or more. Also, it would necessitate writing another program on the receiving end to place the data on disk. Therefore it appears that the most efficient and cost-effective means of data transfer is by magtape. It is recommended that the dose modeling routine be converted to FORTRAN IV and placed on the PNL PDP-11 computer system.

The GETOUT code was restructured into one program rather than the two programs previously required to decay-ing releases or impulse releases. This refinement provides for easier operation of the program by a person who is not familiar with the internal workings of the code.

A rough draft of the final report was written.

INVESTIGATION OF RADIONUCLIDE TRANSPORT IN UNSATURATED GROUNDWATER SYSTEMS - A. K. Tyagi

The bibliography compilation of radionuclide transport in unsaturated groundwater systems was completed and typed on mag cards. Technical papers summarized are related to three categories: 1) modeling of unsaturated flow; 2) transport of solutes and radionuclides; and 3) identification of the model parameters.

The first two categories include the theoretical considerations in modeling, laboratory data, field data, and verification of mathematical models. In the last category, model parameters such as the unsaturated hydraulic conductivity, diffusivity, dispersion coefficients, and unsaturated flux, are described. In addition, the literature pertaining to the measurements of water content, bulk density, and other miscellaneous considerations are included.

The steady-state partially saturated model and the transient unsaturated model, both developed by Reisenauer and others at Pacific Northwest Laboratory, were reviewed in addition to the Philip model for horizontal and vertical flow in unsaturated soil systems. The steady-state model is capable of predicting the distribution of suction head and water content in a three-dimensional space. Problems involving up to 8000 nodes can be solved. Optimal under-relaxation and over-relaxation tech-

niques were used to increase the speed of convergence and maintain stability.

A transient two-dimensional model was developed to predict the hydraulic head distribution in unsaturated porous media. The Crank-Nicolson finite difference method was utilized to solve the mathematical partial differential equation. Functional relationships of the hydraulic conductivity and water content with suction head were derived using the approaches of King, Millington and Quirk, and Campbell. Empirical expression, suggested by Campbell, gave satisfactory results. The model can include up to 6000 nodes.

Modifications in the program computing the hydraulic conductivity and water content with suction head were made to run the program more efficiently on the PDP-11/45 computer.

INTERACTION OF EVALUATION CRITERIA FOR RADIOACTIVE WASTE MANAGEMENT ALTERNATIVES - M. L. Warner

Arrangements were made for access to the "Policy III" computer program via the General Electric System. Two meetings were held with HARC researchers to plan for conducting a judgment analysis exercise on repository siting using PNL personnel. A detailed proposal for this exercise was submitted and approved. An interlaboratory authorization for the participation of HARC in conducting the judgment analysis sessions is being processed.

DATA BASE DEVELOPMENT FOR NUCLEARWASTE MANAGEMENT - G. B. Lane,

T. N. Bishop, and H. P. Foote

Work was initiated on this project during the transition quarter, and additional work was deferred until this quarter.

The Computer Overlay Resources Assessment System (CORAS) will provide the framework for the data base. A number of parameters of interest in nuclear waste management can be included in CORAS such as topography, glaciated areas, flood plains, seismic risk areas, areas underlain by bedded salt deposits, distribution of crystalline basement rocks, etc.

All available CORAS literature, programs, and data were obtained and reviewed in detail. Since the CORAS data base controlling program was written for a PDP-9 computer, a study of PDP-9 software was necessarily included. The CORAS data types and computer storage modes were studied. A data link between the PDP-9 and PDP-11/45 required an understanding of the 11/45's File-Q software and device-independent graphics.

Because of the imminent installation of a PDP-11/55 and an upgrading of the 11/45 (with the attendant system hardware differences from the previous systems), the CORAS data base will require considerable revision. The following will be included in the new CORAS data base:

1. All programming will be done in FLECS for ease of understanding.
2. The revised CORAS will be developed in such manner as to be easily

expanded to include more data, and to be generally similar to existing data bases (e.g., CIRMIS) so that a familiarity with any existing data base carries over to CORAS.

3. Complete revision of data storage with a possible mixing of computer storage techniques in order to enhance rapid data access and retrieval.
4. Expansion of CORAS to include more global area.
5. Ease of use and understanding for individuals of diverse professional disciplines (e.g., geologists, engineers, and businessmen) who are not necessarily computer oriented, but who would be interested in the capabilities of such a data base.

The general structure and course of development of the CORAS data base was defined as follows:

1. The data for each base should be stored in a three-dimensional array referenced by angular coordinates (latitude and longitude) in decimal degrees.
2. The angular resolution should reach 0.01° .
3. Beginning data might include areal geology, hydrology, and land use.
4. Graphic display capabilities should be included.
5. The first CORAS program should be a "setup" program which explains the CORAS system and its needs with respect to the user.
6. The second phase of the setup program includes reading and writing to a large three-dimensional array with goals of maximum speed and efficiency.

7. When 5 and 6 have been accomplished, an editing program should be written so that data may be changed, inserted, or deleted, as required.

In this reporting period, a "set-up" program was written in such a way that only the latitude and longitude of a particular data element are required from the user. The user then answers self-explanatory questions from the "setup" program to extract trial data from a small three-dimensional array. Four output devices (lineprinter, plotter, terminal, and tectronix scope) are incorporated into the "setup" program and are available to the user on command.

It was intended during this quarter to develop efficient methods for reading and writing to three-dimensional arrays. However, further consideration and discussions indicated that an editing program should be the next step in the data base program development. Therefore development of two matrix editing programs was started, with each program attacking identical editing problems from different directions. At this time, the benefits of one program over the other is unknown, but upon completion of the programs their relative efficiencies will be determined.

SEISMIC DATA BASE DEVELOPMENT -

T. N. Bishop, G. B. Lane, and
H. P. Foote

Work on the project was initiated this quarter. The major objective of this study is to aid in understanding the tectonic patterns and seismic risk

(initially in Washington, Oregon, Idaho, Northern California, British Columbia, western Montana, and western Nevada) by setting up a seismic data base that is as complete and useful as possible.

The information in the NOAA data base (115,000 earthquakes) was studied. Certain groups of quakes classified by magnitude, location, and year were filed on disk for further analysis. Techniques learned in dealing with these smaller files will be used with the complete data base, when they are perfected. Preliminary search programs were written.

Cartographic projections were studied in detail, and programs were completed that plot global data (latitude and longitude) such as earthquakes with selected map projections (Mercator, Albeis Equal Area, Lambert's Conformal, Orthographic, or Stereographic). A program also was developed which does the reverse operation--transferring digitized data from a given projection (X-Y coordinates) to global coordinates. This set of programs will give an accuracy of 2/1000 of a degree and optimal visualization of the data.

All data from four sources (NOAA Worldwide Seismic Data Base, Woodward-Clyde Pacific-Northwest Seismic Data Base, and local arrays in eastern and western Washington) were incorporated into the seismic data base. Seismic events will have 18 associated parameters defining their location, time, magnitude, intensity, depth, and identification as an explosion, volcanic event, and/or an event which caused casualties.

A digitizing correction program was written that increases digitization accuracy by a factor of ten, and work is continuing on increasing efficiency of search programs, organization of the data base, and understanding all aspects of the data itself. Also, investigation is being carried out on equations relating body wave magnitudes, surface wave magnitudes, and local magnitudes to select an applicable magnitude scale on which to sort seismic events.

POOL STORAGE OF SPENT NUCLEAR FUEL -
A. B. Johnson, Jr.

A study to assess prospects for long-term performance of spent fuel in pool storage was started during the previous quarter. The study will compile data on experience to date and relate storage conditions to regimes known to cause degradation of fuel cladding materials.

During the quarter, information previously obtained from the sites with spent fuel storage experience was compiled and analyzed. A report summarizing results of the study was drafted and issued for clearance. Indications are that water basins provide an acceptable method for long-term (~25 years) storage of spent fuel.

NUCLEAR WASTE COMMUNICATIONS -
S. M. Nealey, HARC

There are three tasks to be carried out within the waste communications task: a) analysis of official sources of information pertaining to nuclear waste disposal; b) media analysis of newspapers and magazines

that involves two subtasks--content analysis and journalistic analysis; and c) administration of a nuclear waste knowledge-interest questionnaire.

Official Source Issues Analysis

Official statements about nuclear waste disposal have been collected and analyzed, and a methodology for discussing the relationships between issues has been developed. A first draft of the issues is nearly complete at this time. Analysis of issue inter-relationships is under way.

Media Analysis

The content analysis subtask of the media analysis has progressed rapidly and is nearing completion. All the newspaper and magazine articles have been content analyzed, keypunched, and computer analyzed. A bibliography of the nuclear waste articles has been prepared, and a first rough draft of this section of the report is nearing completion.

A staff member was brought on board in April to do the journalistic analysis. The goal of this analysis is to provide a journalist's perspective to the question of how the press in America has been handling the issue of nuclear waste disposal. For comparison purposes, developments surrounding coal as an energy source will also be analyzed. The objectives of the analysis are to: a) show what the press is and is not doing regarding nuclear waste disposal as a subject; b) suggest some insights into intentions of the journalists; c) point out journalistic techniques used to intensify or

make stories more prominent than others and, conversely, point out methods utilized to downplay or sometimes give less credence to stories; d) monitor, primarily through word selection, the influence of headline writers in the press's portrayal of nuclear wastes; e) report on the frequency with which stories on nuclear waste and coal occur within a newspaper and the emphasis given them; and f) critically analyze the press's role in scientific issues that focus on nuclear subjects.

The Seattle Times, New York Times, Tri-City Herald, and Montana Standard have been chosen for analysis. All of the April through June 1977 newspapers will be read and analyzed. At this time about 70% of the newspapers have been analyzed.

Knowledge-Interest Questionnaire

The knowledge-interest questionnaire has been finalized. A bid has been let to Dinner and Klein for the survey data collection. The questionnaire will be administered in August to 1350 adult residents of Washington State and 150 residents of the Tri-Cities area (nuclear neighbors). Administration can commence as soon as approval of the questionnaire is received from the sponsor.

PUBLIC PERCEPTION AND EVALUATION OF RISK - J. A. Hébert, HARC

There are two main subtasks under this task: a risk evaluation survey and a risk perception survey. The risk evaluation survey consists of asking respondents to judge the ac-

ceptability of hypothetical future power generation mixes (coal dominant, nuclear dominant and conservation dominant) which are characterized on three dimensions: amount of power available, amount of risk, and distribution of benefit and risk between current and future generations. The risk perceptions subtask focuses on respondents' beliefs about the hazards of nuclear wastes.

During the current quarter, the components of the two questionnaires have been refined and additional material added. The risk evaluation survey has been shortened to a length that is feasible for administration within a half-hour period.

The risk perception survey has been revised to include the assessment of perceptions of comparative risks and benefits between the nuclear fuel cycle and other electric power technology fuel cycles, especially coal. Also included are reference items on general attitudes toward environmental pollution and its control. It is expected that the revised questionnaire will be able to provide information which will prove useful in clustering the respondent groups. With data from this section we should be able to determine whether concerns about possible long-term adverse environmental impacts are specific to nuclear waste or are regarded as an issue which involves other technological wastes as well. Further questions will probe respondents' concerns about waste management considerations involved in geologic isolation. Pending approval of the data collection instruments, data can be collected in late summer.

8.0 WASTE MANAGEMENT SAFETY ASSESSMENT

W. K. Winegardner and P. J. Pelto - Project Managers

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

The scope of this project was modified during the quarter. The primary objective continues to be safety assessment of alternative waste management schemes for viable nuclear fuel cycles. Both occupational and public safety will be considered. Further, waste management systems will be scoped, defined and evaluated relative to available technology, compatibility with current developments and final waste isolation planning, waste character-

istics and logistics, and system cost. Initial emphasis will be on the evaluation of waste management systems for the once-through fuel cycle. The risk assessment of a conceptual system for managing high-level waste from commercial reprocessing was terminated.

Work continued on the three-report set (see January - March report) to describe PNL-developed computer programs for drawing fault trees and for assessing these trees in terms of risk. Early FY-1978 publication is planned.

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9.0 NRC REQUESTED STUDIES

J. H. Jarrett - Project Manager

The objective of this study is to perform waste management studies upon NRC request.

SUMMARY

As indicated in recent quarterly reports, this program previously has addressed studies relating to the Nuclear Fuel Services Plant in West Valley, New York. A low level of effort has been spent during this

quarter keeping current on events in the West Valley situation. However, no requests have been received, either from NRC or ERDA regarding initiating specific studies related either to the West Valley situation or to others which NRC may wish ERDA to investigate.

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10.0 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, and 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 included:

1. the review of possible methods for performing geologic isolation safety assessments and the specification of the output format for those safety assessments;
2. the completion of a first-generation computer code for simulating the occurrence of repository release scenarios and the development of computer software for data base manipulation;
3. the development of resistance- and induction-furnace methods of making sample glass waste forms for leaching and the preparation of sample waste forms containing ^{233}U , ^{237}Np , ^{239}Pu , ^{243}Am , and ^{244}Cm ;
4. the completion of a comprehensive compilation of hydrologic, contaminant transport, water-dose, and air-dose computer codes of potential use in predicting the consequences of radioactivity releases from geologic isolation repositories;
5. the start of batch experiments to determine the sorption of Tc, Sr,

Cs, Np, and Am for 12 minerals and four solutions, the measurement of Pu and Am sorption on rock tablets, and the measurement of the relative migration rates of Cs, Pu, and Am through various geologic materials by flow-through column methods;

6. the establishment of a library of nontechnical waste management issues and the start of socioeconomic studies related to waste management.

A paper, "Safety Assessment and Geosphere Transport Methodology for the Geologic Isolation of Nuclear Waste Materials," was presented at the OECD/NEA-sponsored workshop on Risk Assessment and Geologic Modeling, May 23-27, 1977, Ispra, Italy.⁽¹⁾

TASK 1 - SAFETY ASSESSMENT CONCEPTS AND METHODS - J. Greenborg

Discussions were held between the WISAP staff and PNL health physicists and radiation biologists to determine the format for presenting the results of WISAP safety assessments. The group concluded that the primary output of the WISAP method should be dose

and dose rate to individuals living at various future times and that these doses and dose rates should be compared with natural background radiation. The group thought that the prediction of population doses and "health effects" to far-future generations was meaningless from a technical standpoint. However, the group concluded that a secondary output of the WISAP method (in the appendix of reports) should be population doses and "health effects" translations in order to better communicate assessment results to the nontechnical public.

TASK 2 - DISRUPTIVE EVENT ANALYSIS - J. A. Stottlemire

A generic method has been developed for analyzing potential containment disruptions at geologic isolation repositories. This method (called repository simulation analysis) is a combination of the simulation and fault tree analysis techniques and has the following steps:

1. Potentially disruptive natural and man-caused events and processes are listed.
2. The interdependencies of the processes are identified and their coupling relationships are quantified to the extent possible (e.g., worldwide warming trend, mean sea level increase, inundation of land over repository, renewed sedimentation and compaction, halokinetic diapirism, stress-induced overburden fracturing, groundwater penetration, and salt dissolution).

3. A stratified model of the site-specific geology is made.
4. The potential failure modes are identified.
5. Probabilities for the events and rates for the processes are determined.
6. Repository response curves (e.g., distance to the biosphere versus time) are derived for combinations of the processes.
7. The occurrence probabilities of combinations of the events are determined by the fault tree technique.
8. The events and their combinations are forced to occur at various times, and their effect is superimposed on the repository response curves for the processes.
9. Containment failures are noted and the failure times are combined with information from the repository response curves to determine the boundary conditions for subsequent consequence evaluation.

Subsequent work will focus on developing submodels for this general method with the help of a team of geologists and geophysicists and on determining consequence evaluation boundary conditions from method output.

The use of this (or any other) safety assessment method requires an extensive data base and computer software to interface the data with the method. Programs have been completed to plot global geologic data, such as earthquakes and volcanos, on selected map projections. Programs have also been completed which perform the reverse operation--the transfer of digitized data from a

given projection to global coordinates. Subsequent development will provide the capability to overlay other geologic, geophysical, hydrologic, and geographic data, such as natural resource concentrations, fault locations, and water source information, so that all relevant data for a specific location can be brought together.

TASK 3 - SOURCE CHARACTERIZATION -

D. J. Bradley

The development of both resistance- and induction-furnace methods for producing glass waste form samples for leaching has been completed. Both methods produce waste form samples of high quality.

Doped glass samples for leach rate measurement containing ^{233}U , ^{237}Np , ^{239}Pu , ^{243}Am , and ^{244}Cm have been produced, and characterization comparisons with the undoped glass are under way. The metallography, x-ray diffraction, and alpha autoradiography analyses completed thus far show that the doping/waste form manufacturing process does not significantly change the glass from its original form with the exception of small increases in porosity which will not adversely affect the leaching experiments.

The leaching solutions chosen for the studies on the actinide-doped glasses are as follows:

1. salt brine based on the analysis of a deionized water dissolved core from the WIPP facility (300 g/l NaCl)
2. high ionic strength groundwater (2.206 g/l $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$)

3. high-sodium groundwater (1.76 g/l NaCl)
4. high ionic strength carbonate groundwater (2.52 g/l NaHCO_3)
5. deionized water.

TASK 4 - TRANSPORT MODELING -

J. R. Raymond

Over 150 hydrologic, contaminant transport, water-dose, and air-dose computer codes were compiled. The hydrologic and contaminant transport models were categorized according to Table 10.1. The water-dose and air-dose models had considerable similarity and did not require a complex categorization.

TASK 5 - TRANSPORT DATA - R. J. Serne

Three additional subcontracts were emplaced during the quarter, bringing the total to nine for the year. These were:

1. Lawrence Berkeley Laboratories - "Theoretical and Experimental Evaluation of Waste Transport in Selected Rocks"
2. Oak Ridge National Laboratories - "Soil Chromatograph K_d Values"
3. Sandia Laboratories - "A Microstructural Investigation of the Interaction of Southeastern New Mexico Geological Media with Waste Radionuclides--A Basis for Ion Mobility Prediction."

Batch experiments to measure the K_d of Pu, Tc, Sr, and Cs for 12 minerals and 4 solutions (same as the first 4 solutions listed under Task 3) controlled Eh-pH

[illegible]

laboratory to measure the sorption of Am, Pu, Np, and Cs on one or more

Sorption measurements were begun at Oak Ridge National Laboratory for

cesium with montmorillonite. An apparatus was constructed to investigate axial filtration as a sorption measurement method.

An apparatus to measure K_d at high pressures was designed at Lawrence Livermore Laboratory, and a decision was made to construct a brass prototype for low-pressure experiments before proceeding with construction of the high-pressure apparatus.

The characterization of a Sandia salt, Hanford basalt, Nevada Test Site granite, and argillaceous material in preparation for sorption measurements was begun at ARHCO.

TASK 6 - SOCIETAL ACCEPTANCE -

A. H. Schilling

A library of bibliographic materials on social issues in waste manage-

ment has been established. Studies were begun on socioeconomic issues, population impact projections, state laws affecting property rights in the states of Louisiana, Texas, Utah, New York, and Ohio, Federal and state agency responsibilities and policies related to waste management, impact management guidelines, and the siting of waste repositories and related facilities.

REFERENCE

1. H. C. Burkholder, J. A. Stottlemire and J. R. Raymond, "Safety Assessment and Geosphere Transport Methodology for the Geologic Isolation of Nuclear Waste Materials." Risk Analysis and Geologic Modeling in Relation to the Disposal of Radioactive Wastes Into Geological Formations, OECD Nuclear Energy Agency, Paris, France, 1977.

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

Monitoring system component evaluations are continuing in order to define potential soil physics and radiochemical monitoring apparatus which may be used by nuclear waste burial site operators and controlling agencies. Several additional state-of-the-art fluid potential and thermal monitoring devices have been identified and evaluated.

Laboratory analyses of numerous base line soil physics and soil chemistry parameters have been conducted. These analyses are being used to define new laboratory experiments to better quantify the transport of radwaste solutions in land burial media.

One-dimensional sediment columns and physical models have been initially developed, and column monitoring systems have been fabricated. These models will be used to simulate or predict transport of contaminants in partially saturated land burial media.

Field activities are continuing in order to develop an operational system capable of monitoring energy

and mass balance components determining the rate and direction of radionuclide transport in partially saturated media.

TASK 1 - EVALUATION OF MONITORING SYSTEMS - S. J. Phillips and G. W. Gee

Specific transducers and monitoring systems capable of accessing fluid and vapor phase water and radiological contaminant transport through burial and burial trench media are being evaluated.

The use, accuracy, limitations, and reliability of each monitoring component potentially used in an arid region under subsurface, partially saturated conditions are being assessed. A heat dissipation ceramic block is being evaluated that is capable of monitoring matrix potential between -0.1 and > -2 bars. This transducer consists of two electronic thermometers: one is located adjacent to, and measures, a transient heat source; the other measures ambient temperature in the porous matrix. The rate of heat dissipation within this transducer is a function of the

properties of the ceramic and the fluid content within the ceramic. The fluid is assumed to be in equilibrium with the porous media into which it is placed. This transducer and associated electronics are capable of monitoring sediment fluid potential below diurnally and seasonally induced temperature gradients in arid regions where quasi-steady-state low thermodynamic potentials exist. Additional fluid potential monitoring transducers, i.e. thermocouple psychrometers, of specific design are being evaluated. A primary psychrometer type currently used utilizes a porous ceramic cup encapsulating a thermocouple junction to which vapor phase H_2O condenses when a cooling current is applied. This unit has proven reliable under severe conditions in arid regions. However, the response time required to measure near-surface potential change is in some cases inadequate. Another design is under study which uses a monel gauge to encapsulate the thermocouple junction and requires much shorter equilibration time. Both types of psychrometers are expected to be required for use in partially saturated groundwater monitoring systems.

Also efforts continue in evaluating active and passive mode in situ systems for detecting radionuclides. A survey has been completed of recently developed logging tools used in the minerals exploration industry. In addition, surveys of in situ neutron activation systems and related monitoring and data acquisition systems have also been reviewed.

TASK 2 - LABORATORY ANALYSIS -

R. J. Serne, D. Rai, and
S. J. Phillips

Soil chemistry and soil physics characterization studies of two soil-sediment types are continuing. Base lines have been determined for fluid retentivity, conductivity, pH moisture percentage, saturation paste chemical composition, cation exchange capacity, organic carbon content, calcium carbonate content, particle size distribution, and selectivity constants.

Selectivity constants are being determined for several macrocations, i.e. sodium, potassium, calcium, and magnesium. Selectivity constants are being calculated from mass action laws using binary exchange reactions. For example, the reaction of Na^+ ions replacing soil bound calcium, $2Na^+ + Ca-X \rightleftharpoons Na_2-X + Ca^{++}$ where X designates the soil phase, yields the following mass action equation:

$$K = \frac{[Ca^{+2}]}{[Na^+]^2} \frac{[Na_2-X]}{[Ca-X]}$$

Because the rigorous mass action equation requires the determination of the solid components' activities, which is not possible for heterogeneous solids, an empirical approach is used. The mass action equation becomes:

$$K^* = \frac{\gamma_{Ca}(Ca^{+2})}{\gamma_{Na}^2(Na^+)^2} \frac{Na_2-X}{CaX} P$$

where K^* is the empirical selectivity constant and P is an empirical activity correction term. By determining $K^*(\text{Na-Ca})$, $K^*(\text{Na,K})$, and $K^*(\text{Ca,Mg})$ on the respective binary systems, the simultaneous interaction of a four-component system (Na, Ca, K, Mg) can be predicted.

To evaluate the movement of solubilized radionuclides percolating through soils, the affinity towards sorption, K_d , must be evaluated. Initial batch experiments are being run on some of the following important isotopes (Sr, Cs, Tc, I, Eu, Ce, Sb, Am, Cm, Pu, Np, Ra, U) using synthetic groundwaters covering the concentration range from about two times the observed saturation extracts to dilute groundwaters and rainwaters.

For those isotopes for which K_d is sensitive to solution composition, systematic factorial design experiments will be planned in such a way that predictor equations can be developed.

TASK 3 - PHYSICAL MODELING OF CONTAMINANT TRANSPORT -

L. D. Kannberg and S. J. Phillips

Studies have been started to solve one-dimensional fluid flux and dispersivity in one-to-one models using transport in isotropic homogeneous materials. These initial cases are being expanded to simulate retarded or accelerated transport of contaminants through burial materials. Pulse height analyses of ^{60}Co and ^{137}Cs solutions used in calibration of one-dimensional columns have been completed. Fluid retentivity evaluations

of synthetic sand mixtures are continuing. These evaluations will be used to determine the interrelationships among the fluids and dissolved solutes within porous media and the physical properties of the media itself, i.e., viscosity, surface tension, compressibility, fluid and gross density, thermodynamic potential, specific discharge, intrinsic permeability, volume, and volumetric porosity. From the evaluations completed to date, single- and two-phase flow of slightly compressible and incompressible flow in unconsolidated media hydrodynamic dispersion, heat, and mass transfer can be modeled.

TASK 4 - FIELD MONITORING AND DATA EVALUATION - S. J. Phillips and G. W. Gee

Installation of field monitoring systems is continuing at an area next to a retired burial facility. Several atmospheric monitoring devices used to measure evaporation parameters have been installed. Additional evapotranspiration parameters controlled by specific plant species inhabiting arid land burial sites are being investigated as to their short- and long-term, i.e. diurnal and seasonal, flux relationships. Temperature flux plates that measure incoming and outgoing thermal transients through porous media systems are being evaluated. These instruments will be used, in part, for quantifying the energy and mass balance of shallow land waste burial sites.

12.0 DETECTION AND CHARACTERIZATION OF MOBILE ORGANIC COMPLEXES OF FISSION PRODUCTS

J. A. Franz - Project Manager

The objective of this program is to determine the important mobile or volatile organic complexes of fission and activation products formed in the storage of low-level waste in shallow land burial.

SUMMARY

A detailed review of nickel and the stability of its organic complexes was written. A detailed review of technetium and the stability of its organic complexes was started. PH titrations of candidate zirconium and nickel complexes were performed which indicate significant stability and solubility at the high pH of Hanford soil. High-performance liquid chromatographic instrumentation was used to test the absorption of several candidate nickel complexes by Hanford soil.

IDENTIFICATION OF NUCLIDES AND COMPLEXING AGENTS

During the first quarter of FY-1977, 10 candidate non-TRU isotopes were identified as existing in sufficient quantities with sufficiently long half-lives to present potential problems due to migration as mobile organic complexes from shallow land burial. They are ^{90}Sr , ^{137}Cs , ^{154}Eu , ^{60}Co , ^{93}Zr , ^{63}Ni , ^{137}Ba , ^{151}Sm , and ^{99}Tc .

Complexing agents derived from decontamination procedures selected

for study include polyphosphates and aminopolycarboxylic acids (EDTA, HEDTA, and DTPA). The principal complexing agents derived from soil humus constituents and decaying organic matter are hydroxycarboxylic acids such as citric, oxalic, tartaric, hydroxy-acetate, formic, acetic, benzoic, 3-hydroxy-5-methylbenzoic, p-hydroxybenzoic, vanillic, gallic, propionic, succinic, and furnace acids.

A general review of known stability data for complexes of these complexing agents and nuclides and a detailed review of zirconium complex stability were completed and written during the second quarter of FY-1977.

A detailed review of the stability of nickel complexes was completed and written during the third quarter of FY-1977. A detailed review of the stability of technetium complexes was completed and is now being written. Our review of the known chemistry of organic complexes of nickel has revealed several key features of aqueous nickel solutions:

- Nickel hydroxide irreversibly precipitates from an aqueous solution in the presence of base at pH 6.7.⁽¹⁾

- DTPA, EDTA, HEDTA form highly stable complexes with nickel.⁽²⁾
- Cobalt, which behaves chemically like nickel, is desorbed from soil by extracts of leaves.⁽³⁾
- Co-EDTA and DTPA are the complexes least absorbed by soil.⁽⁴⁾
- Nickel organic complexes are more stable when a five or six-membered bidentate ring system is formed as in Ni-EDTA or Ni- α hydroxycarboxylic acid.⁽⁵⁾
- Nickel predominantly bonds with a soil carboxyl and a soil phenolic OH simultaneously. Bonding which involves only a carboxyl occurs to a lesser extent.^(6,7)

Our review of the known chemistry of organic complexes of technetium has revealed several key features of aqueous technetium solutions:

- Tc(VII), which will not complex with organic molecules, can be reduced to a lower complexable oxidation state by HCl, thiocyanate ion, organic impurities present in tetraphenylarsonium chloride anion exchange resin, some organic solvents, and ascorbic acid.^(8,9)
- SN(II) reduces Tc(VII) to Tc(IV), which is complexed by DTPA.⁽¹⁰⁾
- Sterilization of the soil stops sorption of Tc by soil (i.e., its sorption is related to microbial activity).⁽¹¹⁾
- Organic matter and pH are the most important parameters influencing retention of Tc(VII) in soil.⁽¹²⁾

STUDY OF MOBILITY CHARACTERISTICS OF ORGANIC COMPLEXES

In an attempt to ascertain the stability and solubility of zirconium organic complexes at soil pH, a few potentiometric titrations were carried out during the second quarter of FY-1977. Additional titrations of zirconium and nickel complexes were done during the third quarter of FY-1977. These titrations were done on an aqueous acid solution of either nickel or zirconium, depending on the experiment ($1.2M$ HNO_3 , $0.2M$ Zr or Ni), containing an equimolar amount of the complexing agent. pH titrations of zirconium nitrate, zirconium tartrate, zirconium gluconate indicate that tartrate and gluconate complexes have high stability and solubility throughout a broad pH range (pH 2 - pH 14). The tartrate complex precipitates out of solution immediately on complexation at pH 2.0. This complex is extremely soluble in aqueous media having a pH greater than 7.0, depending on the ratio of zirconium to tartaric acid. The zirconium-gluconate complex does not precipitate at any pH.

After analyzing our data and finding that it agrees with other investigators:

- zirconium organic complexes are more stable when the organic ligand can form a five-membered chelate ring with zirconium⁽¹³⁾
- the increasing order of ligand coordinating tendencies is $O^{-2} \gg OH^- > RO^- > RCOO^- \gg R-OR > R_3 \equiv N$ and⁽¹⁴⁾

- the presence of hydroxyl or carboxyl groups as substituents on the chain of alpha-hydroxycarboxylic acids tends to render the resultant zirconium compounds more water soluble,⁽¹⁵⁾

we conclude that di- and tri- α -hydroxycarboxylic acids as a general class of compounds form highly stable, water-soluble complexes over a broad pH range. Because of this high stability and solubility over a broad pH range, these zirconium complexes can present the greatest problems in elution through soil. Most other zirconium complexes will partially precipitate and/or be completely destroyed at high soil pH.

The pH titrations of various nickel complexes were performed. EDTA, HEDTA, DTPA, gluconic acid and tartaric acid were stable and water-soluble over a broad pH range. Because of this high stability and water solubility, these five- and six-membered chelate complexes can increase the elution of radioactive nickel through soil.

A portion of the high-performance liquid chromatographic instrumentation was used for soil column work. A 6-in. long by 1-in. (OD) stainless steel column was used to hold the waste top fill Hanford soil (uncontaminated soil was obtained from burial ground trenches). A stainless steel 10- μ filter and a porvick filter were installed at the exit and entry to this column. A 2-ml liquid injection system was attached between the pump and the soil column. A fixed volume fraction collector was used to collect the effluent.

A radioactive spiked (for detection purposes) Ni-EDTA complex at pH 7-8 and a Ni-gluconate complex at pH 2 and pH 7-8 were introduced in separate experiments to the above described system. These preliminary results appear in Figures 12.1-3: 62.14% of the Ni-EDTA complex eluted from the soil column in one lump peak immediately with the solvent front; 46.25% of the Ni-gluconate complex at high pH eluted from the soil column in one lump peak immediately; 28.55% of the Ni-gluconate complex at low pH eluted from the soil column in two incomplete peaks after more than 80 ml of water was washed through the column. More definitive conclusions about these results will be made when more data is obtained in future work.

FIGURE 12.1. Preliminary Elution Curve of Nickel-EDTA Complex from Hanford Soil (62.14% total recovered, not absorbed)

FIGURE 12.2. Preliminary Elution Curve of Nickel-Gluconate Complex (low pH) From Hanford Soil (28.55% total recovered, not absorbed)

FIGURE 12.3. Preliminary Elution Curve of Nickel-Gluconate Complex (high pH) from Hanford Soil (46.25% total recovered, not absorbed)

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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

Major work on the 400-gal demonstration decontamination electropolishing facility was completed with the installation of the high-current power supply and the unpackaging hood for preparation of the items to be decontaminated. Full-scale testing of the demonstration facility is in progress using both beta/gamma and plutonium-contaminated material. All system components are operating satisfactorily except for minor leakage problems in the electrolyte pumping system.

The major item decontaminated during initial testing of the facility was a large plutonium-contaminated stainless steel tank representing more than 15 ft² of surface area. Other items decontaminated during the reporting period included a canister used to transport plutonium nitrate solution and welded stainless steel capsules containing plutonium oxide. The ability to remove uranium contamination from Cascade Improvement Program aluminum scrap also was demonstrated.

More than 2000 ft² of plutonium-contaminated metal components from the decommissioning of the Hanford 231-Z Building plutonium facility have been saved for processing in the demonstration decontamination facility. Construction of a temporary greenhouse facility was started. It is to facilitate sectioning of this material into sizes compatible with the 400-gal electropolishing system.

DEMONSTRATION FACILITY

Major work on the demonstration decontamination facility was completed with installation of the high-current (5600 A) power supply and the open-face hood used to unwrap and preclean the items to be decontaminated. Figure 13.1 shows the arrangement of the major system components in the completed facility.

The power supply is located in a noncontaminated zone above the decontamination facility. The power leads run to a distribution box just above the electropolishing tank. Up to eight anode leads can be used to provide the necessary current capability

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FIGURE 13.1. 400-gal Electropolishing Facility

and current distribution characteristics for large components. The power distribution system also permits use of the tank walls as the cathode and/or up to eight separate leads for auxiliary and internal cathodes. The power supply is run remotely from the decontamination facility using the control unit shown in Figure 13.1.

Safety features of the power supply include current and voltage limiting capability and the ability to shut down within half a cycle in the event of a short circuit. The control system also incorporates a programmer for automatic operation of the power supply, including specification of any desired current-time profile.

The unpackaging hood (Figure 13.1) is used to unwrap the items to be decontaminated and for any necessary

precleaning such as removal of paint, grease, or other nonconductive coatings or material. The metal surfaces are thoroughly wiped in accordance with criticality safety requirements to remove any gross contamination. Then they are sprayed with phosphoric acid to tie down any loose contamination before transport to the electropolishing tank. The end of the unpackaging hood next to the electropolishing tank opens to permit entry and removal of the test pieces. The top of the hood is slotted so that the hoist can be used inside the hood.

The pumps and filters for the electrolyte and rinse solutions are located under the unpackaging hood. This permits removal and replacement of the contaminated filter elements through the floor of the hood. Use of a pumped stream to agitate the

electrolyte has a number of advantages over the simpler and more commonly used air and mechanical agitation methods. Ejecting the high-pressure stream at the bottom of the electropolishing tank produces a rolling agitation; this minimizes splashing and misting and also prevents the buildup of sludge on the tank bottom. The circulating electrolyte can be filtered to remove the sludge and any corrosion products or contamination not in solution. Also, electrolyte is available under pressure for use in internal cathodes for applications to in situ decontamination using pumped stream and brush techniques.

These advantages of pumped-stream agitation also apply to the rinse system. Filtered water from the first rinse tank can be used to spray rinse the decontaminated parts over the electropolishing tank. This serves as an additional rinsing step and, more importantly, helps minimize the buildup of contamination in the rinse tanks by returning the contaminated dragout to the electropolishing tank.

A number of additional process control and safety systems were installed during the reporting period. These included an on-stream density cell for continuously measuring the specific gravity of the electrolyte; several circuits to detect leaks or out-of-bounds solution level changes for the electropolishing and rinse tanks; continuous radiation monitors for airborne contamination; and a monitoring system to ensure adequate ventilation of the electropolishing and rinse tanks. The safety systems automatic-

ally turn off power supply, pumps, and water supply to the decontamination system as well as sound an alarm in the event of leakage or other abnormal operation conditions.

The entire electropolishing facility was designed to facilitate self-cleaning and the maintenance of a very low background contamination level. The use of polished stainless steel to line the sides of the electropolishing and rinse tanks and the adjacent room walls is shown in Figure 13.1. This view also shows the stainless steel floor composed of removable panels that can be cleaned by electropolishing in the decontamination facility.

Full-scale testing of the demonstration decontamination facility is now in progress using both beta/gamma and plutonium-contaminated material. All system components are operating satisfactorily with the exception of the 50-gpm pump used to circulate the electrolyte. Although designed for acid service, the pump experienced successive seal failures, resulting in minor leakage of electrolyte into a containment tank positioned under the pumps and filtration system. The pump manufacturer is attempting to identify and correct the seal problem. Also, arrangements have been made to obtain two different types of zero-leakage pumps for evaluation with the decontamination system.

The largest item decontaminated during initial testing of the electropolishing system was a stainless steel container (16-in. dia by 22-in. high) that had been used as the electropolishing tank for earlier plutonium

decontamination studies. The initial contamination level inside the container was 20,000 dis/min/100 cm² fixed and 2,000 dis/min/100 cm² smearable. The entire container (17.8 ft²) was electropolished in the 400-gal system using the tank walls as the cathode. This reduced the contamination level to nonsmearable, with less than 2,500 dis/min/100 cm² of fixed contamination. The ability to partially decontaminate the inside of the container without using an auxiliary cathode illustrates the good throwing power of the electropolishing process. The remaining contamination was readily removed by electropolishing the interior of the tank for an additional 15 min using an internal cathode.

Most of the contaminated material initially processed in the demonstration decontamination system will come from the decommissioning/restoration of the Hanford 231-Z Building plutonium facility.

More than 2000 ft² of plutonium-contaminated metal components ranging in size from small vacuum system parts up to glove boxes and 2-ft diameter ventilation system ducts have been saved for processing in the demonstration facility. In addition, every effort will be made to obtain representative plutonium-, uranium-, and beta/gamma-contaminated metallic waste from other Hanford contractors and other ERDA sites for evaluation in the decontamination facility.

For example, uranium-contaminated aluminum compressor blades obtained through the National Lead Company of

Ohio have been successfully decontaminated using the electropolishing facility (see Related Projects). This material is representative of the thousands of tons of surface-contaminated metal scrap generated by the Cascade Improvement and Upgrading Program. Arrangements also are in progress to obtain two shipping boxes, 4 x 4 x 7 ft, and several drums of plutonium-contaminated, mechanically-sectioned metal waste from the Rocky Flats Plant.

The 400-gal electropolishing system will accommodate planar components 4 ft long by 2 ft high and cylindrical components 1.4 ft in diameter by 4 ft long. Anything larger than this must be disassembled or sectioned before processing in the electropolishing tank.

A plastic greenhouse is under construction adjacent to the decontamination facility to facilitate sectioning of ductwork and other components too large for the 400-gal electropolishing system. This temporary facility also will be used to evaluate different sectioning techniques pending the establishment of a permanent prototype sectioning/pretreatment facility.

RELATED PROJECTS

Electropolishing was used to decontaminate a product receiving (PR) canister used by the Rockwell Hanford Company for onsite transfer of plutonium nitrate solution (Figure 13.2). The radiation level of the 304L sample chamber, 3-in. dia by 30-in. deep, was reduced from more than 1,000,000 dis/min/100 cm² to background to permit

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FIGURE 13.2. Stainless Steel Product Receiving Canister Used to Transport Plutonium Nitrate Solution. Electropolishing reduced the contamination level inside the 3-in.-dia by 30-in.-deep sample chamber from more than 1,000,000 dis/min/100 cm² to background.

use of the canister for a training class. In another project, 1-in. dia by 7.5-in.-long stainless steel "standards" capsules containing plutonium oxide were electropolished after sealing by welding to remove the surface contamination prior to secondary encapsulation. Less than 4 min of electropolishing was required to reduce the surface contamination levels from 200,000 dis/min/100 cm² to background.

Decontamination tests were conducted on several uranium-contaminated aluminum compressor blades from the (UCCND) Paducah Plant. These blades were from a compressor that had been in service for several years, and were selected to represent contamination as deeply ingrained and difficult to remove as any type of scrap generated by the Cascade Improvement Program. The blades were about 3 in. wide and from 5 to 10 in. long. The

as-received alpha surface contamination levels ranged from about 200 to 2000 dis/min/100 cm² and the beta/gamma levels from about 1000 to 6000 counts/min/100 cm². Electropolishing the blades for less than 10 min in a phosphoric acid electrolyte reduced the surface alpha and beta/gamma radiation levels of most of the blades to background. The metal removed to effect decontamination represented a weight change that ranged from only 0.5% to less than 3%.

A few blades exhibited an initial large drop in contamination level and then maintained a value (<60 dis/min/100 cm² alpha and <200 counts/min/100 cm² beta/gamma) that was relatively unaffected by further electropolishing. This probably reflects internal contamination as some porosity was noted in the blades. Comparison decontamination tests also were conducted using phosphoric-chromic and phosphoric-sulfuric electrolytes and

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