**DO NOT MICROFILM
COVER**

**Nuclear Waste Management
Semiannual Progress Report
October 1983 Through March
1984**

**J. L. McElroy
J. A. Powell**

June 1984

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

**Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute**

PNL-4250-5

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

**DO NOT MICROFILM
COVER**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Reference hereon **PACIFIC NORTHWEST LABORATORY**
operated by **BATTELLE**
for the **UNITED STATES DEPARTMENT OF ENERGY**
under Contract **DE-AC06-76RLO 1830**

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161
NTIS Price Codes
Microfiche A01

Printed Copy
Pages Price
Codes
001-025 A02
026-050 A03
051-075 A04
076-100 A05
101-125 A06
126-150 A07
151-175 A08
176-200 A09
201-225 A10
226-250 A011
251-275 A012
276-300 A013

026-125
051-150
076-175
101-200
126-250
151-275
176-300
201-225
226-250
251-275
276-300

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

NUCLEAR WASTE MANAGEMENT
SEMIANNUAL PROGRESS REPORT
OCTOBER 1983 THROUGH MARCH 1984

Compiled by
J. L. McElroy and J. A. Powell
Nuclear Waste Technology Program

June 1984

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

Pacific Northwest Laboratory
Richland, Washington 99352

NOTICE

PORTIONS OF THIS REPORT ARE REPRODUCIBLE.
It has been reproduced from the best
available copy to permit the broadest
possible availability.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

FOREWORD

This document, PNL-4250-5, is one of a series of technical progress reports designed to report semiannually on radioactive waste management programs at the Pacific Northwest Laboratory (PNL). These programs are funded by the Department of Energy's Offices of Nuclear Energy, Civilian Radioactive Waste Management, and Defense Programs. Only programs that have significant, reportable results are included in this document. This document includes a section on National Waste Terminal Storage programs at PNL.

Technical progress of the Civilian Nuclear Waste Treatment Program is reported in an annual report instead of this document.

CONTENTS

FOREWORD	iii
1.0 DEFENSE WASTE TECHNOLOGY	1.1
1.1 HANFORD WASTE VITRIFICATION	1.1
1.2 IN-SITU VITRIFICATION OF HANFORD WASTE	1.19
1.3 DEFENSE BYPRODUCTS PRODUCTION AND UTILIZATION PROGRAM	1.25
1.4 MODELING RADIONUCLIDE RETARDATION MECHANISMS	1.35
1.5 TANK CORROSION	1.42
1.6 CESIUM CHLORIDE COMPATIBILITY	1.43
1.7 HANFORD GROUT TECHNOLOGY	1.46
1.8 SYSTEM TRADEOFF STUDIES	1.49
1.9 REDUCED WASTE GENERATION - ADMINISTRATIVE SORTING	1.51
2.0 NUCLEAR WASTE MATERIALS CHARACTERIZATION CENTER (MCC)	2.1
SUMMARY	2.1
WASTE MATERIALS INTERACTIONS	2.1
CORROSION	2.5
WASTE-FORM CHARACTERIZATION	2.7
REFERENCE MATERIALS AND HANDBOOK DATA	2.10
REFERENCES	2.13
3.0 WASTE ISOLATION	3.1
3.1 OFFICE OF NUCLEAR WASTE ISOLATION (ONWI)	3.1
3.2 BASALT WASTE ISOLATION PROJECT (BWIP)	3.25
3.3 NEVADA NUCLEAR WASTE SITE INVESTIGATIONS	3.42
4.0 SUPPORTING STUDIES	4.1
4.1 HANFORD DEFENSE WASTE STUDIES PREPARATION OF ENGINEERING AND ENVIRONMENTAL IMPACT DATA FOR DISPOSAL OF HANFORD DEFENSE WASTES	4.1
4.2 HANFORD DEFENSE WASTE STUDIES PREPARATION OF AN ENVIRONMENTAL IMPACT STATEMENT FOR DISPOSAL OF HANFORD DEFENSE WASTES	4.2
4.3 COVER TECHNOLOGY EVALUATION FOR URANIUM MILL TAILINGS	4.3
4.4 SPECIAL WASTE-FORM LYSIMETERS - ARID	4.5
4.5 TRANSPORT ASSESSMENT - ARID	4.7
4.6 KRYPTON-85 COSTS AND HEALTH IMPACTS ASSESSMENT	4.9
4.7 KRYPTON ION IMPLANTATION	4.11
4.8 INTERNATIONAL PROGRAM SUPPORT	4.15
5.0 RECENT WASTE MANAGEMENT PUBLICATIONS	5.1

FIGURES

1.1	Turntable/Melter Combination	1.7
1.2	Melter Discharge Cone	1.9
1.3	Melter Discharge Cone - Base Plate Holding Mechanism	1.9
1.4	Melter Discharge Cone - Insertion and Removal Mechanism	1.10
1.5	Melter Discharge Lid Prototype	1.12
1.6	Discharge Section Lid Installed on Melter Shell	1.13
1.7	The Lid Is Positioned Above the Melter by Remote Control	1.14
1.8	Dowel Ends from Lid Are Inserted in Guide Tubes on Melter	1.14
1.9	Melter Thermocouple Jumper	1.15
1.10	Melter Discharge Section, Showing Thermal System Components	1.17
1.11	Glass Sampler	1.18
1.12	Schematic of Off-Gas Trailer	1.24
1.13	Radioluminescent (RL) Light Panel	1.28
1.14	Radioluminescent Wand	1.29
1.15	Radioluminescent Superwand	1.29
1.16	Military Runway Configuration	1.31
1.17	Civilian Runway Configuration Tested at Central, Alaska	1.31
1.18	Photo of Radioluminescent Lights in Military Runway Configuration	1.32
1.19	Radioluminescent Lights in the Civilian Runway Configuration Tested	1.32
1.20	Visual Approach Slope Indicator	1.33
1.21	Radioluminescent Light Wind T Being Installed at Central, Alaska	1.33
1.22	Configurations of Glide Slope Indicators Evaluated	1.34
1.23	Schematic Flow Diagram Outlining the Radionuclide Retardation Modeling Project	1.36
1.24	Stability Fields of the Predominant Plutonium Aqueous Species Plotted as a Function of pH and Redox Conditions at a Total Plutonium Activity of 1×10^{-6} and 25°C	1.38
1.25	Stability Fields of the Predominant Uranium Aqueous Species Plotted as a Function of pH and Redox Conditions at a Total Uranium Activity of 1×10^{-5} and 25°C	1.38
1.26	Stability Fields of the Predominant Uranium Aqueous Species and Uranium Mineral Solubilities Plotted as a Function of pH and Redox Conditions at a Total Uranium Activity of 1×10^{-5} and 25°C	1.39
1.27	Mass Distributions of U(VI) Aqueous Species Plotted as a Function of pH at a Total Uranium Activity of 1×10^{-5} and 25°C	1.40

1.28	Typical Laboratory "Pit" on 316L S/S Found During Electropolishing (300X)	1.45
2.1	Concentrations of Total Dissolved Uranium Plotted as a Function of Reaction Time for the Measured Solubility of $\text{UO}_2(\text{OH})_2$ at 60°C	2.3
2.2	Calculated Saturation Indices for $\text{UO}_2(\text{OH})_2$ Plotted as a Function of Reaction Time for the Measured Solubility of $\text{UO}_2(\text{OH})_2$ at 60°C	2.4
3.1	Penetration Rates of All Ferrous Materials, Limited Reactant Test	3.4
3.2	Comparison of $\text{Pu}(\text{OH})_4$ Solubility Data 110 Days in 0.4 M and 4.0 M NaCl and NaClO_4 Solutions at 25°C	3.8
3.3	Illustration of Pu Oxidation (+4 to +6) due to Radiolysis and Illustration of the Lack of Cl Complexation	3.9
3.4	Solution pH Versus Annealing Temperature for Cycle No. 4 Permian Basin Rock Salt and Harshaw NaCl Irradiated to 5×10^9 rad at Room Temperature	3.11
3.5	Titration Curves for 1.00-g Permian Rock Salt	3.12
3.6	Plot of Hydrogen Pressure Versus Time, with a Functional Fit to the Data by the Method of Least Squares	3.15
3.7	Plot of the Concentration of Radiolytically Produced Species Versus Time as Predicted by RADIAL at a Dose Rate of 3.5 Mrads/hr and Initial Oxygen Concentration of 1.5 ppm	3.16
3.8	East-West Cross-Section of Major Depositional Systems in Palo Duro Basin	3.20
3.9	GSM Finite-Element Grid	3.21
3.10	Regional Model Study Area	3.22
3.11	Smoothed Thickness of Ogallala Formation	3.23
3.12	Current Status of Color-Coded Soil Classifications for the Greater Pasco Basin	3.27
3.13	Three-Dimensional Plot of Stratigraphy Underlying Hanford Illustrates Method for Displaying Spatial Data	3.28
3.14	PNL pH Electrode	3.29
3.15	PNL Micro-Porous Reference Electrode	3.30
3.16	Concentration of ^{237}Np from Run B-48-03 (glass only) 200°C, 30 MPa	3.32
3.17	Concentration of ^{237}Np from Run B-48-04 (glass + basalt) 200°C, 30 MPa	3.33
3.18	Comparison of ^{237}Np Concentrations from Runs B-48-03 (glass only) and B-48-04 (glass + basalt) 200°C, 30 MPa	3.33
3.19	Concentration of ^{239}Pu from Run B-48-03 (glass only) 200°C, 30 MPa	3.33
3.20	Concentration of ^{239}Pu from Run B-48-04 (glass + basalt) 200°C, 30 MPa	3.34

3.21	Comparison of ^{239}Pu Concentrations from Runs B-48-03 (glass only) and B-48-04 (glass + basalt) 200°C, 30 MPa	3.34
3.22	Fluid Concentrations for Both ^{237}Np and ^{239}Pu from Runs B-48-03 (glass only) and B-48-04 (glass + basalt) Comparing Concentrations of Both Actinides	3.35
3.23	Corrosion of Iron-Base Alloys Exposed to Synthetic Grande Ronde Basalt Ground Water at 25°C	3.38
3.24	Corrosion of Iron-Base Alloys Exposed to Synthetic Grande Ronde Basalt Ground Water at 150°C	3.39
3.25	Corrosion of Iron-Base Alloys Exposed to Synthetic Hanford Grande Ronde Basalt Ground Water at 250°C and ^{60}Co γ -Irradiation Intensity of 3×10^5 rad/hr	3.41
4.1	Engineering Drawing of Special Waste-Form Lysimeter Test Facility	4.6
4.2	Simulated Annual Drainage Values (in cm H_2O) for 6-Year Simulation of Climatic Data for Two Soil Types (silt loam and sand) at the Hanford Site	4.9
4.3	Bench-Scale (260-cm ² substrate surface area) Krypton Trapping Unit	4.13

TABLES

1.1	Chemical Compounds Combined with CAW To Form a Glass	1.2
1.2	HBCM Run Variables and Resulting Melting Rates	1.3
1.3	Chemical Analyses Following Thermal Mockup of Melter Discharge Section, wt%	1.18
1.4	Equipment Remotizing and Testing in Progress Status	1.19
1.5	PSRT Radionuclide Inventory	1.20
1.6	PSRT Radionuclide Release Data	1.21
1.7	Survival Rate of Cherry Fruit Fly Pupae as a Function of Gamma Dose	1.26
1.8	Summary of Military and Civilian Test Program in Alaska (November 19, 1983 to February 19, 1984)	1.30
1.9	Estimated Metal Attack in the Thermally Aged WESF CsCl Capsules	1.45
1.10	Estimated Quantities, Both Current and Future of Special Case and RH-TRU Wastes	1.50
1.11	Effect of Test Variables on Smearable Contamination Levels and Decontamination Factors (DF) for Freon Spray-Cleaning of Plutonium-Contaminated Glove Box Areas	1.53
2.1	MCC's Schedule for Preparation and Characterization of Approved Testing Materials (January - June 1984)	2.11
3.1	Corrosion Rates Observed in General Corrosion Studies	3.3
3.2	Irradiation-Corrosion Penetration Rates of Ferrous Materials	3.5
3.3	Heating and Irradiation Effects in Permian Rock Salt	3.12
3.4	Compositions of Various Saturated Salt Brines at 25°C	3.13
3.5	Compositions of Steel Sheet Used in U-Bend Specimens	3.44
3.6	Compositions of Steel Plate Used in Slow-Strain-Rate Tests	3.45
3.7	Results of Slow-Strain-Rate Tests of 304 Stainless Steel at 150°C	3.45
3.8	Results of Slow-Strain-Rate Tests of 304L Stainless Steel at 150°C	3.46
4.1	Radon Flux Measurements, pCim-2sec-1, Made on the Earthen Covers During March 1984	4.5
4.2	Description of Bench-Scale Deposition Experiments Performed Through March 1984	4.14

1.0 DEFENSE WASTE TECHNOLOGY

The objective of the Defense Waste Technology activities is to develop technology to recover or immobilize and package radioactive wastes from the Defense nuclear fuel cycle for useful applications or for ultimate disposal.

1.0 DEFENSE WASTE TECHNOLOGY

J. M. Latkovich and C. A. Geffen - Program Office Managers

1.1 HANFORD WASTE VITRIFICATION

(AR-05-10-02 - 80602)

J. E. Minor - Program Manager

The objective of the Hanford Waste Vitrification (HWV) Program is to apply vitrification technology to a selected Hanford waste stream(s), developing a process and equipment to be utilized in a Hanford waste facility. The HWV Program consists of two parts: Hanford Waste Vitrification Plant (HWVP) support and Waste Stream Characterization and Immobilization (WSCI) support. The objective of the WSCI support is the development of technology applicable to the immobilization of high-level waste from the Hanford Site. The technology developed will not be specific to any facility. It will be based on a high-priority waste stream defined in the Hanford Waste Management Plan and by Rockwell Hanford Operations (Rockwell).

Summary

During this period the program was re-scoped to support a facility designated as the Hanford Waste Vitrification Plant (HWVP). The HWVP has the mission of vitrifying those components of all Hanford liquid high-level wastes which require terminal geologic disposal. The former B Plant Immobilization Pilot Plant (BIPP) was scoped to vitrify only current acid waste (CAW) from PUREX and neutralized B Plant acid waste (NBAW).

The HWVP will vitrify pretreated neutralized current acid waste (NCAW) rather than CAW. Future process development will center on NCAW from PUREX and other pretreated streams that are identified as requiring geologic disposal.

Remotized component development has included testing of a melter turntable mockup; melter discharge lid remotability; and melter through-wall thermocouple testing.

WSCI generic process development activities during this period have included melter feed rheology studies; melter feed system development; studies of glass foaming; and effluent control system studies.

Conceptual design of the HWVP vitrification system has been rescheduled for FY 1985.

To provide greater continuity and clarity for the reader, this report combines the results of work in two programs.

Process DevelopmentMelter Feed Rheology Studies -

C. O. Harvey

Glass formers are most commonly added to the liquid waste to be charged to an electric melter for vitrification as a finely ground frit. This produces a homogeneous, intimate mixture of the glass formers and waste. However, these slurries, especially those made using neutralized waste that already contain considerable insoluble material, are difficult to pump to the melter at precisely controlled low flow rates. This is because the particles are abrasive, and they tend to settle rapidly and plug the pump, feed lines, and nozzle orifices. For years the solution to this difficulty was

sought through proper design of the hardware. The current HWVP approach to finding a solution includes modifying the chemistry and rheological properties of the slurry, as well as equipment development, to improve the dependability of the melter slurry feed system.

The ideal resolution to this difficulty would be to find glass formers that are completely soluble in the liquid waste. Soluble nitrates and borates were successfully tested with simulated current acid waste (CAW) for all the glass formers but the silica, as presented in Table 1.1. The silica was added to the solution either as a colloidal suspension of 50 wt% $<1\text{-}\mu$ particles in water or as SiO_2 ground to pass through a 325-mesh sieve ($44\text{ }\mu$).

The feed made with the colloidal suspension was a Bingham plastic fluid. When it was at rest, the fluid quickly gelled, preventing any settling of particles, even after months without agitation. When the stress yield point of the gel was exceeded, the fluid flowed freely. Laboratory tests showed that feed left standing for 16 hr in tanks, pumps, and 1/4-in.-dia stainless steel tubes could be circulated easily by starting the pump.

TABLE 1.1. Chemical Compounds Combined with CAW To Form a Glass

Desired Oxide Glass Former	wt% Oxide in a Frit	Soluble Compounds Used Instead of Frit
SiO_2	62	None
B_2O_3	15	$\text{N}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
Na_2O	15	NaNO_3
Li_2O	7	LiNO_3
MgO	1	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

The $44\text{-}\mu$ SiO_2 settles rapidly but can be resuspended, while $44\text{-}\mu$ frit is very difficult to resuspend and forms immovable plugs in the hardware.

The coarser SiO_2 and frit particles can be suspended in the waste solution by the addition of 2000 ppm of polyelectrolytes, as previously reported. The effects of gamma radiation on these polymer-stabilized slurries were explored; simulated melter feeds were exposed to ^{137}Cs capsules for a dose estimated at least an order of magnitude higher than that from the current flow sheet melter feed. Settled volume and settling rates for the irradiated samples were essentially the same as for the control samples. Thus, it appears that polymer suspending agents will be stable in HLLW. This preliminary finding is of particular significance since the candidate waste was changed from CAW to neutralized current acid waste (NCAW). The colloidal silica does not produce a Bingham plastic fluid in the basic waste. Moreover, tests to evaluate rheology modification suggest that the use of colloidal silica reduces the melting rate, as reported in more detail in the Melter Tests sections.

Simulated CAW prepared in the laboratory to the concentration specified by the current reference process flow diagram was a complete solution at 80°C , but it crystallizes as it cools to room temperature. The result is a 21 to 25% supernatant over a polycrystalline monolith. If CAW were to be a process feed stream for the HWVP, these results would require a careful reevaluation of the waste concentration levels in a CAW process flow diagram and complementary adjustments in the glass-former slurry concentrations.

Melter Feed System Development -

H. T. Blair

After more than 2 years of review and testing, it was concluded that a commercially available pump for metering the HLLW/glass former slurry to the melter does not exist. Commercially available slurry pumps designed for controlled flow at rates less than 40 gph (150 L/hr) depend on elastomers for dependable service. The radiation levels predicted in the melter feed would render the most resistant elastomers useless in about 1 month. Therefore, a pumping concept that was being tested at Savannah River Laboratory (SRL) was investigated. A prototype all-metal air displacement slurry (ADS) pump with a pneumatically driven, double-acting valve was designed, built, and tested for 1060 hr at an average flow rate of 135 L/hr in a CAW/colloidal silica slurry. The pump never failed due to plugging or wear during the test. There were several weld failures, but the welds are peculiar to the prototype and do not exist in the second-generation design currently being fabricated.

Melter Tests - J. M. Perez

In the previous report, a very slow melting rate was reported for the 112-hr test conducted in the pilot-scale ceramic melter (PSCM). The feed for that run was made by combining simulated CAW and glass formers composed of soluble nitrates, borate, and colloidal silica as described in the section on Melter Feed Rheology Studies. The low melting rate was determined to be caused by sodium and boron not being fed to the melter in appropriate concentrations. When the run was completed, the feed makeup tank was drained and a large deposit of $\text{Na}_2\text{B}_4\text{O}_7$ was

found near the bottom of the tank. Thus the feed to the melter was deficient in those two major fluxing agents. More recently a series of four runs was made in the high-bay ceramic melter (HBCM) to compare the melting behavior of feeds in which the physical or chemical form of the glass formers was varied to modify the feed rheology. The variables and resulting melting rates are summarized in Table 1.2.

These results verify the beneficial effects of a proper Na_2SO_4 content on feed melting. They also show that colloidal silica, which produces the most desirable feed properties, does not compromise the melting rate, while frit, which produces the most troublesome feed transfer properties, melts the fastest. These results suggest that an engineering compromise must now be developed to produce a melter feed with both satisfactory rheology and melting behavior.

During the 112-hr PSCM test, the feed nozzle, through which the feed flows into the melter chamber, was successfully cooled by a closed-loop, free-convection heat pipe. The advantages of such a device are that there are no moving parts to wear out and there are no remote connections to be made for coolant to or from the nozzle. The volume of working fluid is also just over 1 L. However, a condensor is required that has a horizontal surface of 4 ft². During the series of HBCM tests, the heat pipe-cooled and feed nozzle was demonstrated to

TABLE 1.2. HBCM Run Variables and Resulting Melting Rates

<u>Glass-Former Variable</u>	<u>Melting Rate, L/hr</u>
Ground SiO_2 w/o Na_2SO_4	11
Na_2SO_4 & ground SiO_4	12-13
Na_2SO_4 & ground frit	15
Na_2SO_4 & colloidal SiO_2	12-13

work just as effectively with the condensor standing edge. This greatly reduced the amount of melter top shadowed from crane access by the condensor.

Glass Foam Control - D. S. Goldman

The previous year-end report described preliminary results of a new laboratory method to evaluate the foaming tendency of glasses collected from melter experiments. The method involves remelting the glass in a laboratory furnace, decreasing the pressure isothermally, and determining the pressure at which bubbling, due to gaseous supersaturation, occurs in the melt. This pressure is referred to as the reboil pressure, which is an overall measure of the dissolved gas content. Glasses having a greater dissolved gas content are expected to be more prone to foaming and would be indicated by greater reboil pressures. Consistent with this hypothesis, reboil pressures were found to be greater in glasses collected from melter experiments that had experienced foaming and were found to be independent of the feed composition (Hanford, West Valley, and Savannah River).

Once a correlation was established between the laboratory results and melter observations, effort was directed toward defining the gases responsible for the foaming. The approach taken was to analyze the glasses used in the laboratory test for their dissolved gas content and to correlate these results with the measured reboil pressures. Also, mass spectrometric analyses were conducted on the gases contained in glass foam collected from the melter. Conclusions from these studies are as follows:

1. Reboil pressure correlates with dissolved water content for all glass compositions tested. Infrared spectral analysis of

polished glass sections were used as a measure of the dissolved water content.

- a. Calculations show that a 0.005 wt% loss of water from the glass at melt temperatures could release a volume of water vapor nearly equal to the entire melt volume. Water release could thus be a potent cause of foaming.
 - b. Water has "reverse" solubility in most silicate melts, meaning that its solubility decreases with decreasing temperature. Thus, water release could occur with unstable convection and rapid flow of a melt volume into a cooler region of the melter. This potential problem demands convective flow and temperature stability in design and operation of the BIPP melter.
 - c. Glasses analyzed after reaching the reboil pressure in the laboratory test were found to contain about half of their original water content.
2. Reboil pressure correlates with dissolved oxygen content for most glass compositions tested. Dissolved oxygen content is reported to be controlled by the concentration of multivalent ions in the glass. Oxygen release is expected to arise from redox reactions involving these multivalent ions.
 - a. Direct colorimetric analysis of iron in these glasses indicated the absence of ferrous iron, so redox reactions involving ferrous and ferric iron have been discounted as a cause of foaming.
 - b. A ceric sulfate titration procedure has been developed to measure the total amount of oxidized multivalent species in the glass as a means to infer a total dissolved oxygen content. It is this parameter that correlates with reboil pressure for most

glass compositions studied. The most likely candidates affecting the dissolved oxygen content include tetravalent cerium and hexavalent chromium in the glass. Independent evidence from pulsed polarography and UV-VIS spectroscopy confirm the presence of hexavalent chromium.

- c. Redox reactions between hexavalent and trivalent chromium will release more oxygen with changes in melt oxygen activity or temperature than will most other redox couples.
3. The dissolved water and oxygen contents of most glass compositions are correlated, suggesting that the same process that oxidizes the melt also hydrates the melt.
4. Mass spectrometric analyses of the gases contained in glass foam collected from the melter revealed the presence of both water and oxygen, thus supporting the analytical results described above. This analysis was conducted at elevated temperatures to minimize potential problems with water adsorption in the vacuum system (unlike earlier analyses).
5. The laboratory test revealed that reboil pressure significantly increased with time during a melter experiment using simulated Hanford CAW feed. It is not clear whether the reboil pressure stabilized at the termination of the experiment, so prediction of longer-term foaming tendency could not be deduced from this melter run. The laboratory test is sufficiently rapid that it should be used to evaluate whether chemical stability has been achieved during the melter run and should be used as an additional basis to conclude the run.

Effluent Control System Development -

R. D. Peters

Laboratory results were received from analysis of off-gas effluent samples taken during the 5-day pilot-scale test, PSCM-17. Ruthenium, which was spiked in the simulated CAW feed, was found to be predominantly gaseous in the 300°C melter exhaust. However, after quenching the off gas through an ejector venturi scrubber to 30°C, no ruthenium was detected in the gas stream either as a gas or aerosol. Gross melter exhaust emissions were found to be much lower than in previous tests, probably as a result of the lower melter feed rate. Measured aerosol collection efficiencies for the high-efficiency mist eliminator (HEME) and the hydrosonic scrubber were somewhat erratic due to insufficient on-line sampling time for the relatively low melter emission rates. Low efficiencies ($DF < 4$) are indicated for collection of aerosols which carry elemental calcium, silicon, and aluminum, and high efficiencies ($DF > 10$) are indicated for collection of sulphur, sodium, lithium, and cesium. No other feed-originating, aerosol-borne elements were detected leaving these high-efficiency devices.

The concentration of HNO_3 in the scrub recirculation liquor steadily increased and was up to 270 g/L by the end of the 5-day run. This corresponds to 75% collection efficiency of NO_x by the ejector scrubber. A thermosyphon evaporator successfully concentrated 2300 L of scrub liquor to 70 L.

The control of volatile fission product in liquid-fed melter off-gas system was evaluated. The following topics were covered:

- review of key pilot-scale nonradioactive tests performed at PNL
- properties of gaseous ruthenium effluents
- methods for removing ruthenium from gas streams
- methods for removing iodine
- iodine-scrubbing performance of bubble-cap column (NO_x absorber).

PNL tests demonstrate that during steady melter feeding conditions, the elements cesium, technetium (represented using manganese), antimony, tellurium, and strontium behave as aerosols, both in untreated melter off gas and in quenched off gas. The element selenium is readily volatilized from the melter, but exhibits aerosol behavior after off gas passes through the binary scrubber.

Liquid-fed ceramic melter (LFCM) tests conducted at PNL and elsewhere indicate that ruthenium behaves predominantly as an aerosol, especially after melter off gas has been quenched. There are reports, however, of volatile ruthenium persisting beyond a primary scrubbing step, as observed during calcination experiments. It is, therefore, prudent for HWVP to include a ruthenium adsorber. The most promising solid sorbents are silica gel and the molecular sieves zeolon 900H and UC13X. The current approach in the BIPP flowsheet is to allocate 1% of the total ruthenium as gaseous and the balance as a solid particulate. This approach is consistent with observations of ruthenium behavior during LFCM tests as reported in the literature.

Iodine is expected to totally volatilize from the BIPP melter and to remain a gas in the effluent treatment system. The most effective means of controlling this element are those currently proposed in the BIPP preconceptual design: caustic scrubbing via the NO_x absorber (which will preferentially

remove interfacing acid halogens such as HF), followed by a bed of silver-impregnated solid sorbent.

The effectiveness of the NO_x absorber and solid sorbent bed for I_2 removal is uncertain. This is because gas-liquid equilibrium data for I_2 in the air-caustic system is limited, and the efficiency of solid sorbents at the anticipated low I_2 partial pressures is unknown. Bench-scale studies using tracer radioiodine have been planned in order to address these uncertainties.

Equipment Remotizing and Testing -

D. H. Siemens, D. E. Larson and S. M. Berry

Turntable

Testing of the turntable mockup located in the high bay extension (HBE) of the 324 Building has been completed. The secondary seal that isolates the canister thimble from the turntable when the canister access cover is removed will require redesigns. The turntable/melter combination tested is shown in Figure 1.1.

During initial testing of the turntable system, it was not possible to achieve proper alignment of the right-angle drive unit with the internal canister thimble mechanism. This was corrected by installing an off-set key that allowed the drive unit to be properly indexed when the canister thimble was aligned at the canister fill location. Future designs should incorporate matched drilled flanges on the drive unit to accommodate indexing and alignment. Repeated testing of the turntable indicates that the chain/sprocket drive extension system will contribute to misalignment of the canister at the fill location due to slack developing in the chain. The system, as

8307484-1cn

FIGURE 1.1. Turntable/Melter Combination

designed, has no provision for tensioning. Future designs should incorporate a tensioning device, or perhaps a peripheral ring-drive system could be used. A system where all bearings are exterior to the turntable containment tank would be most desirable.

In general, all other remote tests of the turntable were successful; however, minor design-related items did appear throughout the testing phase. For example:

- The turntable access hatch cover should be modified to lower the center of gravity.
- The annular space for the water seal and cover should be enlarged (widened) to prevent binding of the cover.
- The gap in the canister grapple that interfaces with the canister flange is too narrow.
- The potentiometer sensing/indexing unit should be relocated to enhance remote changeout.
- Redesign of the input/output drives and sockets from square to taper appears warranted to improve remote assembly.

The load cell system for determining canister weights and the inflatable metal bellows seal system between the melter and turntable functioned well. Repeatability and accuracy of the load cell signal through the modified electrical connector gave excellent results even after the connection had been repeatedly made/broken remotely. The bellows seal system made an extremely tight seal between the melter and turntable. Leakage rates for the bellows seal indicate a range of 3 to 10 standard ft³/hr (scfh) for vacuums of 5 to 20 in. of water, respectively, with bellows inflation pressures of 60 to 70 psig.

Melter Overflow Discharge Insert

During the canister-filling process, the molten-glass stream that leaves the melter overflow cavity flows down into the canister via a discharge cone assembly. This cone does not normally contact the glass stream, but its replacement does provide a means for recovering should glass material come in contact with the cone walls and plug unit. The discharge cone is designed to be replaceable using canyon-remote (crane-only) techniques with handling equipment that is used through the canister access port on the turntable system. Testing was done to evaluate the remote handling aspects of the discharge cone and the associated equipment design.

The discharge cone is a hollow, tapered, conical section surrounded by insulative materials on the lower half (larger diameter end) as shown in Figure 1.2. As molten glass normally will not adhere to carbon steel, material was selected for fabrication of the tapered section of the discharge cone. The lower half of the discharge cone is insulated with Kaowool® to reduce heat loss in the glass stream, and thus help prevent possible glass freezing problems here. The exterior of the cone in the insulated area is fabricated from 300-series stainless steel for corrosion resistance. In the event the discharge cone cannot be removed with the remote handling equipment, the unit is designed with a shear plane 7-1/2 in. from the bottom. This will allow the cone to fail at the shear plane when the turntable is pulled from beneath the melter, shearing off the cone at the same time. The cone is held in place by cams on a base

8400257-24cn

FIGURE 1.2. Melter Discharge Cone

plate (Figure 1.3). The cams grip the serrated grooves along the cone's lower portion. Features are included on the handling equipment (Figure 1.4) to enable the engagement and release of the cams.

The discharge-cone handling equipment consists of several pieces of hardware in order to remotely insert and remove the cone assembly. The insertion mechanism is a pneumatic cylinder mounted to a base plate (Figure 1.4). The base plate provides vertical orientation for the cylinder assembly, as well as an attachment for the lower set of guide vanes to aid in centering the insertion mechanism in the canister liner.

Three modifications to the original design were required, each to three different pieces of equipment. The first modification consisted of trueing the inside bottom edge of the discharge cone. This change allowed the discharge cone to drop clear of the cam grippers during the removal operation. The second modification was to correct the

FIGURE 1.3. Melter Discharge Cone - Base Plate Holding Mechanism

8400257-21cn

FIGURE 1.4. Melter Discharge Cone -
Insertion and Removal Mechanism

spread and length of the discharge cone and handling equipment yoke arms. This change enabled the hooks of the lifting yoke to engage the handling-equipment cross bars during lifting of the cone. The third modification, consisting of four changes, was to the removal adaptor ring:

- increasing the depth of the ring by 2-1/2 in.
- raising the centerline of the crossbars by 3/4 in.
- adding an inner guide ring to ease alignment of the lifting yoke arms inside the removal adaptor ring for remote operations

- adding size equally spaced guide bars around the periphery of the removal ring to improve alignment of the mechanism during cone removal.

The prototype discharge cone was remotely installed in, and removed from, the mock melter shell, twice with direct visual observation of operations and twice in a totally remote mode.

During the initial testing (i.e., with the turntable out from beneath the melter shell), it was observed that due to slight radial misalignment between the turntable access port and the discharge cone, atop the insertion tool, the cone tended to catch in its stepped insulated area on one of the ejector cams and become locked into place by the cam grippers during installation. This was corrected by adding the six guide bars on the removal ring that was previously mentioned.

Subsequent testing with the turntable beneath the melter in normal operating configuration revealed that during installation of the discharge cone, the top of the cone would hit the bottom of the melter shell adjacent to the inlet cone that leads into the overflow section of the melter mockup. This situation was also caused by the slight radial misalignment between the melter and the discharge cone atop the installation tool located in the canister thimble. Increasing the air pressure to the cylinder of the installation tool from 45 psig to ~70 psig provided sufficient force that the cone would bounce off the edge of the melter shell bottom and continue up into the proper position. This bouncing effect, demonstrated by the discharge cone at the higher

air pressure, did not appear to dent or distort surfaces of the cone assembly.

The described modifications to the equipment allowed the remote testing to be completed with no difficulty. It should be noted that standard rubber air hose and fittings were used for test purposes, and that one of these lines was torn off its connector once on the pneumatic cylinder as a result of being caught on the upper adaptor plate during extension of the cylinder shaft. This feature will be modified for actual remote operations.

The remote testing program demonstrated that:

- The discharge cone and the respective holding mechanism (cam grippers) function as designed for remote installation purposes.
- Should the discharge cone remain stuck after release of the cam grippers, the ejector cams will act on the cone to force its release from the melter.
- The installation and removal equipment and discharge cone are designed for successful remote operation with the aforementioned modifications.

Other design modification recommendations were generated from the test program:

1. All outside surfaces of the discharge cone, except the area acted upon by the ejector cams, should be sloped to minimize areas of potential "hang-up" during installation.
2. The air supply to the ports on the cylinder system should be hard-piped to an area above the top adaptor plate.

Melter Discharge Lid Remotability

During canister filling, the glass stream leaving the melting cavity requires external heat to maintain its molten state. This

heat is provided by silicon carbide heating elements in the melter discharge lid. A prototype melter discharge section lid was built and tested to determine the handling characteristics of the lid during remote installation and removal from the discharge section of a melter. These installation and removal tests were performed using a radio-controlled crane and impact wrench, first with direct viewing of the operation and then with closed circuit viewing as would be done in-cell.

The lid is constructed of ceramic materials as shown in Figure 1.5 and covered with a stainless steel metal plate for handling, bolting to the melter, and attachment of associated equipment. The sides are also covered with metal to protect the ceramic material during installation. The lid, containing eight silicon carbide heating elements, is remotely guided into place and fastened to the melter using near-standard canyon-remote flanging technology (Figure 1.6). Two long guide dowels are provided to aid lid positioning during installation and to ensure that the heaters are not damaged during installation by impact with other components.

The prototype discharge lid was remotely installed on, and removed from, the melter shell five times using crane-only techniques. In Figure 1.7, the lid is remotely positioned above the discharge opening on the melter shell. In Figure 1.8, the ends of the long guide dowels have been inserted in the guide tubes located on the side of the melter shell.

The first two tests remote installation/removal of the discharge lid were performed with direct viewing. Three subsequent installation/removal tests were performed with closed-circuit viewing. All tests were performed without difficulties: the remote lid

FIGURE 1.5. Melter Discharge Lid Prototype

installation can be characterized as a smooth operation with or without direct viewing.

As part of each installation test, the eight remote nuts were tightened on the lid using a remote-operated impact wrench. Neither the lid-lowering operation nor the

impact-wrench ratcheting (even after 1 min or more of prolonged wrench vibration) was found to cause heating-element damage detectable by element-resistance measurements. Resistance measurement sensitivity was better than $\pm 0.001 \Omega$.

8400879-8cn

FIGURE 1.6. Discharge Section Lid Installed on Melter Shell

Through-Wall Thermocouple Test

A test was conducted to determine the feasibility of remote installation and removal of the through-wall melter thermocouple assembly developed during previous verification testing of the concept.

The concept consists of inserting metal sheathed thermocouples through a spiral wound pipe in the hot-cell shielding wall, then through a jumper with long radius bends, and finally into a thermowell in the melter. The thermowell is connected to the melter with a remote flange. The jumper is

8400879-15cn

FIGURE 1.7. The Lid Is Positioned Above the Melter by Remote Control

connected to the thermowell flange on a seat positioned by two dowels through a collar. The wall end of the jumper is positioned in a vee slot which aids in guiding the jumper into place. The assembly is shown in Figure 1.9. To perform the test, the jumper and thermowell were handled with the remote

8400879-4cn

FIGURE 1.8. Dowel Ends from Lid Are Inserted in Guide Tubes on Melter

TV viewing system mounted on the HBE crane in the radio-controlled mode.

The tests successfully demonstrated the remote operability of the system, and the following observations were made:

- The thermowell was easily installed and removed remotely. During remote removal,

8401775-14cn

FIGURE 1.9. Melter Thermocouple Jumper

when flange nuts were being loosened, the loosened nut tended to reengage the thread by a fraction of a turn because of vibration of the assembly from the impact wrench.

- The thermocouple jumper was remotely installed and removed with and without installed thermocouples. It was observed that the jumper design could be improved by placement of the bail or modifying the thermowell doweling configuration, so that the jumper would initially contact a dowel first to aid in pivoting the jumper into place for final placement. The impact wrench-operated crimp nut worked very well in holding the thermocouples in the jumper during its removal.
- Ten 1/8-in.-dia aluminum wires, 25 ft long, were inserted into the 3/4-in. pipe channel between the wall and into the thermowell. The first five went in easily, and the last five went in with increasing difficulty. As the pipe became filled, the wire ends increasingly tended to stall at the junctions between the wall and jumper and between the wall and the thermowell. This situation can be corrected by chamfering the receiving ends on the jumper and thermowell.
- Removal of the jumper with all thermocouples was successfully accomplished. The crimping nut held the thermocouples in the jumper when tightened and made it easy to pull the thermocouples through the wall.

Mockup of Thermal Characteristics of Melter Discharge Section

Tests of this unit were to determine heat transfer characteristics and operating parameters of a melter discharge section and

to verify the structural integrity of the discharge section components.

During canister filling, the glass stream leaving the melting cavity requires external heat to stay molten. The function of the overflow section is to provide a thermally insulated containment and a flow path for the glass-product stream leaving the melter. Heating elements are used to provide this heat, thus maintaining the glass in a molten, flowing state.

Eight coaxial heating elements of silicon carbide provide direct heat along the overflow trough and pour spout. The heaters are designed to maintain an operating temperature of ~1050°C in the overflow section. The operating temperature is monitored using thermocouples (T/Cs) which enter through a T/C nozzle on the lid of the overflow heater. The overflow section heater is insulated with a cast material that is corrosion-resistant.

The overflow section, Figure 1.10, consists of a containment box that houses a metal trough and dam with a refractory that is similar, as to heat transfer characteristics, to current melter designs. Refractory materials include Monofrax®, Alfrax-66®, firebrick, and Kaowool® (blanket and bulk fiber). Heat is provided by four SiC coaxial heating elements and four spiral elements. Two plate heaters are provided to simulate the thermal presence of molten glass within the melting cavity. The thermal effect of glass product within a canister (located in the turntable below the trough opening) is simulated using a disk-shaped steam jacket. The steam jacket is located at the base of a mock discharge insert included in the test assembly.

Thermal testing included measuring the temperatures within the mockup during

FIGURE 1.10. Melter Discharge Section, Showing Thermal System Components

various steady-state operating conditions and observing the extent of damage to the refractory lid or trough components as a result of nonsteady-state thermal stresses.

Test data indicated that the metal trough and dam components functioned well. Throughout all steps, except for simulation of a heating element failure, the trough temperatures remained sufficient to maintain glass flowability. Cooling of the dam appeared sufficient to prevent glass from leaking beneath the trough into the discharge area.

Extensive damage of the cast refractory wall adjacent to the dam was noted. This damage was due to warpage of the dam caused by a temperature gradient extending radially outward from the center of the dam to its

cooled edges. It is recommended that a deformable material, e.g., Kaowool® or an air gap, be left between the dam and adjacent refractory walls. In the test assembly, the dam was cast into the refractory.

Three of the spiral-type SiC heating elements malfunctioned during the last part of the thermal test simulation of a heating element failure. One coaxial SiC heating element was found to be near failure upon visual inspection after the test.

At the conclusion of the test, a yellow powder was found in the off-gas line and covered the refractory surfaces inside the mockup. A white powder was found on the spiral heating elements. Chemical analyses were performed on these powders and are

summarized in Table 1.3. Table 1.3 indicates that the material on the heating elements is primarily SiO_2 rather than Al_2O_3 as had been anticipated. The refractory scale was found to be primarily Al_2O_3 with a small amount of other compounds presumably responsible for the yellowish color. The off gas was high in SiO_2 , MoO_2 , Fe_2O_3 , Cr_2O , and Al_2O_3 . The SiO_2 source may have been from the heating elements.

Glass Sampler

Tests were conducted to evaluate the remote operation of a glass sampling concept (Figure 1.11) developed during previous concept verification testing. In this concept, a sampler is placed within the neck of a glass-receiving canister. The canister is then placed in the turntable and rotated under the melter glass stream. As the glass stream is collected in the sample cup, the increasing sample weight balances a counterweight on the opposite side of a pivot. Additional glass causes the sample arm to deflect until a critical point is exceeded, and the arm falls into a final stable con-

TABLE 1.3. Chemical Analyses Following Thermal Mockup of Melter Discharge Section, wt%

Oxide	Off-Gas	Refractory	On Elements
Al_2O_3	37.4	7.83	0.72
B_2O_3	--	0.90	0.26
CaO	4.49	1.12	0.25
Cr_2O	0.54	6.52	0.03
CuO	0.04	3.31	0.03
Fe_2O_3	0.81	19.0	0.31
K_2O	--	--	0.5
MoO_2	0.40	10.9	--
NaO	1.45	5.68	--
SiO_2	1.51	23.0	40.0
TiO_2	--	0.67	0.24

8401520-2

FIGURE 1.11. Glass Sampler

figuration. During arm deflection, a second pivot on the sample cup keeps the cup upright to prevent sample loss.

Tests conducted on the sampler included:

- sampler arm tripping, using lead shot, to determine a range of sample weight collected
- installation of sampler into a canister using a remote-operated crane
- removal of sampler from a canister using a remote-operated crane
- transfer of the sample cup from sample arm into sampler retainer/transport cask using a remote-operated crane
- canister loading into the turntable to observe effects of loading on sampler position in the canister.

The sampler operability and remotability tests proceeded very well, and successfully demonstrated the viability of this concept.

Equipment Remotizing and Testing in Progress

Several equipment test programs are in progress. The equipment tests and their status are provided in Table 1.4.

Canister Closure Weld

A contract has been placed with Manufacturing Technology, Inc. (MTI) to perform a series of primary (canister lid) and secondary (canister secondary lid) canister lid closure welds using the reference inertial welding process. Primary and secondary canister lid weld samples have been fabricated and shipped to MTI for weld testing.

Canister Weld Closure Examination

Ultrasonic testing was selected as a reference nondestructive testing technique to verify the integrity of the canister lid welding process. Preliminary tests have been conducted to assess the performance of ultrasonic testing to detect flaws in the

inertial weld of the lid to the canister. Using various frequencies, the capability was demonstrated of detecting side-drilled holes as small as 1/16 in. in diameter in simulated canister-closure samples. The verification notches and reference flaws were also readily detected.

1.2 IN-SITU VITRIFICATION OF HANFORD WASTE (AR-05-10-02 - 80441)

V. F. FitzPatrick - Program Manager

The objective of this program is to develop and evaluate the in-situ waste vitrification concept to confirm its feasibility for large-scale use.

Summary

Work during this reporting period focused on three tasks, 1) analysis of the samples from the pilot-scale radioactive test, 2) corrosion testing of silicon carbide (SiC)-coated graphite electrodes, and 3) design of the large-scale system.

TABLE 1.4. Equipment Remotizing and Testing in Progress Status

<u>Equipment System</u>	<u>Objective</u>	<u>Status^(a) March 31, 1984</u>
SRL Electrical Connectors (Concept Adaptation)	Verify remotability and performance features of SRL and other electrical connectors to provide power to the melter overflow heater and instrument signals.	Testing in progress.
Nozzle Cleaner	Evaluate use of air and water flow to cool and remove debris from core-cutting surface (used to clean solids buildup from melter nozzles).	Testing in progress.
In-Melter Viewing Remotability	Assess remote installation, removal, and operation of camera in mock-melter assembly.	Testing in progress.

(a) Testing in progress indicates that the equipment has been designed, fabricated, and installed; the test procedure has been completed; and test operations have been initiated.

Analysis of samples from the pilot-scale radioactive test indicates that the vitrified soil retained greater than 99% of all of the radionuclides. Losses from the melt to the off-gas treatment system ranged from $\leq 0.03\%$ for particulates such as plutonium and strontium to 0.8% for a more volatile element such as cesium. All radionuclide losses from the melt were contained in the off-gas system, and no radionuclides migrated beyond the vitrification zone.

SiC coating successfully retarded electrode oxidization above grade. Corrosion in the subsidence zone, previously unobserved because of minimal subsidence, was very high. This deficiency has created sufficient uncertainty to necessitate reviewing the performance of molybdenum as a temporary fallback position for initial large-scale testing. Future testing of graphite/coating systems will focus on isotropic graphite, with a combination of reaction and chemical vapor deposition coatings with increased thickness.

Detailed design of the large-scale system, which comprised 92 sheets, was completed ahead of schedule in mid-February. All engineered equipment, such as scrubbers, blowers, control systems, etc., has been ordered and over 80% has been received and acceptance tested. Bids for fabrication and assembly of the process system have been received and evaluated, and the low bidder was judged to be responsive. A contract for system fabrication will be awarded in early April 1984.

Pilot-Scale Radioactive Test Analysis -
C. L. Timmerman

A major objective of the ISV program during FY 1983 was to vitrify actual radioactive materials in place. To accomplish

this, a mobile pilot-scale off-gas treatment unit for the radioactive field test was constructed in a semi-trailer. The power system and off-gas treatment system were improved designs, building upon experience gained with the pilot-scale field test system. Two nonradioactive tests were performed to provide equipment checkout and operator training prior to the radioactive field test. A successful pilot-scale radioactive test (PSRT) was performed in June 1983, using a makeup site containing known quantities of ^{241}Am , ^{239}Pu , ^{238}Pu , ^{137}Cs , ^{106}Ru , ^{90}Sr , and ^{60}Co (see Table 1.5).

The primary objectives of the radioactive test were to 1) demonstrate containment and confinement of the radioactive material, 2) verify equipment performance of the power and off-gas systems, 3) identify losses to the off-gas system, and 4) characterize the behavior of the radioactive material in the vitrified soil.

The test successfully demonstrated the processing containment of radionuclides within the vitrified mass or in the off-gas system. (Operational details and preliminary analytical results were reported in the previous report in this series, PNL-4250-4.) No environmental release of radioactive material was measured during testing operations. The vitrified soil had a greater

TABLE 1.5. PSRT Radionuclide Inventory

Radionuclide	Total Curies	Original Concentration, nCi/g
^{241}Am	0.0095	370
^{239}Pu	0.0053	210
^{238}Pu	0.0018	70
^{137}Cs	0.020	780
^{106}Ru	0.021	820
^{90}Sr	0.680	26,600
^{60}Co	0.010	390

than 99% retention of all radionuclides. Losses to the off-gas, as indicated in Table 1.6, varied from <0.03% for particulate materials (plutonium and strontium) to 0.8% for a more volatile element such as cesium. The off-gas system performed effectively in containing any volatile or entrained radioactive components. Vitrified soil analysis revealed a relatively uniform distribution of all radionuclides within the glass, except ruthenium and cobalt. Their nonuniform distribution may be correlated to the smaller amount of sample of these radionuclides, or less mass may produce a more random distribution. Migration of radionuclides outside the vitrification zone did not occur, as indicated by soil samples surrounding the block.

Electrode Performance Testing and Analysis -
K. H. Oma, W. C. Morgan, and C. L. Timmerman

A key task in the technology development effort for the in-situ vitrification (ISV) process (Brouns and Timmerman 1982) has been to evaluate electrode material performance. The objective of the work was to identify an economical electrode system that will last

the duration required for large-scale ISV operation. Based on modeling studies, the electrodes should last for up to 400 hr of operation, depending on the required melt depth and electrode separation (Oma et al. 1983). For radioactive waste site applications, it is desirable to leave the electrodes in the melt, as recovery for reuse would introduce additional radionuclide handling and containment difficulties.

A review of candidate electrode materials and designs was completed early in the ISV Program when initial testing of the engineering-scale laboratory system was under way. Molybdenum (Mo) was thought to be the most compatible electrode material for vitrification because it has a high melting point, high strength, and high corrosion resistance. Molybdenum was successfully tested on five engineering-scale tests and one pilot-scale test. Molybdenum is, however, expensive. The review established that graphite was the prime alternative to molybdenum.

The electrode must perform in four differing environments: 1) above the melt, 2) in the melt zone, 3) in the subsidence zone, and 4) below the melt. For the past

TABLE 1.6. PSRT Radionuclide Release Data

<u>Radionuclide</u>	<u>Melt Retention, %</u>	<u>Release to Off Gas, %</u>	<u>Soil-to-Off-Gas DF</u>
Transuranics			
²⁴¹ Am	99.99	0.01	1.3×10^4
²³⁹ Pu/ ²⁴⁰ Pu	99.98	0.02	4.4×10^3
²³⁸ Pu	99.98	0.02	4.5×10^3
Fission Products			
²³⁷ Cs	99.23	0.77	1.3×10^2
¹⁰⁶ Ru	99.82	0.18	5.6×10^2
⁹⁰ Sr	99.97	0.03	3.1×10^3
⁶⁰ Co	99.94	0.06	1.8×10^3

2 1/2 years, graphite electrodes have been tested in laboratory, engineering-scale and pilot-scale tests. The results of pilot-scale testing during FY 1983 showed that the portion of electrode above grade is very susceptible to oxidization; electrode diameter reductions of 50% were observed in all three pilot-scale tests. Graphite corrosion rates as high as those observed in the pilot-scale tests were deemed unacceptable for large-scale testing. Several coating materials that might retard the high oxidization rates were evaluated, with silicon carbide (SiC) identified as the most promising. A series of laboratory screening tests was conducted to ascertain the amount of protection that might be achieved with a SiC coating. The results were sufficiently promising that engineering-scale and pilot-scale performance testing of SiC coated electrodes was incorporated into the FY 1984 program scope.

Standard graphite electrodes come in 6-ft lengths, and the pilot-scale testing up through the end of FY 1983 was limited to test depths of 6 ft. Some electrodes were modified to incorporate joints; however, the number of tests and the amount of data were limited. Therefore, it was necessary to investigate coupling/extension techniques that provided acceptable mechanical/corrosion/electrical performance.

The electrode performance assessment for FY 1984 was defined to be twofold: 1) to determine the corrosion resistance of the SiC coating, both above grade and in the subsidence zone and 2) to determine the mechanical/corrosion performance of electrode joints. In previous tests no significant amount of subsidence had been observed because of the relatively shallow depths achieved during testing (~6 ft). Subsidence

up to 33% of the melt depth, however, is anticipated with the large-scale system.

The results of the engineering-scale electrode performance assessment are summarized briefly below:

- Silicon-carbide effectively stops graphite electrode corrosion above grade ground level.
- A layer of glass adheres to the SiC in the subsidence zone and protects the graphite electrode from air oxidation. If the SiC coating is disrupted by corrosion, the glass will not adhere to the exposed graphite, making it susceptible to oxidation once subsidence occurs.
- Metal oxides in the melt are reduced by the direct reaction with noncoated graphite and form metallic globules. On SiC-coated graphite, the reduction occurs primarily when cracks or pinholes occur in the coating, resulting in an undercutting of the coating substrate adjacent to the point of attack. This leads to sloughing of the coating as subsidence occurs. Corrosion of the electrodes is greatly accelerated at points of contact with these molten globules.
- Elimination of cracks and pinholes in the SiC coating may greatly extend the life of the coating and the electrode.
- To achieve an electrode free of pinholes and cracks, it is proposed that isotropic-extruded graphites with reaction and chemical vapor deposition (CVD) coatings of SiC be tested in the laboratory. If successful, this electrode-coating system should be tested during future pilot- and large-scale ISV tests.
- For graphite electrodes, the male/female joint offers significant advantages over the conventional pin-and-socket joint.

The poor electrode performance in the subsidence zone has produced sufficient uncertainty to necessitate reviewing the performance of molybdenum electrodes as a temporary fallback position. This uncertainty relative to the near-term testing requirements for the large-scale system, particularly the initial acceptance tests scheduled for December 1984, dictates a conservative approach and the selection of molybdenum for the initial large-scale tests.

To ensure having a qualified electrode available for initial large-scale testing, the following specific actions will be pursued as part of the program:

1. Initiate immediately a laboratory-scale program to define the performance of SiC coatings on isotropic graphite. Combinations of reaction and chemical vapor deposition coatings of SiC will be investigated. It is believed that the change to an isotropic grade of graphite, combined with thicker coatings of SiC, can improve the corrosion performance in the subsidence zone.
2. Conduct the currently scheduled pilot-scale electrode corrosion test using molybdenum electrodes to increase the performance data base because molybdenum electrodes will be used as a temporary fallback position for initial large-scale tests.
3. Continue engineering and pilot-scale testing of promising SiC-graphite electrode configurations and, in parallel, examine the potential for employing other coatings.

Large-Scale Development - J. L. Buelt, J. G. Carter, C. R. Hymas, and K. H. Oma

In the first half of FY 1984, the most significant accomplishment was completion, ahead of schedule, of the definitive design of the large-scale in-situ vitrification process. Completion constituted the preparation of 92 drawings, their review by representatives from both participating DOE contractors (Pacific Northwest Laboratory and Rockwell), and incorporation of the comments. The design's completion and the receipt of >80% of the standard process equipment allowed for the bidding process for fabricating and assembling process equipment in the three process trailers to be completed. With these advancements, the large-scale process is expected to be completed on schedule by the end of FY 1984.

Definitive Design

The definitive design drawings completed in this half-year fulfill the technical requirements needed to proceed with fabrication and assembly of the large-scale process. The design details the process and electrical equipment and the interconnecting jumpers and structural support. The process equipment is contained in the following three trailers:

- the off-gas trailer (see Figure 1.12), containing all off-gas treatment equipment
- the support trailer, containing the electrical transformation and protection equipment and the off-gas cooling system

FIGURE 1.12. Schematic of Off-Gas Trailer

- the control trailer, containing the process control station and support equipment such as the motor control center, air compressor, and scrub-solution supply tank.

The 92 drawings include an overall site plan of all three trailers and supportive equipment; engineering flow and piping and instrument diagrams; off-gas equipment, containment module, and off-gas trailer arrangements and details; electrical and instrumentation assemblies; and arrangements and details of the support and control trailers.

As part of the design effort, considerable review was made by PNL and Rockwell representatives in specialties from radiological and industrial safety, process engineering, and quality assurance. Their review effected a number of modifications during design to implement a safer and more reliable process. The following is

a list of some of the more significant modifications:

- Provide a HEPA filter on the inlet of the control trailer's heating and ventilation system for worker protection.
- Provide a HEPA filter on the outlet of the off-gas trailer's ventilation system for environmental protection in the event of a backflow from the off-gas equipment.
- Provide fuse protection on the primary of the auxiliary power transformer.
- Provide a dual off-gas line for redundancy in the event of off-gas line failure.
- Extend the operating platform on the support trailer and provide a railing for added worker safety during voltage tap changes.
- Provide an electrical/interlock as a redundancy to the process control system to shut down electrode power in the event of blower failure.

Procurement

All but eight pieces of the 49 government-furnished equipment needed for the large-scale process have been received and inspected. These items will be supplied to the winner of the trailer fabrication contract for assembly into the three trailers. The government-furnished equipment includes off-gas cooling equipment, wet scrubbers, HEPA filter housings, blowers, pumps, an air compressor, process control equipment, and electrical transformers and controllers. Of the remaining items to be delivered, none is expected to delay completion of the large-scale process by fiscal year end.

Fabrication Contract

The bidding process has been completed for the fabrication and assembly contract for all three trailers. Because of the magnitude and complexity of this order, significant inspection and acceptance test procedures have been specified. The basic fabrication requirements include conformance to ANSI/ASME B31.1 for all radioactive process piping, the National Electric Code (NFPA-70) for all electrical systems, and all structural steel welding in accordance with AWS D1.1. Both preliminary and final acceptance test procedures have been specified to be performed at the completion of the fabrication/assembly at the seller's and buyer's facilities, respectively. The contract is expected to be awarded in early April 1984 and completed in August 1984.

References

Brouns, R. A., and C. L. Timmerman. 1982. "In Situ Thermoelectric Stabilization of Radioactive Wastes." In Proceedings of the Symposium on Waste Management '82,

ed. Roy G. Post, pp. 449-463, University of Arizona College of Engineering and U.S. Department of Energy, Tucson, Arizona.

Oma, K. H. et al. 1983. In Situ Vitriification of Transuranic Wastes: Systems Evaluation and Applications Assessment. PNL-4800, Pacific Northwest Laboratory, Richland, Washington.

1.3 DEFENSE BYPRODUCTS PRODUCTION AND UTILIZATION PROGRAM

(AR-05-15-25 - 80576 -

GE-0347-03/80401)

G. L. Tingey - Program Manager

The objective of this program is to identify and develop safe and cost-effective applications for nuclear byproducts, and to optimize the supply of these byproducts, especially those available from Hanford. During FY 1984, this program will focus on developing irradiation for food and other agricultural products in the Northwest, supporting activities for defense energy sources for a 500-W_e power generator, and developing an adequate supply of safe, cesium-137 sources qualified as irradiation sources.

Summary

Irradiation of cherries and apples using the cobalt-60 facility at PNL has begun. Irradiation at doses less than 20 krad kills more than 90% of the pupae from cherry fruit flies. The capability of the surviving insects to reproduce will be evaluated this summer; but from the large kill it is assumed that the survivors will be sterile. Little or no degradation of the fruit by irradiation at doses up to 100,000 rads has been observed. Preliminary indications are that some small delay in ripening of the cherries may even occur. The experimental study of the effect of irradiation of apples is continuing, and a second series of tests on cherries is planned during the 1984 harvest.

The testing of radioluminescent (RL) lights in Alaska has been completed for the 1983-84 year. With the approach of summer and decreasing darkness available for testing, the lights have been returned to the "lower 48" for summer testing and evaluation. Tests were conducted at Allen Army Airfield and Donnally Landing Zone near Delta, Alaska; Eielson Air Force Base near Fairbanks; and at Central, Alaska. Military pilots were able to acquire the lights from 4 miles or greater and to land C-130, A-10 and other aircraft safely. Civilian pilots reported that they could acquire the lights from 2 to 4 miles distance and land. Landing aids such as alignment panels were found to be acceptable, but visual approach slope indicator designs need more evaluation. An unplanned emergency evacuation that occurred after a local resident was badly burned would not have been possible without runway lighting such as that provided using the RL lights.

Irradiation of Northwest Agricultural Products - D. E. Eakin

Export of Northwest agricultural products is currently limited because of the potential for the spread of insects harmful to production. Therefore, a reliable means of disinfestation is required. This need has increased the interest in irradiation as a means for both disinfestation and preservation. Although several agricultural products are being considered for irradiation treatment, apples and cherries for export appear to be of greatest present interest. Thus, to date, research conducted as part of this program has concentrated on apples and cherries. Other commodities, however, such as potatoes, onions, hay, grain, and cattle hides are expected to be included later.

Cherries were irradiated to evaluate:

1) the effectiveness of irradiation as a method of insect control and 2) its effect on product quality. To determine the insect control effectiveness, a batch of cherries was purposely infested with codling moth larvae and another batch infested with cherry fruit fly pupae by the U.S. Department of Agriculture (USDA) laboratory at Yakima. These cherries were then irradiated to nominal doses of 0, 4, 6, 8, 12, and 20 krads in the PNL cobalt-60 facility. After irradiation, the codling moth larvae were transferred to apples for continued growth. In these tests, too few larvae survived to differentiate among the irradiation treatments. In the tests with cherry fruit fly pupae irradiation, substantially reduced the survival rate. Table 1.7 shows the survival rate as a function of gamma dose.

As shown in the table, even low doses of irradiation result in a major reduction in survival rate. Of primary importance is the ability of the insects to reproduce. To test this, the surviving pupae were transferred to apples, which will be stored until the summer of 1984 to evaluate the reproduction rate of the irradiated insects.

The product quality is being studied by irradiating the cherries at levels of 0, 20, 40, 60, 80, and 100 krads in the PNL

TABLE 1.7. Survival Rate of Cherry Fruit Fly Pupae as a Function of Gamma Dose

<u>Dose Received, krad</u>	<u>Number of Surviving Pupae</u>
0	218
3.5	92
5.3	72
7.0	53
10.5	37
17.4	15

cobalt-60 facility. Cherries from five different packing houses were tested over a 6-week period. Tests were conducted up to 100 krad to measure the effect of irradiation up to the maximum dose permitted by the proposed FDA regulation. The actual dose used in a commercial irradiator would be between the minimum required for insect control and the maximum without adversely affecting the product quality.

Following irradiation of the cherries, they were transported to the USDA laboratory in Wenatchee, Washington, and prepared for chemical and physical testing. For each irradiation dose, the product was divided into 10 groups of 30 cherries each. Quality tests were conducted on these 10 groups after the following storage periods:

1. tested immediately
2. held in ripening room (68°F) 4 days
3. held in cold storage (31°F) 7 days
4. held in cold storage 7 days and then in ripening room 4 days
5. held in cold storage 14 days
6. held in cold storage 14 days and then in ripening room 4 days
7. held in cold storage 21 days
8. held in cold storage 21 days and then in ripening room 4 days
9. held in cold storage 28 days
10. held in cold storage 28 days and then in ripening room 4 days.

Quality tests included stem diameter, stem discoloration, fruit size, visual color, photometric color measurements, firmness, percent soluble solids, pH, and acidity based on titration. Respiration measurements were also made by holding a batch of cherries from each dose level at 32°F for 3 days and then placing 15 cherries from each batch into a respiration jar at 68°F. The atmosphere in each jar was then sampled for CO₂, O₂, and analyses of volatiles on

each of the next 4 days for a total of four samples. Because of the large number of samples and individual tests, results are not detailed here. In summary, however, significant differences could be detected in the quality of the cherries as a function of irradiation dose level. Rather, there was even some indication that irradiation may have improved the product quality at the longer storage times. Future tests are planned to confirm and quantify this observation. There were significantly more differences in quality between batches (packing house/orchard) and even cherries within a batch than between irradiation doses. In all cases, irradiation was less detrimental to cherry quality than is standard methyl bromide fumigation.

For the apple irradiation testing, apples were obtained from six packing houses and divided into six lots for irradiation at six time intervals. Thus, an equal number of apples from each packing house is irradiated at each dose level at each time interval. The initial irradiation was done on freshly packed apples (no controlled atmosphere storage). Irradiation tests have been or will be conducted following 2, 4, 6, 8, and 10 months of controlled atmosphere storage. Following irradiation, the apples are placed in cold storage for 2 months. After removal from cold storage, quality tests are conducted on 20 apples from each dose level and each packing house. Quality tests are then conducted on five apples following 3, 7, 10, and 14 days ripening time. The quality tests include pH, visual inspection, moisture, and firmness. The first irradiated apples have been visually inspected and no differences observed between different radiation doses. However, pressure tests, inspection of the interiors, and other measurements indicated that minor quality

changes occurred at the higher doses. The results from this batch will be analyzed to determine the significance of the differences. The apple irradiation project is only half over, and additional results must be analyzed before a decisive conclusion is reached on impacts of quality changes. During the 1984 crop year, testing will be conducted to determine the effectiveness of irradiation for insect control.

Radioluminescent (RL) Light Testing in Alaska - G. A. Jensen

The iterative process of design modification of tritium-powered radioluminescent (RL) lights that began in 1982 has now produced a prototype system for use at tactical military airfields and rural Arctic and sub-Arctic airfields. This process resulted in several short-term civilian and military evaluations in Alaska and a long-term civilian evaluation at Central, Alaska. All work has been a cooperative venture between the State of Alaska Department of Transportation and Public Facilities (DOT&PF), Department of Energy (DOE-HQ) and its operations offices at Oak Ridge, Tennessee (DOE-OR), and Richland, Washington (DOE-RL), and contractor personnel at Oak Ridge National Laboratory (ORNL) and Pacific Northwest Laboratory (PNL). The Alaskan Air Command, U.S. Air Force, the Alaska Air National Guard, Alaska and North Carolina Army Air National Guard, and Alaska Region Federal Aviation Administration (FAA) flights standards personnel also participated in these evaluations at different times.

RL light panels, wands, and superwands used in these tests are shown in Figures 1.13, 1.14, and 1.15. The light panels and superwands incorporated a new tritium tube design developed by ORNL during the

84C468-1

FIGURE 1.13. Radioluminescent (RL) Light Panel

spring and summer of 1983. This development was in response to the need for greater brightness identified during tests and evaluations conducted at the "Brimfrost 83" exercises earlier that year. Preliminary design of the support fixtures and hardware was begun by Alaska DOT&PF and PNL personnel and completed during August at ORNL.

Evaluation using a prototype of the panel as the basic light element and supporting fixtures was made at Camp Mackall, North Carolina, during the fall. Observers and pilots were able to acquire the lights from 4 to 6 miles. The omni-directional superwand was developed during this period (Figure 1.14). The superwand represents an improvement over the first generation wand (Figure 1.15) used during "Brimfrost 83" testing in Alaska. Since response to the

Individual Light
Tubes Inside High-
Impact Structure

FIGURE 1.14. Radioluminescent Wand

84C468-1

FIGURE 1.15. Radioluminescent Superwand

second generation was good, the lights were brought to Alaska for winter tests and evaluation. The following summarizes the results of the military and civilian test program in Alaska from November 19, 1983, through February 19, 1984, when the lights were removed from Central, to Anchorage, Alaska, for return to the "lower 48" and further tests (Table 1.8).

The lights were installed at several locations for military evaluation. Figures 1.16 and 1.17 show the basic configurations of the lighting system used in these tests. Pictures of these configurations are shown in Figures 1.18 and 1.19. Both configurations were modified periodically by increasing or decreasing the amount of lights in the threshold area to determine the effects on pilot acquisition and definition of the lights or landing aids. Since these evaluations were primarily for military use of the lights, most of the flying was done with the runway configuration shown in Figure 1.16. This is designed to meet Military Airlift Command regulations for nighttime operations. Military pilots were able to acquire the light from 3 to 6 miles distance and found the runway marking usable for alignment and landing from 2 to 6 miles. Some difficulty was experienced by A-10 pilots in high winds, but most felt that they could have landed to the lights under these conditions had they been permitted to do so. C-130, O-2, and C-12 pilots reported no difficulty landing, and generally rated the RL lights as satisfactory to outstanding. Many A-10 pilots also gave the lights an outstanding rating. On several occasions, a visual approach slope indicator (VASI) shown in Figure 1.20 was evaluated. Military pilots acquired the light from the VASI from 1 to 2 miles out but found it unusable. Attempts were made to increase

TABLE 1.8. Summary of Military and Civilian Test Program in Alaska
(November 19, 1983 to February 19, 1984)

Test Location	Test Date(s)	Aircraft Participating	Sorties		Runway Configuration	Acquisition Distance, mi	Weather				
			Landings	Flyovers			Temp., °F	Wind	Visibility	Precipitation	Moon
Allen Army Airfield	Nov 19	Cessna 208	8-10	--	Civilian	1-3	-9	Light & variable	Clear 15+	0	Full
		C-12	1			3-4					
		UH-1	1-4			2-3 1/2					
Allen Army Airfield	Nov 20 & 21	O-2	0	2	--	2-5	Cold	High Turbulence	Clear	0	Full
Allen Army Airfield	Nov 22	O-2 C-12	Several 2	Numerous Numerous	Military	4-5 4-6	Cold	High	Partly Cloudy	0	Full
Allen Army Airfield	Nov 23	Cessna 208 C-130	2-4 8-10	--	Military	1 1/2 2-3 ^(a)	Cold	None	Cloudy	Snowing Hard	--
Donnally Landing Zone	Nov 28	Flying	--	--	--	--	42	40+ mph	Cloudy	--	--
	Nov 29	Cancelled									
Donnally Landing Zone	Nov 30	C-130	20	--	Military	3-4 ^(a)	40	20+ mph	Cloudy	--	--
	Dec 1	C-130	30		Military	3-4 ^(a)	40				
	Dec 2	Flying Cancelled	None				10-15	Light	Cloudy	Heavy Snow	--
Allen Army Airfield	Dec 5	A-10	0	15-20	Military	4+	15	Calm	15+	0	Broken Cloud Cover
	Dec 6	A-10	0	24	Military	3-6	15	17-20 knots Gust to 26 knots	10+	0	Broken Cloud Cover
Eielson AFB	Dec 12	A-10	8-10	25	Military	4+	-30	Calm	15+	0	60% Moon
Eielson AFB	Dec 13	A-10	8-10	20-25	Several ^(b)	4+	-30	Calm	15+	0	70% Moon
Eielson AFB	Dec 14	A-10	2-4	10-15	Several ^(b)	4+	-30	Calm	15+	0	70% Moon
Central, Alaska	Dec 19	Several	Several		RL Civilian	3-7		Varied			
Central, Alaska	Feb 8	Cessna 206	2-3	--	RL Civilian	3+	-34	Calm	15+	Thin	Quarter
		Cessna 206	2-3		RL Civilian Flarepot V Lead-in	3+					
		Cessna 206	2-3		RL Civilian Flarepot Y Lead-in	3+					
Central, Alaska	Feb 9	Cessna 206	2-3		RL Civilian	1 1/2-2	-34	Calm	2	Indefinite	Cloud Cover
		Cessna 206	2-3		RL Lead-in Flarepots	2-3					
Central, Alaska	Feb 15	Cessna 206	Several		RL Civilian	2-4 ^(c)	-34	Calm	Unlimited	0	Full
		Cessna 206			VASI	1 1/2-2 (usable) ^(c)					
		Cessna 206			Flarepots	4-5					

(a) C-130 pilots were allowed to fly only a short final approach. They acquired the lights upon turning to align themselves with the runway.

(b) Primary purpose of these tests was to evaluate and attempt to improve acquisition of the visual approach slope indicator (VASI).

(c) Purpose of these tests was to evaluate several visual approach slope indicators.

the light output of this VASI, but this did not improve the acquisition or usefulness of the system.

Installation of the lights on the runway was completed December 19, 1983, at Central, Alaska. The lights were removed February 21, 1984. The civilian configuration was tested at Allen Army Airfield (Figure 1.17) prior to installation at Central. A 15-watt

strobe beacon was used as a navigational aid to bring pilots to the general vicinity of the airfield. This beacon was located on a DOT&PF building about 1/4 mile from the airfield. A glide slope indicator (Figure 1.20) and a wind T (Figure 1.21) were also installed later in December. Evaluation questionnaires were provided to Air Taxi and other pilots flying to the Central

FIGURE 1.16. Military Runway Configuration

FIGURE 1.17. Civilian Runway Configuration Tested at Central, Alaska

airstrip, and in general, other pilots reported acquisition distances from 2 to 7 miles. Nominally, acquisition distance averaged about 3 miles. An unplanned medical evacuation of a burn victim was completed New Year's Eve, made possible only by the RL lights being on the runway at that time. FAA flight standards personnel and Transport Canada personnel also viewed the lights.

The test team and FAA flight standards personnel evaluated the RL runway lighting system and navigational and landing aids such as alignment or lead-in lights, the strobe, flarepots as edge markers and lead-in lights, various VASI configurations and combinations of these various landing

aids. The flarepots were evaluated to determine whether they could be used to lead pilots to the airfield if the strobe fails. In all approaches, the RL runway light was acquired from ~3-1/2 miles distant, alignment was possible at 3 miles and positive runway definition occurred at ~2 to 2-1/2 miles. Reduced visibility reduced the acquisition and visibility proportionally. In clear weather, pilots normally had full vision of the runway at 2 miles. Flarepots worked well for runway alignment but were not judged as effective as the strobe as a navigational aid. The strobe could be identified from 7 to 11 miles out compared to 4 to 5 miles for flarepots. The RL glide slope indicator was normally not clearly

FIGURE 1.18. Photo of Radioluminescent Lights in Military Runway Configuration

FIGURE 1.19. Radioluminescent Lights in the Civilian Runway Configuration Tested

visible from more than 1-1/2 miles out and difficult to use beyond 1/2 mile. Use of RL lights for runway alignment was preferred over flarepots for this purpose since night vision was not compromised. Use of alignment lights did not improve acquisition distance but significantly improved the ability to align the aircraft earlier than without them. Although flarepots were found

to be visible from about 50% further than RL lights, with the strobe light, visible from 7 to 11 miles, flarepots were of no advantage. Furthermore, their reliability and permanent nature make RL lights an overwhelming choice over flarepots.

One evening of testing was devoted to evaluation of several VASI configurations. The configurations evaluated for glide slope

FIGURE 1.20. Visual Approach Slope Indicator

84C468-3

FIGURE 1.21. Radioluminescent Light Wind T Being Installed at Central, Alaska

indicators, shown in Figure 1.22, were positioned 500 ft down the runway with 10 ft between front racks (when 2 racks were used) and 57 ft between the front fixture and the back fixture. All systems were judged usable from 1/2 to 2 miles by the pilots flying the aircraft. The DOT&PF observer and one of the FAA pilots flying in the aircraft regularly saw the glide slope indicator and found it usable from 1-1/2 to 2 miles distant. It is important to note that the most distinct and easiest configuration to use was not necessarily the one producing the most light (Figure 1.22b). Pilots' comments indicated that the simpler L configuration (Figure 1.22d) was easier to become accustomed to than the "top hat." Also, the pilot who reported problems acquiring and using the glide slope indicators felt that

his astigmatism reduced his acquisition and distance in using the system.

Taxiway Lights at Fairbanks International Airport

Blue superwand taxiway lights were installed on 150-ft spacing on one of the taxiways on the south side of the main runway at Fairbanks International Airport. This taxiway is used by small air carriers and private aircraft. Response to this installation has been limited to date; however, because the lights are dim, the 150-ft spacing appears inadequate. Thus, additional lights were supplied by ORNL for installation on the runway. Several of these were struck by snow removal equipment and other accidents, but only the support

FIGURE 1.22. Configurations of Glide Slope Indicators Evaluated

fixtures were broken; the lights themselves were undamaged and have been reinstalled for further testing.

Summary of the Evaluations

Evaluation of the data obtained in the military and civilian testing in Alaska during 1984 is incomplete, but the following summarizes the findings of these tests:

- Acquisition distance of tritium RL lights ranges from 1 to 4 miles for civilian pilots and from 3 to 6 miles for military pilots, with some reports of greater distances.
- Runway definition occurs for military pilots at distances of 2 to 4 miles and civilian pilots at distances from 2 to 3 miles out.
- Alignment can be enhanced using runway alignment (lead-in) lights, and the uses of these extra lights for this purpose may be more effective than increasing the light emission from the threshold area.
- A navigational aid such as a strobe light is needed to lead civilian pilots to the airfield. Once the pilot is near the airfield, the RL lights are a good landing aid.
- FAA flight standards pilots evaluating the lights felt that they could be used with operators' specifications and pilot training. A reliable wind indicator and a beacon or strobe as a navigational aid are needed.
- The lights worked well in Alaska under the weather conditions of the tests. Maintenance was minimal and involved only occasional cleaning and removal of snow. Thin (less than 1/16 in.) hoarfrost layers on the light cover actually enhanced the output of light. Evaluation

is needed, however, to define clearly the encountered problems with thicker layers of hoarfrost.

- An improved glide slope indicator is needed. The top hat (Figure 1.20) is somewhat confusing and difficult to use. Evaluation of an L-shaped configuration showed promise, but further work in this area is needed.
- Blue RL lights show promise for taxiway use. A closer spacing than the normal 150 ft is probably required unless the light output is increased.
- Pilots' vision can be an important factor. This was identified by one of the FAA flight standards pilots and is indicated also by the lower response of older pilots as compared to that of younger observers in the aircraft.

1.4 MODELING RADIONUCLIDE RETARDATION MECHANISMS (AR-05-10-02 - 80813)

J. R. Morrey - Program Manager

The final objective of this program is to develop a capability to reliably predict retardation of radionuclides in soils and geological strata. To accomplish this requires three major developments: 1) selecting and upgrading a baseline geochemical code; 2) constructing a streamlined, efficient geochemical code which will receive initializing information from the baseline code and be coupled to the appropriate aqueous transport code; and 3) updating and expanding a selected thermodynamic data base. When met, these objectives together will provide DOE with the desired capability. This will be accomplished by explicitly accounting for the physical and chemical retardation processes which are operative in chemical and transport processes.

Summary

This program was initiated in April 1983, with four technical tasks: 1) development of an accurate and internally consistent

thermodynamic data base; 2) selection and modification of a parent geochemical code; 3) development of a compact, efficient geochemical subroutine that will couple to transport codes; and 4) coupling the geochemical and transport code to simulate transport of radionuclides in groundwaters.

Figure 1.23 illustrates the logical association of the four technical tasks in this program. Appropriate thermodynamic data are gleaned from the literature and analyzed via the code SOLUPLOT and then made self-consistent with the rest of the data base via the code MCRT. The resultant thermodynamic data file is then used by MINTEQ along with a sample file which has previously been created by the problem definition code PRODEF. MINTEQ can be used alone to predict complex heterogeneous equilibria

and, when completely modified, will create a minimum-basis, site-specific thermodynamic data base to be used by the coupled code to predict the fate of radionuclides in aqueous flow systems.

Development of the thermodynamic data base for the parent and the streamlined geochemical codes includes the addition of pertinent thermodynamic data for inorganic aqueous species and solids containing important radionuclides. Current efforts are focused on expanding the data base's thermodynamic data for uranium, plutonium, technetium, neptunium, and thorium. Data accepted from published sources are documented and checked for thermodynamic internal consistency with computer codes before inclusion. Thermodynamic data for those elements in the parent geochemical

FIGURE 1.23. Schematic Flow Diagram Outlining the Radionuclide Retardation Modeling Project

code will also be expanded where possible to extend the range of aqueous speciation and solubility calculations to temperatures greater than 100°C. Because complexation of dissolved radionuclides with organic constituents may play an important role in migration of these toxic constituents in aquatic environments, expansion and documentation of the thermodynamic data base relative to pertinent aqueous complexes of important organic ligands will be initiated in FY 1985.

Selection and improvement of a parent geochemical code, have been included because it is first necessary to properly scope site-specific problems with a sophisticated geochemical code too large and slow to be coupled to a transport code. The code MINTEQ (Felmy et al. 1984) was chosen after comparison of several extant codes: EQ3/EQ6 (Wolery 1979), developed at the Lawrence Berkeley National Laboratory; EQUILIB (Morrey et al. 1978), developed at PNL for geothermal applications; PHREEQE (Parkhurst et al. 1980), developed at the U.S. Geological Survey; GEOCHEM (Sposito & Mattigod 1980), developed at the University of California at Riverside; and REDEQL.UMD (Harriss and Magnuson 1983), developed at the University of Minnesota for the Environmental Protection Agency. MINTEQ was chosen because it has a full complement of adsorption algorithms, is relatively easily structured, and has associated with it a carefully edited thermodynamic data base. This code was developed at PNL by modifying the code MINEQL, originally developed at the Massachusetts Institute of Technology.

MINTEQ is being improved in several ways to make it easier and more reliable to use: 1) improving convergence reliability, 2) adding high-temperature competency, 3) adding high-ionic-strength competency,

4) adding conservation of water, 5) improving ease of use, 6) modifying to model closed solid systems with finite quantities of soluble materials, 7) adding the capability to model solid solutions, and 8) adding the capability to create a site-specific data base to be used by the coupled geochemical code in modeling transport phenomena. Items (1), (3), (4), (5), and (6) have already been accomplished. Modifications have been made to substantially enhance the performance of MINTEQ, though extensive testing has yet to be done before the code will be documented and released.

Development of the compact geochemical code to solve chemical equilibria extremely quickly and efficiently was preceded by a careful analysis of algorithms proposed in the literature for solution of this type of problem. These investigations, coupled with modeling tests, convinced us that the Newton-Raphson technique will be the most efficient provided that the system is close to equilibrium at all times. The code is now being written and tested.

Thermodynamic Data Base

Recently published thermodynamic data for the inorganic aqueous species and solids of uranium, plutonium, and technetium are being carefully reviewed and evaluated for possible inclusion in the data base of the parent geochemical code. The accepted data will be checked for thermodynamic internal consistency using the MCRT code (Wolery 1983). The MINTEQ (Felmy, Girvin, and Jenne 1984; Felmy et al. 1984) and SOLUPLLOT (Bethke 1978) codes are similarly being used to evaluate the importance of these new data and their relative stabilities to other aqueous species and solids.

Prior to evaluating the reviewed thermodynamic data with the MINTEQ and SOLUPLLOT codes, the MCRT code (Wolery 1983) is used to: 1) check the internal consistency of the accepted thermodynamic data, 2) calculate $\log K_{r,298}^\circ$ and $\Delta H_{r,298}^\circ$ values for the speciation and solubility reactions, and 3) check the mass and charge balance of the formulated speciation and solubility reactions. These reactions and thermodynamic data are then merged with the existing data base of the parent geochemical code. Output from the MCRT code provides documentation for the accepted thermodynamic data and for checking the internal consistency of the data.

SOLUPLLOT, now operational on the VAX computer facility in the Geosciences Research and Engineering Department at PNL, calculates equilibrium stability fields for predominant aqueous species and solids as a function of pH and redox conditions for a user-specified chemical system at a given temperature. The stability fields are calculated from an input data file that contains the Gibbs free energies of formation ($\Delta G_{f,298}^\circ$) and heats of formation ($\Delta H_{f,298}^\circ$) for the aqueous species and solids of interest. By altering this input file with respect to the number of aqueous species and solids and their thermodynamic data, SOLUPLLOT may be used to graphically analyze their relative importance and the stability relationships between different constituents.

Figures 1.24 and 1.25 show the Eh-pH stability fields (marked by dashed lines) of the predominant aqueous species for the carbonate-free systems Pu-H₂O and U-H₂O, respectively, at 25°C as calculated by SOLUPLLOT. Thermodynamic data for the aqueous species and solids of plutonium and uranium were accepted for the calculation

FIGURE 1.24. Stability Fields of the Predominant Plutonium Aqueous Species Plotted as a Function of pH and Redox Conditions at a Total Plutonium Activity of 1×10^{-6} and 25°C. (Stability fields calculated under carbonate-free conditions and with the thermodynamic data currently under review in this project.)

FIGURE 1.25. Stability Fields of the Predominant Uranium Aqueous Species Plotted as a Function of pH and Redox Conditions at a Total Uranium Activity of 1×10^{-5} and 25°C. (Stability fields calculated under carbonate-free conditions and with the thermodynamic data tabulated in Lemire and Tremaine (1980).)

FIGURE 1.26. Stability Fields of the Predominant Uranium Aqueous Species and Uranium Mineral Solubilities Plotted as a Function of pH and Redox Conditions at a Total Uranium Activity of 1×10^{-5} and 25°C. (Stability fields calculated under carbonate-free conditions and with the thermodynamic data tabulated in Lemire and Tremaine (1980).)

of these figures from data currently under review in this project and from the tabulation of Lemire and Tremaine (1980). Mineral-solubility calculations may also be superimposed onto the stability fields for the predominant aqueous species. For example, Figure 1.26 shows the Eh-pH regions (marked by solid lines) where the solubilities of the solids $\text{UO}_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, U_3O_8 , U_4O_9 , and UO_2 are exceeded with respect to the uranium aqueous species given in Figure 1.25 and a total uranium activity of 1×10^{-5} at 25°C. Therefore, based on the available thermodynamic data, these solids should precipitate from solution in these Eh-pH regions. The SOLUPLLOT code depicts only the stability fields of the most dominant aqueous species. Because thermodynamically lesser important aqueous species may have important roles in sorption and biological processes, the SOLUPLLOT calcula-

tions must also be supplemented with the mass distributions of aqueous species computed by a geochemical code. Figure 1.27 shows the mass distributions of uranium aqueous species calculated by MINTEQ as a function of pH and under carbonate-free, oxidizing conditions. Note that the dominant aqueous species in Figure 1.27 correspond also to the dominant uranium species in Figure 1.25 at oxidizing conditions.

Parent Geochemical Code

The Newton-Raphson method of convergence used in MINTEQ is unreliable unless initial estimates of activities of basis species are close to the equilibrium values. Three additional methods of convergence have consequently been added to make initial estimates no longer necessary. One of these, the Marquardt method (Marquardt 1963), changes the magnitude of the change vector for the basis species by adding a constant to the diagonal of the Jacobian matrix formulated in the Newton-Raphson method. The second is a back substitution method on the independent species that is operational when mass balance error is greater than 20%. The third is a deDonder (deDonder 1936) shift algorithm which simultaneously adjusts all the components in a chemical reaction. Though still being tested, these methods have greatly improved convergence performance in the cases analyzed.

It is particularly time-consuming to define a problem to be run by MINTEQ. Furthermore, unless intimately familiar with the structure of MINTEQ, the user can spend excessive amounts of funds and time in properly structuring the problem. Consequently, we have written a code called PRODEF which helps the user define the

FIGURE 1.27. Mass Distributions of U(VI) Aqueous Species Plotted as a Function of pH at a Total Uranium Activity of 1×10^{-5} and 25°C . (Mass distributions calculated under oxidizing, carbonate-free conditions and with the thermodynamic data tabulated in Lemire and Tremaine (1980).)

problem by interactively responding to questions provided by the code. This code is designed to check logical and chemical errors which otherwise would render a solution meaningless.

Though high-ionic-strength competency was not scheduled to be achieved until FY 1985, it has now been added to the new version of the parent code (MINTEQ2). Currently, the user has the option of designating Debye-Hückel (Westall et al. 1976), Davies (Davies 1962), or Pitzer (Pitzer & Kim 1973) methods of calculating activity coefficients for aqueous species.

We still plan to also add Helgeson's (Helgeson et al. 1981) method of calculating activity coefficients as an option because by so doing we can determine whether large deviations occur as a result of using dif-

ferent methods of calculating activity coefficients and we can thereby obtain some measure of confidence in high-ionic-strength predictions.

With the deDonder (deDonder 1936) algorithm added, MINTEQ2 can now model problems that start with finite quantities of solids. Previously this was not possible with soluble salts.

In addition to thoroughly verifying the operation of the new MINTEQ2, the following remain to be done: complete high-temperature competency (after the thermodynamic data base has been prepared), add conservation of water, add solid-solution modeling capability, and add the capability of generating the intermediate site-specific data base for the coupling program (after its format requirements have been defined).

Coupling Geochemical Code

A prototype streamlined geochemical code is now being assembled. It is being structured to include activity coefficient calculations, adsorption (Langmuir isotherm and the triple layer model), mass balance on water, and solid-phase precipitation and dissolution on a large enough array of components to promise reasonable modeling capability. These features are not all available in other codes recently written (e.g., MININR, Felmy, Reisenaur et al. 1984; FIESTA, Jennings et al. 1982; and CHMTRN, Miller & Benson 1983).

Assumptions underlying the simple cell-flow model are now under close scrutiny. The cell-flow model assumes that all of the fluid phase in a bin is transported simultaneously to the next bin; the solid matrix is treated as a homogeneous medium (i.e., grain-size effects are not accounted for). Scaling of small and large laboratory columns, and scaling of laboratory columns to field cases is particularly simple with the simple cell-flow model, but the accuracy of this simplified scaling is coming under question.

Methods have also been investigated to simulate grain-size effects (particularly hydrodynamic dispersion) in conjunction with the simple cell-flow model. The most promising of these is the Markov chain approach which introduces a single disposable parameter to deal with deviations from homogeneity. Scaling laws for this model have also been derived.

References

- Bethke, C. M. 1978. Program SOLUPLLOT. The Pennsylvania State University (Computer Center), University Park, Pennsylvania.
- Davies, C. W. 1963. Ion Association. Butterworth's, London.
- deDonder, Th. 1936. L'Affinite. Revised by P. Van Rysselberghe, Gauthier-Villiers, Paris.
- Felmy, A. R., S. M. Brown, Y. Onishi, R. S. Argo and S. B. Yabusaki. 1984. MEXAMS - The Metals Exposure Modeling System. EPA-600/3-84-031 (NTIS PB 84157155), Environmental Protection Agency, Washington, D.C.
- Felmy, A. R., D. C. Girvin and E. A. Jenne. 1984. MINTEQ: A Computer Program for Calculating Aqueous Geochemical Equilibria. EPA-600/3-84-032 (NTIS PB 84157148), Environmental Protection Agency, Washington, D.C.
- Felmy, A. R., A. E. Reisenauer, J. M. Zachara and G. W. Gee. 1984. MININR: A Geochemical Computer Program for Inclusion in Water Flow Models--An Application Study. PNL-4921, Pacific Northwest Laboratory, Richland, Washington.
- Harriss, D. K., and V. R. Magnuson. 1982. "Generalization of Water Quality Criteria Using Chemical Models--Development of the REDEQL.UMD System of Computer Programs for Aqueous Equilibria." Preprint, University of Minnesota, Duluth, Minnesota.
- Helgeson, H. C., and D. H. Kirkham. 1981. "Theoretical Prediction of the Thermodynamic Behavior of Aqueous Electrolytes at High Pressure and Temperatures: IV. Calculation of Activity Coefficients, Osmotic Coefficients, and Apparent Molal and Standard and Relative Partial Molal Properties to 600°C and 5 Kb." Am. Jour. Sci., 281:1249-1516.
- Jennings, A. A., D. J. Kirkner and T. L. Theis. 1982. "Multicomponent Equilibrium Chemistry in Groundwater Quality Models." Water Resources Research, 18:1089-1096.
- Lemire, R. L., and P. R. Tremaine. 1980. "Uranium and Plutonium Equilibria in Aqueous Solutions to 200°C." Jour. Chem. Eng. Data, 25:361-370.
- Marquardt, D. W. 1963. "An Algorithm for Least-Squares Estimation of Nonlinear Parameters." J. Soc. Indust. Appl. Math., Vol. 11, No. 2.

Miller, C. W., and L. V. Benson. 1983. "Simulation of Solute Transport in a Chemically Reactive Heterogeneous System: Model Development and Application." Water Resources Research, 19:381-391.

Morrey, J. R., D. W. Shannon and R. P. Smith. 1976. "Use of a Chemical Equilibrium Computer Code to Analyze Scale Formation and Corrosion in Geothermal Brines." Soc. Petrol. Eng. of AIME Paper No. spe 6592.

Parkhurst, D. L., D. C. Thorstenson and L. N. Plummer. 1980. "PHREEQE--A Computer Program for Geochemical Calculations." U.S. Geological Survey Report No. PB81-167801.

Pitzer, K. S., and J. J. Kim. 1973. "Thermodynamics of Electrolytes. IV. Activity and Osmotic Coefficients for Mixed Electrolytes." J. Phys. Chem., 77:268.

Sposito, G., and S. V. Mattigod. 1980. GEOCHEM: A Computer Program for the Calculation of Chemical Equilibria in Soil Solutions and Other Natural Water Systems. Dept. of Soil & Environmental Sciences, University of California, Riverside.

Westall, J. C., J. L. Zachary and F. M. M. Morel. 1976. MINEQL--A Computer Program for the Calculation of Chemical Equilibrium Composition of Aqueous Systems. Technical Note No. 18, Department of Engineering, Massachusetts Institute of Technology.

Wolery, T. J. 1979. Calculation of Chemical Equilibrium Between Aqueous Solution and Minerals: The EQ3/6 Software Package. UCRL-52658, Lawrence Livermore Laboratory, Livermore, California.

Wolery, T. J. 1983. EQ3NR--A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations: User's Guide and Documentation. UCRL-53414, Lawrence Livermore National Laboratory, Livermore, California.

1.5 TANK CORROSION (AR-05-15-10/80681)

J. R. Divine - Program Manager

The primary objective of this study is to provide the operating personnel of the Hanford waste storage tanks with corrosion data to define acceptable, safe operating

specifications for compositions, temperatures, and mixtures.

The secondary objectives are to attain an understanding of the corrosion mechanism in these solutions, to produce corrosion data under nominal storage conditions, to provide a basis for extrapolating from existing chemistries and temperatures, to acquire the data needed for use with new conditions, and to provide surveillance of the corrosion in the tanks.

Summary

The double-shell slurry compositions generally had significantly increased corrosion rates with increasing temperature. On the other hand, most future PUREX compositions either decreased or remained unchanged in corrosiveness.

The higher caustic concentrations in both waste types produced the higher corrosion rates with the corrosion rate increasing with increasing caustic concentration. At this time, temperatures above 140°C (284°F) are not recommended for hydroxide levels above about 4 M though this limit is expected to be relaxed slightly when the results of longer term tests are obtained.

Introduction

Historically, interest in the corrosion of radioactive waste tanks goes back to the early fifties. Several test programs related to the bismuth phosphate and PUREX processes were conducted both in the laboratory and in the field (in-tank). These early tests were conducted in solutions up to about pH 13 and, in field tests, at temperatures estimated at 250 to 300°F (120-150°C). Uniform corrosion rates of 0.5 mils/yr (13 µm/yr) or less were measured in both the liquid and vapor phases; pitting rates of up to 3.7 mils/yr (95 µm/yr) were

observed. In other, more concentrated, waste forms, corrosion rates of up to 12 mils/yr (300 $\mu\text{m}/\text{yr}$) were observed.

When the environmental impact statement (EIS) was prepared for the 241-AN and AW double-shell waste storage tanks, the available data were garnered from literature and from Savannah River and Hanford sources. Based on these data, it was possible to state that the double-shell slurry (DSS) specified in the EIS could be put in the tanks without additional testing, provided that the temperatures were kept close to or below the proposed operating values.

Results

Earlier reports described results of tests in double-shell slurry at temperatures at or below 100°C. In those conditions, after 1 year, the corrosion rates were all within 0.5 mils/yr, with no stress-corrosion cracking.

During the last report period, the 12-month tests of future PUREX compositions, at 100°C, were completed. These solutions were generally found to produce corrosion rates below the 1 mils/yr design allowance. The exceptions were dilute hydroxide/nitrite solutions. In these cases severe corrosion, greater than 2 mils/yr, with localized attack, occurred in the most dilute cases, 0.001 M OH^- and 0.01 M NO_2^- . With slightly higher concentrations, about 0.2 M OH^- and <0.1 M NO_2^- , stress-corrosion cracking occurred in the 70°C test.

With increased temperature, corrosion rates generally increase. The exceptions are the more dilute cases where the localized corrosion is reduced, probably due to the increased efficacy of the nitrite to produce passivation.

After 4 months at 140°C, most of the compositions tested were still acceptable; the exceptions were the most dilute and the most concentrated compositions. Thus operation at 140°C is acceptable for the most common waste compositions.

However, at 180°C after 4 months the following tentative assessment is made:

- 10 M hydroxide, independent of other constituents, produces corrosion rates of greater than 2 mils/yr (this is still lower than pure caustic at the same temperature).
- 7-9 M hydroxide produces corrosion rates of 1.5 to 2 mils/yr independent of the other constituents.
- 4-5 M hydroxide can produce corrosion of up to 1.5 mils/yr, but other factors can reduce the rate to between 0.5 and 1.0 mils/yr.
- Corrosion rates are less than 0.5 mils/yr if the hydroxide is between 0.5 and 1.2 M.
- At or below 0.5 M hydroxide, the corrosion rate depends strongly on certain of the other components; at the present time complexant in DSS, nitrite, and possibly nitrate appear crucial.

As a consequence of the data to date, operation above 140°C must be carefully reviewed to ensure that concentration limits are not exceeded. Generally the corrosion rates have decreased with time, but this cannot be guaranteed.

1.6 CESIUM CHLORIDE COMPATIBILITY

(AR-05-15-10/80682)

G. H. Bryan - Program Manager

The objective of this study is to evaluate the compatibility of WESF-produced CsCl with 316L stainless steel capsule material under the thermal conditions that would be

encountered in a geologic repository. A secondary effort involves a defining of the magnitude, severity, and origin of pitting found on the outer surface of freshly decontaminated and exposed capsules.

Summary

The compatibility of WESF^(a)-produced cesium chloride with 316L stainless steel is being evaluated under the maximum thermal conditions that would be expected in a geologic repository. Six WESF-produced CsCl capsules are held at a nominal CsCl/metal interface temperature of 450°C for times up to 4 years. When a test is completed, the outer capsule is opened and the inner capsule removed. The inner capsule is sectioned and metal samples obtained from various locations. The capsule samples are subjected to metallographic examination to determine the extent of metal attack by the CsCl. A secondary effort involves defining the magnitude, severity, and origin of pitting found on the outer surface of the inner capsule.

Aging Tests - G. H. Bryan

A total of eight WESF CsCl capsules is required for the compatibility studies. Two of these were sectioned and examined immediately after they were filled with CsCl. The remaining six capsules are aged at a nominal 450°C for times of 0.25, 0.5, 1, 2, 3 and 4 years. The six capsules placed in individual insulated containers are allowed to self-heat to the desired test temperatures.

The WESF CsCl capsules required for the test have been provided by Rockwell Hanford

Operations. The Oak Ridge National Laboratory is sectioning the capsules and providing metallographic examination of the specimens.

To date, two capsules were examined immediately after filling with CsCl, and the three capsules aged at a nominal 450°C for 0.25, 0.5 and 1 year have been examined. The estimated metal attack on these capsules is shown in Table 1.9.

The results indicate the attack is significant for the geologic disposal conditions for which the capsules were tested. The corrosion rates are, however, much greater than those observed for pure cesium chloride under similar test conditions (Fullam 1972), probably due to the greater concentration of impurities in WESF material. The lower corrosion rate observed in the capsule heated for 8784 hr suggests a lower impurity content in the salt from this capsule than that in the two capsules tested for shorter times. It should be noted that these studies performed at high temperatures should not be interpreted to infer high corrosion rates for lower temperature applications of the capsules.

WESF Pitting Study - J. R. Divine

Pits observed on the exterior surface of the inner WESF capsule were observed on four 316L stainless steel capsules and appeared to be associated with the contact points of the rack in the WESF electropolishing unit used for decontamination of the capsules.

A number of pits produced on a section of 316L stainless steel capsule material in the laboratory were examined (see Figure 1.28). They were typically about 0.1 mm in diameter (about one-third the size observed in the WESF capsules), with one or more spherical

(a) The Waste Encapsulation and Storage Facility at the Hanford Site.

TABLE 1.9. Estimated Metal Attack^(a) in the Thermally Aged WESF CsCl Capsules

Exposure, hr	Ring No. 1		Ring No. 2		Ring No. 3		Ring No. 4	
	Average Temp., °C	Attack, μm (mils)	Average Temp., °C	Attack, μm (mils)	Average Temp., °C	Attack, μm (mils)	Average Temp., °C	Attack, μm (mils)
2208	415	60 (2.4)	455	30 (1.2)	420	30 (1.2)	354	35 (1.4)
4392	430	110 (4.3)	449	80 (3.2)	400	85 (3.4)	350	50 (2.0)
8784	432	30 (1.2)	460	20 (0.8)	415	60 (2.4)	356	20 (0.8)

(a) Minimum attack estimated from photomicrographs.

FIGURE 1.28. Typical Laboratory "Pit" on 316L S/S Found During Electropolishing (300X)

inclusions present. Localized corrosion-product regions were highly enriched in phosphorus, while the inclusion itself was predominantly tantalum (electropolishing bath rack materials). The immediate area surrounding these inclusions had apparently experienced rapid dissolution rates. Shallow intergranular attack, ~10 μm in depth, was present adjacent to the pit itself on the capsule surface up to a 1 mm from the contact point.

The WESF electropolishing unit was reviewed to find the cause of pitting on the stainless steel capsule material. The major

concern is the electropolishing process and the residual chemicals acting either alone or synergistically. It is known from the literature that sodium phosphate solutions, with excessive chloride, can lead to severe pitting and stress-corrosion cracking, and that impure phosphoric acid can cause pitting.

Operating procedures were examined step-by-step and potential problem areas identified. Although several potential problem areas exist that could cause corrosion, no one stands out as significant. Based on work to date in the experimental portion of this program, discussions with WESF personnel, and a review of equipment drawings, pitting is believed to have occurred in the electropolishing rack. It is nearing the end of its life, and poor electrical contact is maintained between the rack and the capsule. As a consequence, excessive current passed through the rack/capsule contact point(s) and caused accelerated attack at those points.

Reference

Fullam, H. A. 1972. Compatibility of Cesium Chloride and Strontium Fluoride with Containment Materials. BNWL-1673, Pacific Northwest Laboratory, Richland, Washington.

1.7 HANFORD GROUT TECHNOLOGY

(AR-05-15-10 - 80760)

R. L. Treat - Program Manager

The objective of this program is to provide Rockwell Hanford Operations with technical support for disposing grouted low-level wastes in shallow land sites.

Summary

Improvements were made to mathematical models and the data base for performance assessments of disposed grouts. A preliminary performance assessment of grouted Hanford Facility waste was performed. A panel of senior PNL scientists with waste management experience endorsed the current performance assessment strategy. Plans were prepared for complying with NEPA requirements for grout disposal. Criteria were developed for formulating grout recipes. Several grout formulae were tested for set time, shrinkage, and water separation. Candidate grout formers and wastes were analyzed. Input was provided to Rockwell work statements for testing candidate pumps and mixers at vendors' facilities. A batch grout mixer was modified to enable the continuous production of grouts.

Scenario Development and Analysis -

A. E. Reisenauer and W. E. Kennedy, Jr.

The ground-water transport of wastes from a grouted disposal site is one scenario that can lead to human exposure. Using the Hanford Meteorological Tower data to calculate evapotranspiration rates and hourly precipitation, a model of unsaturated flow was compared with the performance of the 300 North Area lysimeter for 1979 to 1982. The UNSATID model results showed good agreement with neutron-probe measurements of

stored water in the soil profile. The results indicate that small amounts of drainage take place below a soil depth of 8 m, assuming cheatgrass evapotranspiration on the surface. Several improvements to the UNSATID model were made to account for the water mass balance more accurately.

Soil samples from the side wall of the AP Tank Farm excavation were collected for characterizing the near-surface soil profile. The excavation is due west of the site being considered for grout disposal. These samples will be analyzed to provide soil data needed to verify the UNSATID model. Existing soil profile data are currently being used for a simplified unsaturated flow model to estimate maximum rates of water transport in the unsaturated zone below the evapotranspiration zone. Annual input water levels of up to 6 in. are assumed available for migration over the grout monolith.

A preliminary performance assessment for grouted Hanford Facility wastes was completed. Exposure scenario/pathway analyses and dose-to-man calculations were performed that consider both phosphate and sulfate Hanford Facility wastes in addition to a combined phosphate/sulfate waste mixture. The results indicate that grout disposal of phosphate waste will not yield significant doses to the maximally exposed individual. However, based on preliminary isotopic concentration data, ^{90}Sr may be present in the sulfate wastes in concentrations that could yield significant doses to the maximally exposed individual. In addition, preliminary ground-water pathway analyses using solubility coefficients indicate that, in the long-term, $^{239/240}\text{Pu}$ concentrations may exceed EPA drinking water limits in ground water.

This preliminary performance assessment was based upon very conservative assumptions due to the lack of specific data for these grouted waste streams. More detailed analyses are planned as specific waste characteristics and long-term performance data on the durability of the grouted waste product are developed.

Peer Review of Assessment Strategy -
S. L. Stein

The strategy for assessing the performance of a grouted disposal system was presented to a peer review panel comprised of senior PNL personnel with expertise in various aspects of nuclear waste management. The panel endorsed the current approach, but recommended that source-term data be enhanced through laboratory and lysimeter testing. It also recommended that an approach for complying with NEPA requirements be established as soon as possible.

NEPA Compliance Plan - S. L. Stein

A strategy for complying with NEPA requirements for grout disposal was prepared. The approach includes a back-up position for preparing the necessary NEPA documents in the event of a delay in the schedule for the Hanford Defense Waste Environmental Impact Statement (HDW-EIS). It also provides the flexibility to make an independent decision on the acceptability of grout disposal of Hanford Facility wastes.

Grout Formulation Criteria - R. L. Treat

Criteria were established for formulating grouts for low-level waste disposal at Hanford, as summarized below:

- Grout formers shall have stable, long-term sources of supply.
- Processing and chemical uncertainties and variabilities shall be considered.
- Grout angle of repose shall be less than 5 degrees.
- Grout shall harden to a compressive strength of at least 50 psi within 28 days.
- No free-standing water shall exist after 28 days.
- Temperature of grout shall not exceed pore-water boiling point (~250°F).
- Within the constraints above, grouts shall be tailored to yield leach-resistant, lowest-cost products.
(Grouts shall meet or exceed a Leach Index of 6 according to ANS 16.1.)^(a)

Process Testing - R. L. Treat

Modifications to an existing grout batch mixer were completed. These modifications will permit the continuous production of grouts for periods of up to about 15 min. This process will enable the production of large quantities of grout (~200 gal) for scale-up testing. The modified process, if shown adequately reliable, could be inexpensively built in a single, small module. Four mixing tests were conducted using water to simulate the liquid waste and Portland 1-P cement to simulate the blend of dry grout formers. Solids-to-liquid ratios were varied from 10 to 20 lb/gal. Grout production rates ranged from 10 to 13 gal/min. Test durations were only a few minutes due to the high rates of cement consumed. An

(a) Draft leach--test procedure being prepared by the American Nuclear Society Standards Committee Working Group 16.1.

attempt was made to pump the 20 lb/gal grout with a diaphragm pump. This grout was very viscous and had an angle of repose of about 5 degrees. During 5 min of pumping, pump rates diminished from about 20 gal/min to zero. Even though a solids-to-liquids ratio this high is not anticipated, the potential for solids to accumulate between the diaphragm and diaphragm pump housing remains, which can ultimately lead to pump failure. The failure of this pump test, coupled with the low discharge pressure capability of the pump, suggests that the diaphragm-type pump is not suitable for the Hanford application.

Vendor Tests - R. L. Treat, S. O. Bates, and R. O. Lokken

Work statements were written for testing candidate mixers and pumps for the Transportation Grouting Facility. Grout samples were also prepared according to recipes specified in the work statements. The grout samples were subsequently analyzed to provide assurance that the grouts produced by the vendors could be safely disposed.

Analyses of Grout Materials - R. O. Lokken

Candidate grout formers were analyzed by the following methods to establish a data base for comparing grouts formulated with different recipes:

- Induction-Coupled Plasma Emission Spectrometry
- BET Surface Area^(a)
- True Powder Density
- Tap Density

Candidate wastes for grouting were also analyzed. Simulated phosphate Hanford

Facility waste was found to vary significantly in its sodium, sulfur, and organic contents, depending on the lot of TURCO® decontamination solution used to prepare the simulated waste. An actual radioactive sample of the phosphate waste was obtained from Rockwell and will undergo analysis.

Grout Testing - R. O. Lokken

Several grouts were prepared according to preliminary formulae prepared by Oak Ridge National Laboratory (ORNL). The purpose of these preparation tests was to ensure that preparation procedures and materials are adequate when final formulae are established. These tests showed that phosphate Hanford Facility waste grouts could not be produced without foaming unless a defoaming agent, such as tributyl phosphate, was added. These tests also showed that the potential grout design objective of a small quantity of free-standing water in a 250-ml graduated cylinder after 2 hr did not indicate the extent of free-standing water after longer periods of time. For example, one sample showed 0.41 vol% free-standing water after 2 hr, but 2.24 and 2.05 vol% after 24 and 48 hr, respectively. Moreover, a free-standing water test in a larger diameter vessel showed the level of free-standing water had about doubled.

Another test involved the production of grouts with 4 and 14 pounds of dry solids per gallon (lb/gal) of simulated waste. Upon setting and air-drying, the former grout shrank and cracked badly, whereas the latter grout appeared dense and had no

* Trade name of Turco Products, Carson, California.

(a) The Brunauer-Emmett-Teller equation.

cracks. This test highlights the importance of wet curing of grouts containing low solids contents.

A third test involved the production of grouts using a 50/50 vol% blend of phosphate and sulfate Hanford Facility wastes. After 5 days, only grouts produced with a 14 lb/gal mix had set. The setting may be attributable to the higher proportion of Portland cement relative to the water content.

1.8 SYSTEM TRADEOFF STUDIES

(AR-05-15-20 - 80762)

R. W. McKee - Program Manager

The objective of this study is to evaluate through system tradeoff studies, the relative cost effectiveness of various alternatives for managing the Special Case/RH categories of Defense TRU Wastes. The study results will facilitate preparation of waste management strategy for these wastes.

Summary

The four DOE sites that have Stored Special Case (SC) and Remote-Handled (RH) Transuranic (TRU) wastes have been visited to obtain information on wastes inventories and characteristics and waste processing plans. Waste inventory information, transportation and Waste Isolation Pilot Plant (WIPP) disposal requirements and preliminary generic waste management alternatives have been described in a letter report. Efforts are now being directed towards refining the alternative selection and waste inventory data and towards developing a comparative analysis of the alternatives.

Technical Progress

Discussions were held with waste management officials at the four major DOE SC/RH-TRU waste sites (Hanford, Idaho National

Engineering Laboratory, Los Alamos National Laboratory, and Oak Ridge National Laboratory). From these discussions it was concluded that much of the SC-TRU and RH-TRU waste is not well characterized and that waste management alternatives are not firmly established for this category of TRU waste. Also, it was found that current volume estimates of both stored and newly-generated SC/RH-TRU waste are significantly different from previous estimates. Following the DOE site visits, a preliminary letter report was prepared for the Transuranic Waste Systems Office (TWSO), that summarized the inventory information for currently stored and newly generated SC/RH-TRU waste. Generic waste management alternatives were identified for further analysis, and transportation/packaging/WIPP disposal regulations and requirements were also discussed in the letter report. This baseline information will be used in the Systems Tradeoff Studies to estimate costs and evaluate risks associated with the SC/RH-TRU waste retrieval, packaging, transportation, and disposal operations at each site.

SC/RH-TRU Waste Inventories

Preliminary analysis of the available SC/RH-TRU waste information shows that most of the current RH-TRU waste results from hot-cell operations. However, a growing component of the RH/TRU waste volume results from planned operation of PUREX, Process Facility Modification Plant (PFMP), Fast Flux Test Facility (FFTF), and the Experimental Breeder Reactor-2 (EBR-2). Some of the TRU wastes at three of the sites are experimental reactor spent fuel rods and may require reprocessing or they could be packaged as high-level waste and sent to a commercial repository.

The total volumes of currently stored and projected future SC/RH-TRU waste are summarized in Table 1.10 and compared for the four major storage/generator sites on the basis of volumes both including and excluding the waste containers and the estimated volume requiring processing to meet WIPP requirements. These data show that SC-TRU waste at the INEL and LANL sites is mostly contact-handled and most of the SC-TRU waste at Hanford and ORNL is remote-handled. The Hanford SC/CH-TRU waste becomes RH-TRU waste when removed from current casks for reprocessing and repackaging to meet WIPP disposal requirements.

SC/RH-TRU Waste-Processing Requirements

It is estimated that 10 to 20% of the stored TRU waste at INEL contains hazardous chemicals and toxic materials that are incompatible with the planned waste certification and treatment facilities. Special process steps/facilities will be needed to prepare this volume (~6,000 m³) of SC/CH-TRU waste for disposal at WIPP. Similarly, special process/reprocessing facilities will be

needed to prepare large volumes of RH-TRU waste currently stored at ORNL, LANL, and Hanford for disposal at WIPP. The RH-TRU waste at ORNL contains neutron sources that will require special shielding considerations for safe treatment, transportation and disposal. Similarly, hot-cell waste generated at LANL and Hanford is highly radioactive and processing will be required to meet the WIPP criteria for fissile content and the radiation dose rates at the surface of the RH waste canister.

One process alternative being considered in the System Tradeoff Studies is to ship all RH-TRU waste to a common site for processing. This option increases transport costs and risks, but has the potential to reduce overall costs by eliminating the need for duplicating costly remote-operated processing facilities. Another interesting option would be to utilize the fuel rod reprocessing capability proposed for the Hanford PUREX Plant (i.e., the PFMP) for processing the experimental reactor fuel type of waste stored as TRU wastes at Hanford, LANL, or ORNL.

TABLE 1.10. Estimated Quantities, Both Current and Future^(a) of Special Case and RH-TRU Wastes

	Volume Including Container, m ³		Volume Excluding Container, m ^{3(b)}		Volume Requiring Processing, m ^{3(b)}	
	SC/CH-TRU	RH-TRU	SC/CH-TRU	RH-TRU	SC/CH-TRU	RH-TRU
Hanford	387	438	0	495	0	370
INEL	7,500	289	6,750	260	6,750	18
LANL	2,834	79	2,390	71	2,390	22
ORNL	18	1,457	16	860	16	562
Total	10,739	2,263	9,156	1,686	9,156	972

(a) Estimated through 1996.

(b) Containers assumed to be 90% filled.

1.9 REDUCED WASTE GENERATION -

ADMINISTRATIVE SORTING

(AR-05-20 - 80761)

R. P. Allen - Program Manager

The objective of this program is to provide analytical data for ways in which newly generated waste can be changed from the transuranic (TRU) waste category into the low-level waste (LLW) category.

Summary

Tests were conducted to evaluate high-pressure Freon® spray-cleaning as an in situ decontamination technique for use in the direct conversion of TRU-contaminated glove boxes to LLW. Although high-pressure Freon cleaning has been effective in removing smearable contamination for power reactor applications, the average decontamination factors obtained for the removal of smearable plutonium contamination from interior stainless steel and Plexiglas® surfaces were less than 10, as compared with 20 for hand scrubbing with Freon and 200 for scrubbing with a commercial cleaner.

The use of Freon sprays to remove plutonium contamination from holdup areas also was evaluated. Areas tested included a glove box window gasket, the intersection of a wall and floor, threads protected by a nut, and a crevice, 0.25 in. deep, between two stainless steel plates. The Freon readily penetrated the holdup areas and removed contamination. However, as in the previous tests, only modest decontamination factors (2 to 20) were achieved. Freon losses were

very high, and the contamination dislodged from the holdup areas was redeposited nearby, necessitating a separate cleaning operation. The primary advantage of the use of high-pressure Freon for in situ decontamination would appear to be for operations where aqueous techniques cannot be used due to criticality safety or component-damage constraints.

Freon Decontamination Studies

A study (Chikalla and Powell 1982) conducted during FY 1982 demonstrated that the size reduction of glove boxes and similar large TRU-contaminated components can provide substantial savings in packaging, storage, retrieval, transportation and WIPP disposal costs for Hanford waste. Although decontamination of sectioned waste to non-TRU levels was included as part of this study, this approach was not the lowest cost treatment option because of the relatively high cost of sectioning material into the small size (8 by 8 in.) required for optimum processing by vibratory finishing (McCoy, Arrowsmith and Allen 1980).

One way of reducing decontamination costs is to eliminate the sectioning operation by using in situ decontamination techniques to convert components directly into non-TRU waste. This approach has not been used extensively in the past, primarily because of the difficulty of adequately decontaminating and monitoring crevices, gasket seals, and other potential contamination holdup areas. Two recent developments now warrant a reconsideration of this direct conversion approach. One is the tenfold increase in the levels defining TRU waste to greater than 100 nCi/g as specified in DOE Order 5820.2. This change should

®Freon is a registered trade name of E. I. du Pont de Nemours, Nemours Bldg., Wilmington, Delaware.

®Plexiglas is a registered trade name of Rhom and Haas Co., Independence Mall West, Philadelphia, Pennsylvania.

substantially reduce the extent and cost of decontamination required and help alleviate the problem of monitoring components.

The other development is the availability of new and potentially more effective in situ decontamination techniques. Previous studies (Platt 1979) have shown that in situ electropolishing, for example, can reduce plutonium-contaminated metallic glove box surfaces from levels greater than 1000 nCi/g to less than 1 nCi/g. In addition to this electropolishing technique, work by commercial firms (Fowler 1982) has demonstrated that high-pressure Freon spray cleaning is very effective in removing smearable fission-product contamination from a variety of metallic and nonmetallic surfaces. The objective of the studies described in this progress report was to evaluate the effectiveness of Freon spray cleaning for removing TRU contamination from representative surfaces and holdup areas as a possible alternative technique for directly converting components to LLW.

The Freon decontamination tests were conducted using a commercial Freon spray cleaning system consisting of a high-pressure pump capable of supplying Freon at a pressure of 2000 psi and a flow rate of 2.1 gpm; a reservoir, filter and low-pressure pump that continuously circulated the Freon through the filter; and a vacuum return system to collect and recycle the Freon. The effect of nozzle configuration was investigated using single-pencil, fan or cone jets with a separate vacuum collection line. Some tests used a spray head with three fan jets mounted in a line with the vacuum return attached for immediate collection and return of the Freon. Other experimental parameters investigated in addition to nozzle type were pressure, flow rate, applica-

tion time, type of surface and component geometry. Decontamination effectiveness was evaluated by taking smear samples from areas of approximately 100 cm². Selected areas also were cleaned using conventional hand-scrubbing techniques for comparison.

The initial Freon decontamination tests were performed with the spray nozzles and vacuum return line inside a representative plutonium-contaminated glove box with a stainless steel floor and Plexiglas walls. The results, summarized in Table 1.11, indicate that the decontamination effectiveness for plutonium is less than would be expected based on the good results obtained for fission-product contamination. Discounting the variations inherent in smear readings, there was no consistent variation in effectiveness with pressure, nozzle type or surface material. The best results were obtained with hand scrubbing, and cleaning with a commercial cleaner was substantially more effective than scrubbing with Freon.

Additional tests were performed so as to understand and improve the decontamination performance of the spray system. Alcohol was added to the Freon to further reduce the surface tension and enhance wetting, but with no significant effect. A 0.2- μ m absolute filter was installed that reduced the recontamination levels on clean control coupons from the recycled Freon to almost background values, but with no change in decontamination effectiveness. Based on the manufacturer's recommendations, special nozzles were obtained to permit optimum operation at full system capabilities; and the equipment, nozzle, and glove box were grounded to eliminate possible problems with electrostatic adhesion of particulate. Despite these modifications, the average decontamination factors obtained for the

TABLE 1.11. Effect of Test Variables on Smearable Contamination Levels and Decontamination Factors (DF) for Freon Spray-Cleaning of Plutonium-Contaminated Glove Box Areas

Test Condition/Technique	Location	Before, dpm	After, dpm	DF
Single-Head Fan (100 psi)	Floor	1×10^6	1×10^6	1
Single-Head Fan (100 psi)	Wall	2×10^6	3×10^5	7
Pencil-Jet (150 psi)	Floor	1×10^7	4×10^6	3
Pencil-Jet (150 psi)	Wall	6×10^4	8×10^4	--
Pencil-Jet (500 psi)	Floor	4×10^6	2×10^6	2
Single-Head Fan (2000 psi)	Floor	2×10^6	2×10^5	10
Triple-Head Fan (2000 psi)	Floor	7×10^6	3×10^5	23
Triple-Head Fan (2000 psi)	Wall	2×10^6	2×10^6	1
Scrub Using Clean Freon	Floor	4×10^6	2×10^5	20
Scrub with Addition of Freon Fan Spray	Floor	8×10^6	4×10^5	20
Scrub Using Commercial Cleaner	Floor	8×10^6	4×10^4	200

removal of smearable plutonium contamination from glove box stainless steel and Plexiglas surfaces remained less than 10.

The evaluation of in situ Freon cleaning techniques was completed with a final series of tests that included the use of a fixture to maintain exact nozzle spacing and angle while spraying test coupons, the cleaning of representative surface areas inside a walk-in glove box using the three-jet spray head, and tests on material sprayed while inside a rotating basket to simulate the processing of sectioned material. All test results confirmed the earlier work in showing incomplete removal of the smearable contamination and only modest decontamination factors. These latter tests also were designed to investigate the effectiveness of the Freon spray in removing plutonium contamination from representative holdup areas, such as the groove in a glove box window gasket, the intersection of a wall and floor, threads protected by a nut, and a 0.25-in.-deep crevice between two stainless steel plates. The Freon readily penetrated

the holdup areas and removed contamination, but only sufficiently to give decontamination factors of 2 to 20. Freon losses by evaporation were very high, resulting in redeposition of the contamination removed from the crevice areas. Based on the results of these tests, it is concluded that the use of Freon spray techniques for in situ decontamination of plutonium does not offer a significant advantage over other conventional methods except for operations where the use of aqueous techniques is prohibited due to criticality safety or component damage constraints.

References

- Chikalla, T. D., and J. A. Powell, compilers. 1982. Nuclear Waste Management Semiannual Progress Report April Through September 1982. PNL-4250-2, Pacific Northwest Laboratory, Richland, Washington, pp. 1.11-1.14.
- Fowler, D. E. 1982. "Decontamination Applications With Freon 113." Decontamination of Nuclear Facilities, pp. 4-29 to 4-36. Canadian Nuclear Association/American Nuclear Society.

McCoy, M. W., H. W. Arrowsmith and R. P. Allen. 1980. Vibratory Finishing as a Decontamination Process. PNL-3336, Pacific Northwest Laboratory, Richland, Washington.

Platt, A. M., compiler. 1979. Nuclear Waste Management Quarterly Progress Report October Through December 1978. PNL-2378-4, Pacific Northwest Laboratory, Richland, Washington, pp. 12.1-12.8.

2.0 NUCLEAR WASTE MATERIALS CHARACTERIZATION CENTER

The objective of the Nuclear Waste Materials Characterization Center (MCC) is to provide an authoritative data base that will include information on the components of the waste emplacement package (the spent fuel or processed waste form and the engineered barriers), their interactions with each other, and the effects of their environment. The MCC works with waste-form producers and repository developers to standardize test methods and obtain materials data and submits these to the Materials Review Board (MRB). After test methods and data have been approved by the MRB, the MCC publishes the approved methods and data in the Nuclear Waste Materials Handbook.

2.0 NUCLEAR WASTE MATERIALS CHARACTERIZATION CENTER (MCC)

(AR-05-15-10/DB-60-20-20/AR-05-15-30 - 80145)

J. E. Mendel - Program Manager

SUMMARY

The MCC is using three different facilities (controlled hood, glove box, and hot cell) to produce radioactive glass testing materials and to prepare spent fuel for use in the repository test programs. The MCC is also doing an in-depth characterization of these materials using the shielded analytical instruments that have been set up for this purpose. The first issue of a document that will be updated periodically to describe the status of MCC-supplied reference and testing materials was distributed: Approved Reference and Testing Materials for Use in Nuclear Waste Management Research and Development Programs, PNL-4955-1.

Development of MCC-14 and 105 test methods continued. A draft of MCC-14.4 basalt compliance test method was reviewed by the Basalt Waste Isolation Program (BWIP), and the MCC has responded to their comments. Equipment, including titanium pressure vessels, is being assembled to initiate MCC-14.4 testing. Development testing of MCC-105.1 and of MCC-105.3 corrosion tests has been initiated.

Testing was initiated to develop MCC-certified leach data so that the ARM-1 (Approved Reference Material) glass can serve as a reference material for the MCC-1 and MCC-2 leach test. Part of that data was included in the submission of the MCC-1 static leach test for full approval by the Materials Review Board (MRB). Initial results show that the ARM-1 glass is more

leach resistant than PNL 76-68, the interim reference material.

WASTE MATERIALS INTERACTIONS -

R. G. Strickert (Task 1 Leader) -
R. L. Erikson, K. M. Krupka, M. McCulloch,
D. Rai, J. W. Shade, R. W. Stephens, and
R. W. Fulton

MCC-14.4 Waste-Form Compliance Test Method for Basalt

The development of the MCC-14.4 test method was initiated in FY 1984 and involves the cooperative efforts of the MCC and BWIP in design of the testing criteria, experimental procedures, and the experimental testing matrix. The compliance test is to be used to establish that a nuclear waste form material is in compliance with the BWIP acceptance requirements and specifications for a nuclear waste repository in basalt.

Data from the test will include radio-nuclide concentrations in synthetic basalt ground water that has contacted basalt and a waste form in a closed, agitated system at a fixed temperature for a defined period of time.

During the first half of FY-84, experimental procedures and test parameters were established. A draft version of the MCC-14.4 test method was completed and has been reviewed by the BWIP staff. Their comments are currently being incorporated into the final version of the test method, which is to be submitted to the Materials Review Board (MRB) in June 1984. Equipment

(titanium reaction vessels, ovens, etc.) and testing materials needed for MCC-14.4 are being set up and prepared.

Experiments to be initiated in the second half of FY-84 will be using MCC 76-68 glasses doped with ^{239}Pu , ^{237}Np , or ^{238}U . The effect of temperature and the solution/solids ratio on the steady-state solution concentrations of the various radionuclides will be examined.

A series of materials interactions tests, also related to MCC-14.4, were begun in late FY-83 and have now been completed. These tests consisted of reaction vessels containing 1 to 1 mixtures of crushed and sized uranium-doped 76-68 glass and basalt contacting deionized water for up to 90 days at either 90 or 150°C. Uranium and other cation analyses were made on quenched and filtered solutions. Measurements of pH and, in some cases, Eh were also made. The quenched pH values of both systems were 9.5.

Preliminary evaluation of the results from the 0.0018- μm filtrates at 90°C suggests that saturation with dissolved silica is achieved in both systems in the presence of basalt, but that boron and alkali metals continue to be released. Silica concentrations from 0.45- μm filtrates were ~40% above saturation, indicating that some colloidal material was passing through the larger filter. Differences in uranium concentrations in the different filtrates were also apparent. Whether this is due to the presence of uranium colloids or sorption of uranium on the silica colloids has not been determined. (See discussion on $\text{UO}_2(\text{OH})_2$ solubility experiments below.)

Solubility-Controlled Concentration Data for Radionuclide Elements in Nuclear Waste

During the reporting period, the solubility of U(VI) hydroxide was determined in carbonate-free, deionized-distilled water at 60°C. The experiments were conducted in glass vessels and MCC-3 type Teflon vessels previously described in Chikalla and Powell (1983) and Materials Characterization Center (1981), respectively. The initial solid reactants, consisting of a mixture of $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ (the mineral schoepite) and $\text{UO}_2(\text{OH})_2$, and the final reaction solids were identified by x-ray diffraction analysis. The concentrations of total dissolved uranium were observed to decrease with increasing pH over the measured pH range of 3.7 to 5.7.

The filtered uranium concentrations are shown as a function of reaction time in Figure 2.1. The uranium concentrations (based on 0.015- μm filters) measured in solutions resulting from these 60°C experiments appear to be ~25-50% lower than concentrations measured in identical experiments we conducted at 25°C and the same pH range [FY-83 results described in McElroy and Powell (1984)]. The current experiments also show that schoepite does not appear to be the stable form of U(VI) hydroxide in water at 60°C and 1 atm, as previously suggested from other studies [e.g., Robins (1966)]. X-ray diffraction analysis of the final solubility reaction solids indicated that the schoepite component in the starting mixture had converted at 60°C entirely to $\text{UO}_2(\text{OH})_2$.

The MINTEQ geochemical code (Feimly et al. 1983a,b) and thermodynamic data for uranium taken from the compilation by Langmuir

FIGURE 2.1. Concentrations of Total Dissolved Uranium Plotted as a Function of Reaction Time for the Measured Solubility of $\text{UO}_2(\text{OH})_2$ at 60°C . The open and filled symbols represent solutions passed through 0.015- and 0.0018- μm filters, respectively. Uranium analyses based on solution aliquots taken from the glass reaction vessel are indicated by the circle symbols. The remaining symbols represent uranium analyses for solution samples taken from the Teflon reaction vessels.

(1978) were used to calculate the aqueous speciation for the dissolved uranium in the 60°C U(VI) hydroxide solubility experiments. The results indicate that the dissolved uranium is composed of significant concentrations (between 10 and 45% of the total mass of dissolved uranium) of the U(VI) species - UO_2^{2+} , UO_2OH^+ , $(\text{UO}_2)_2(\text{OH})_2^{2+}$, and $(\text{UO}_2)_3(\text{OH})_5^+$.

The ion activity products (IAP) and saturation indices [SI, where SI is defined as $\text{SI} = \log (\text{IAP}/K_{r,T})$] for the equilibrium reaction

were calculated from the 60°C speciation results and compared to the equilibrium constant ($\log K_{r,60^\circ\text{C}}$) for reaction (1). An

aqueous solution is defined as being at equilibrium with a certain solid [e.g., $\text{UO}_2(\text{OH})_2$] if $\text{SI}=0$, oversaturated if $\text{SI}>0$, and undersaturated if $\text{SI}<0$. The SI values calculated with respect to $\text{UO}_2(\text{OH})_2$ based on the 60°C U(VI) hydroxide solubility experiments are shown as a function of reaction time in Figure 2.2. For comparison, ± 0.3 SI units about the zero value represent a useful error band for apparent solubility equilibrium.

A preliminary assessment of these SI results indicated that 1) there is a significant quantity of colloidal sized U(VI) hydroxide in the 0.015- to 0.0018- μm size range and 2) the uranium analyses based on the 0.0018- μm filtered solutions may provide a more accurate derivation of long $K_{r,T}$ for $\text{UO}_2(\text{OH})_2$. Solubility experiments involving

FIGURE 2.2. Calculated Saturation Indices for $\text{UO}_2(\text{OH})_2$ Plotted as a Function of Reaction Time for the Measured Solubility of $\text{UO}_2(\text{OH})_2$ at 60°C . The open and filled symbols represent solutions passed through $0.015\text{-}\mu\text{m}$ and $0.0018\text{-}\mu\text{m}$ filters, respectively. Solution aliquots taken from the glass reaction vessel are indicated by the circle symbols. The remaining symbols represent uranium analyses for solution samples taken from the Teflon reaction vessels.

U(VI) hydroxide and the thermodynamic analysis of the experimental results are continuing.

During the second quarter, FY-84, the effect of fluoride (basalt ground water contains ~ 35 ppm fluorine) in complexing the reduced states of actinide ions was experimentally investigated. Neptunium (IV) hydrous oxide solubility was determined in the presence of 100 ppm fluoride aqueous solutions of neutral to basic pH at room temperature. Iron or sodium dithionite was used to maintain neptunium as Np(IV) . The pH values of slightly alkaline sodium dithionite suspensions decreased to about 7, where sodium dithionite is not an effective reducing agent. These experiments will be

started again using higher alkaline concentrations. However, for the iron system at measured pH values of 7.5 to 10, Eh values (as measured by a platinum combination electrode) were between -0.2 and -0.3 volts. Neptunium (IV) is the expected dominant oxidation state under these conditions.

Measurements of the neptunium concentrations in filtered ($0.0018\text{ }\mu\text{m}$) aliquots of the solutions are at instrumental detection limits ($7.7 \times 10^{-9}\text{ M}$). These neptunium concentrations results are the same as those obtained for similar experiments, but without fluoride present (Rai et al. 1984). Therefore, the results show that Np(IV) hydrous oxide solubility is very low under reducing conditions and is not measurably

affected by the fluoride, which is contrary to observations reported in the literature. Further analyses of the solution and solid phases are continuing.

CORROSION - M. D. Merz (Task 2 Leader) -
R. Wang and W. E. Anderson

This task has the objective of codifying and obtaining validation of test methods for corrosion evaluation of metallic container and canister materials in nuclear waste repository environments. General corrosion wastage is being addressed by tests such as MCC-101, 102, and 105.1-105.5 and stress corrosion by MCC-103P and 104. Further development and revision of these methods are ongoing as test results and effects of test technique are examined by the MCC. The site waste-package programs and the MCC are gaining experience with these types of test methods, and the MCC is codifying the methods to ensure consensus approval by corrosion investigators and the scientific community. Because of the availability of site-specific information on the basalt site at Hanford, benchmark tests for basalt are being conducted first. Selection of a reference brine composition and salt composition has delayed MCC corrosion testing and test validation for salt.

Test Method Development

MCC-101 Static-Immersion Corrosion Test Method

This test method was revised according to recommendations by the Office of the Chairman of the Materials Review Board (OTC-MRB) during the last reporting period and will be published in PNL-3990. No further work on this test method is planned since reposi-

tory-relevant tests MCC-105.1 (basalt) and MCC-105.3 (salt) have been codified based on MCC-101 and will be used for repository corrosion testing by BWIP and Office of Nuclear Waste Isolation (ONWI) waste package investigators and since investigators for the tuff repository are developing a different type of test.

MCC-102 Unstressed, Flowing, Immersion Corrosion Test Method

This test method was revised according to comments by OTC-MRB and is ready for publication in PNL-3990. This method was the precursor to MCC-105.4 (flowby test), which was submitted to the BWIP for review for application to evaluating corrosion under flowing basalt ground water.

MCC-103P Stress-Corrosion-Cracking Susceptibility Test Method

No further development of this test method has occurred since approval by MRB and publication in the Handbook during FY-83.

MCC-104 Stress-Corrosion-Cracking Rate-Tension Test Method

A six-day test according to MCC-104 was performed to determine whether the crack-marking technique proposed in the method was workable. Tests were done in basalt ground water, both aerated and deaerated, and in a reference demineralized water. The small crack-growth increment, $\sim 2 \mu\text{m}$, produced during 20 cycles over six days was not unequivocally identified, but corrosion of the fracture surface was not a problem in these test environments. The thin low-carbon steel, $\sim 0.16 \text{ cm}$, used in these preliminary

tests exhibited tearing fracture that obscured the marking. Tests on thicker steel more representative of container thicknesses are planned.

A workshop with site investigators and experts in stress-corrosion cracking was held February 1 and 2, 1984. MCC-104 and the testing in progress for salt, tuff, and basalt were reviewed, and recommendations of experts were recorded. The MCC-104 test method and other fatigue-crack-growth testing being done by the site investigators are based on the same concept. The advanced technique, however, for observing small crack-growth increments proposed in MCC-104 has not yet been demonstrated. A large extrapolation of data to repository-relevant, required, low cracking rates is necessary if the demonstrated techniques, such as remote gauging of crack growth, are used. The MCC is continuing to review the methods proposed and being implemented by ONWI and BWIP investigators to obtain further consensus approval and to develop the statistical basis for the data.

MCC-105 Test Method for Long-Term Corrosion in Repository Environments

Test methods are being developed and codified for basalt, salt, and tuff. Five test methods on general corrosion have been identified, MCC-105.1 through MCC-105.5, for application to the three types of geologic media. Because the conditions in each geologic medium are different, different methods are required for each.

The MCC is integrating activities on validation of each test method with each of the waste-package programs for salt, basalt, and tuff. The MCC has initiated benchmark testing for basalt with BWIP's concurrence.

A static test method for salt drafted by MCC has been reviewed by ONWI and is being revised before benchmark testing is begun. The methods for tuff are in a preliminary stage. The MCC will start benchmark testing to support consensus approval of test methods for corrosion and to substantiate data quality and reliability.

MCC-105.1 Basalt Static System. The benchmark conditions for this test method were agreed upon by the MCC and the BWIP, and testing was initiated by the MCC. The benchmark tests in progress are 30, 120, and 300 days at 100°C, with no radiation and with crushed basalt plus bentonite packing material. The MCC reviewed changes suggested by OTC-MRB and incorporated other changes that resulted from discussions with BWIP and Westinghouse Hanford Company (WHC) investigators. An updated draft of the development test method, with changes recommended after September 30, 1983, is being prepared. The MCC will prepare a draft of MCC-105.1 along with 30-day and 120-day test data for submission to the MRB later this year. Significant developments on the test method during the last 6-month period were a method for preparing the crushed basalt, definition of a reference ground water (GR#4), and availability of A27 cast steel for benchmark testing.

MCC-105.2 Tuff Static System. The development of a method(s) for tuff is in a preliminary stage, and Nevada Nuclear Waste Storage Investigation (NNWSI) has not received formal response to date. The MCC will continue to review NNWSI progress in definition of corrosion testing in order to modify the preliminary drafts of MCC-105.2.

MCC-105.3 Salt Limited Reactants System.

A draft of MCC-105.3 was reviewed by ONWI and several changes were recommended. A key area of concern is identification of benchmark conditions. Dried brine A, though used extensively in waste-package testing may be inappropriate as a reference medium, and other, inclusion brines are being considered. The MCC is currently developing a mixture of dried Permian Basin No. 1 brine with Permian Basin No. 3 inclusion brine additions as a reference medium for this closed-system, limited-reactants test.

MCC-105.4 Basalt Flowby System. The MCC codified a test method wherein the corrosion specimens are placed in packing material (basalt plus bentonite) such that water access is diffusion-limited to simulate long-term postclosure conditions in a basalt repository. This method was reviewed by BWIP investigators and returned to MCC for further revision. BWIP has planned to develop this test through PNL and WHC subcontractors, and MCC will revise the method after more experience is gained. The MCC plans to submit MCC-105.4 to the MRB later this year and to begin benchmark testing.

MCC-105.5 Basalt Water Vapor System. Investigators for BWIP have requested the MCC to codify a test method wherein the corrosion specimens are placed in a slowly refreshed water vapor environment to simulate conditions in the operational period of the basalt repository. WHC investigators have devised a procedure and designed an apparatus for this type of testing. The MCC will begin codifying this method in FY 1985.

Benchmark Testing

The MCC is performing benchmark testing according to MCC-105.1 and plans to begin testing according to MCC-105.3. Testing according to MCC-105.2 will be initiated if the method becomes sufficiently defined. The benchmark tests initiated according to MCC-105.1 (basalt static system) are at 100°C for 30, 120, and 300 days with no radiation. Procedures for incorporating radiation at ^{60}Co exposure levels of 10^3 R/hr are being developed and equipment for this testing will be built in FY-84.

WASTE-FORM CHARACTERIZATION - S. C. Slate
(Task 3 Leader) - G. R. Robinson,
J. W. Shade, P. A. Scott, and J. R. Friley

Test methods are being developed to provide data for four major uses: 1) comparison of waste forms, 2) support of data bases for more complex test methods such as MCC-14, 3) support of the design of waste production processes, and 4) certification that waste forms meet waste acceptance criteria. Test methods 1 through 13 were initially selected to compare waste forms and to provide basic data for complex interactions tests. With the inclusion of the third and fourth uses this year, it was necessary to review the usefulness of the original 13 methods and to determine what additional new tests would need to be developed. The status of existing waste characterization test methods as a result of this review is shown below:

- Completed test methods: MCC-6, 11, 12
- Tests being prepared for final submission: MCC-1, 2, 3

- Tests being prepared for initial submission: MCC-7, 13
- Tests indefinitely delayed: MCC-4, 5, 8, 9, 10.

New test methods will be identified in this and future years in response to the need to show that waste forms comply with waste-acceptance specifications and other requirements within the waste management system. The new tests will be used to supply three basic types of information: 1) data on physical and chemical condition of the canister and waste form; 2) data showing a waste form does not exceed certain limitations; and 3) data showing the waste form and canister perform adequately under accident and storage conditions. MCC-15 is an example of a new test that has been identified for development this year to meet the new needs recently established for transportation and disposal.

Test Method Development

The following six sections are short summaries of the progress made on each of the test methods under development this year.

MCC-1P (Rev. 1) and MCC-2P Static Leach Test Methods

In February 1984, MCC-1P (Rev. 1) was submitted to the MRB for full approval. The submission included a document that presented MCC's final resolution of the eleven issues contained in the Appendix of MCC-1P. Only minor changes in the procedures were required to resolve these issues. The submission also included 28-day "certified" data obtained on the ARM-1 glass. These data are part of a long-term (>1 year) test program in which data will be collected on the ARM-1 glass using both MCC-1 and MCC-2.

The data will be certified and included with each sample of ARM-1 glass issued to other investigators for testing.

In June 1984, MCC-2 will be submitted to the MRB for final approval. This submission will include high-temperature ARM-1 leach data and an Appendix-issue report similar to the one prepared for the MCC-1 submission.

MCC-3 Agitated Powder Test Method

This test method is being revised according to suggestions from the MRB Procedures Panel in 1983. Several key technical issues unique to MCC-3 still remain: particle size effects; quench effects; effect of low Eh; and ARM-1 performance. Tests are under way now in these areas to provide the necessary data by September 1984, when MCC-3P will be submitted to the MRB for final approval. Test results will be available in the next reporting period. Special emphasis is being placed on integrating MCC-3 and MCC-14 data needs this year because of their strong interdependence.

MCC-4 Low-Flow-Rate Leach Test Method

This test method was revised and the example data were replotted as a result of the suggestions made by the MRB Procedures Panel in 1983. Replotting of the data resulted in no major changes in the procedure. The method is undergoing final preparation for resubmission for provisional approval although its further development is indefinitely postponed.

The MCC believes that MCC-4 does not provide the type of data that will sufficiently evaluate waste-form performances in the repository environments presently projected.

MCC-7 Method for Preparation of Isothermally Heat-Treated Forms

An earlier version of MCC-7 was modified this year so it could provide data to meet waste-form production and certification needs. MCC-7 is a procedure for heat-treating waste-form samples according to a specified matrix of temperatures and times. The general approach has been used for years and is well developed. Once treated, the specimens can be used in other characterization tests or their microstructure can be evaluated directly by using MCC-13. The data from this method will be used to help establish cooling and storage requirements for waste forms. The method was submitted in March 1984 to the MRB for approval by the Procedures Panel.

MCC-13S Recommended Practice of Determining the Microstructure of a Waste Form

The MCC has recognized a general need for standardized methods to determine the microstructure of waste forms either in the as-produced condition or as modified by a performance test or environmental treatment. The purpose of MCC-13 is to describe standard procedures for preparing specimens, using the examination techniques, and presenting and evaluating the data. The uses, limitations, and calibration methods for each procedure will also be identified. MCC-13 will be the primary means by which specimens produced by MCC-7 will be evaluated.

The method includes four principal techniques that have been used regularly in the past: 1) light microscopy; 2) scanning electron microscope/energy dispersive x-ray analysis; 3) electron microprobe analysis;

and 4) x-ray diffraction analysis. This first version of MCC-13 has been written and will be submitted to the MRB Procedures Panel.

MCC-15 Waste/Canister Accident Testing and Post-Test Analysis Method

The purpose of this new test method is to provide data on the performance of large-scale canisters containing simulated waste forms under standard accident conditions. There are two major areas where these data are needed. First, transportation agencies need data on the release of respirable particles from the canister as a result of impact-type accidents. These data are needed to establish the level of containment for the waste during shipping. Second, draft waste acceptance requirements require data that show that a canister will not breach and that the waste form will not be excessively damaged by a 9-m drop onto an unyielding surface. This requirement is based on operational safety regulations.

This method will specify the impact conditions, waste-form analysis techniques, canister-measurement techniques, and statistical methods for evaluating the data. Large-scale canisters with simulated waste will be dropped 9 m in orientations that will cause the most severe damage to the waste form and the canister. Waste-form damage will be assessed principally by measuring the size distribution of particles down to $\sim 1 \mu\text{m}$ dia. Deformations of the canisters will be measured for use in fracture mechanics analyses that will establish canister integrity.

Procedures used on past large-scale impact tests at PNL have been adapted for this procedure. Detailed analyses are under way to establish the adequacy of the proposed

test methods. Tests will be conducted this year on full- and partial-scale canisters and will emphasize characterization of the Defense Waste Processing Facility canister and glass. This method will be submitted to the MRB Procedures Panel in September 1984.

REFERENCE MATERIALS AND HANDBOOK DATA -

J. L. Daniel (Task 4 Leader) -
G. B. Mellinger, J. O. Barner, H. E. Kjarmo,
J. F. Williford, and G. R. Robinson

MCC-D1 One-Year Leach Test Data for PNL 76-68 Glass

Data Package MCC-D1 was resubmitted to the OTC-MRB with the revisions specified in previous MRB review. The full data package has been distributed to MRB members for decision on acceptance for the Data Handbook.

MCC-D2 One-Year Leach Test Data for SRL-131 Glass

Data Package MCC-D2 was submitted to the OTC-MRB. The chairman's review is currently in progress. Concurrently, the MCC-D2 data package was published in PNL-3990.

Shielded Analytical Facilities for Characterization of Radioactive Nuclear Waste Materials

The three MCC shielded instruments for analysis of radioactive materials, and the hot cell facilities for specimen preparation, continue to be used successfully. Primary application during this period has been in characterizing radioactive MCC reference materials.

The shielded ICP^(a) spectrometer is being modified with the addition of a sequential scanner module, to be used concurrently with the direct-reader primary unit. The scanner will allow analysis of solutions for any additional elements not included in the fixed array of 26 elements of common interest. Thus it greatly increases the ICP's versatility by providing a convenient method of total analysis of unusual materials or experimental compositions. Installation of the scanner module began on March 19 and is expected to require about 30 days including operator training.

J. L. Daniel and H. E. Kjarmo attended the second Workshop on Examination of Radioactive Materials by Electron Beam Methods, March 29-30, 1984, at Savannah River Laboratory. Representatives from 12 diverse laboratories participated. Details of the MCC shielded scanning electron microscope and energy dispersive spectrometer were described, and factors influencing data quality from radioactive specimens were discussed.

Reference Materials

The first issue of the document Approved Reference and Testing Materials for Use in Nuclear Waste Management Research and Development Programs (PNL-4955-1) was distributed. The report describes the nine reference materials available from MCC at the time of publication and includes a brief characterization summary for each. The document will be issued periodically with

(a) Inductively coupled argon plasma atomic emission.

updated information regarding new materials and additional characterization data.

Demand has increased from the nuclear waste repository projects and glass producers for additional MCC reference materials of particular composition and specimen form specific for the projects. MCC, therefore, is now using three different facilities (controlled hood, glove box, and hot cell) to produce the reference materials required. A strong effort is being made by MCC to produce these on a schedule supportive of the users' test programs and to

select compositions and doping levels of radioactive components acceptable for the R&D programs of more than one glass manufacturer and repository project. In addition, detailed characterization of these and previously produced materials must be conducted. The schedule planned for the period January-June 1984 is given in Table 2.1. ATM-1c has been completed; the special specimen forms required by NNWSI were made and delivered. ATMs 7, 8, and 9 are all in progress and generally on schedule.

TABLE 2.1. MCC's Schedule for Preparation and Characterization of Approved Testing Materials (January - June 1984)

Identification	Description	Radioactive Isotopes (g/g Glass)	Quantity Planned	Facility Required	Estimated Fabrication Completion
New Materials					
ATM-1c	NNWSI Glass-I (U-doped 76-68 type)	UO ₂ (3.98E-2)	3 kg (Includes special specimen forms)	Hood	Feb 84
ATM-7	BWIP Glass-B (Doped Barnwell type)	Am-241 (6.5E-5) U (2.0E-2) Th-232 (1.0E-4) Ra-226 (8.0E-6) Sn-113 (3.6E-9) Se-75 (2.5E-9)	2 kg (Includes powdered specimens)	Hot Cell	Apr 84
ATM-8	NNWSI Glass-II (Actinide doped 76-68 type)	UO ₂ (4.1E-2) NpO ₂ (4.0E-3) PuO ₂ (1.0E-3) Tc ₂ O ₇ (5.0E-3)	3 kg (Includes special specimen forms)	Glove Box	Mar 84
ATM-9	SRL Defense Glass; ONWI, BWIP	To be determined; expected to include U, Pu, Am, Np, Tc	3 kg	Glove Box	May 84
Specimen Preparation					
ATM-101	HB Robinson spent fuel (crushed and sized powder)	--	250 g	Hot Cell	Feb 84
Characterization of Existing Materials					
ATM-2, 3, 4	76-8 Glasses (Actinide doped)	Am, Np, Pu	--	Glove Box	--
ATM-5	76-68 Glass (Fully radioactive)	Complete High-Level Waste	--	Hot Cell	--
ATM-6	BWIP Glass A (Doped Barnwell type)	U, Cm, Th, Np, Pu, Tc, Cs, Se	--	Hot Cell	--

A follow-on schedule for the period July 1984-September 1985 will be proposed for comment by potential users in April.

ARM-1

Static leach tests were conducted on the approved reference material ARM-1 using MCC-1 and MCC-2 methods. Detailed data analysis is under way for tests through 56 days' duration; 1-year tests are still in progress. Data will be used to establish approved reference leach test values for field calibration of equipment and test methods by users of MCC-1 and -2. Initial data analysis indicated that this glass may be more stable (slower leach rate) than the MCC 76-68 glass.

Reference Spent Fuel ATM-101

Nine HB Robinson spent fuel rods were transferred from EG&G to MCC for use as reference material. The tenth rod originally selected for the purpose was found to be defective and so was rejected by MCC and not replaced. Characterization began with collection of fission gas for analyses by EG&G/EXXON at Idaho Falls before shipment; data are being compiled at Idaho Falls for the analytical report. The nine rods were cut by EG&G into sections of one-third full rod length for ease in shipping. At MCC/PNL the 27 rod segments have been repackaged into individual airtight storage containers.

Characterization of this spent fuel at PNL has begun with gamma scanning of fuel rod segments in the order in which they are being distributed for test use; segments N-9C, -9B, and -9T are complete, and segments N-126, L-8C and C-5C are scheduled. Burnup and radionuclide analyses on specimens taken from rod N-9C have started.

Ceramography on samples from segment N-9C is scheduled for April 1984.

Distribution of the HBR fuel was initiated with ground and sized powder prepared from sections cut from segment N-9C for the BWIP. Using a closely controlled automated mortar and pestle, 400 g of powder were prepared. Particle size distribution was as follows:

- 60+115 mesh (preferred size), 222 g (55%)
- 115+250 mesh (acceptable), 88 g (22%)
- 250 mesh (fines), 92 g (23%)

ATM-101 spent fuel is also being used in two other test programs so far. Segment C-5C was transferred to WHC for their use in NNWSI repository program tests. Segment N-9B was transferred to CSFMPO for oxidation tests in connection with the dry storage program.

Foreign Travel: CEC Leach Test Round Robin

J. L. Daniel traveled to Battelle-Frankfurt and to Harwell (the United Kingdom Energy Research Establishment) in connection with a progress review meeting for the Static Leach Test Round Robin conducted by the Commission of the European Communities (CEC). The MCC was the only U.S. participant in the round robin test, which uses a high-temperature method (to 190°C) based on the MCC-2 test method. The MCC also provided consultation to Battelle-Frankfurt in data analysis and preparation of the final CEC report in a format comparable to MCC's 76-68 round robin report (PNL-4249). A comment copy of the CEC report has been received from CEC. Completed results of the CEC round robin seem to show generally better internal consistency (interlaboratory precision) for the 12 selected participants than was achieved in the MCC round robin

with its 27 diverse participants. Some instances of laboratory inconsistencies were noted, suggesting systematic bias in those cases. MCC test data in the CEC round robin were generally comparable with consensus averages for the 12 laboratories. The main difficulty encountered by all participants was the excessive leakage of leachant at test temperatures of 150°C and 190°C. MCC substituted a modified Teflon vessel for those tests, successfully reducing the loss rate to acceptable limits. The report concludes that the test results demonstrate that the method as written and applied is in a state of statistical control.

REFERENCES

- Chikalla, T. D., and J. A. Powell. 1983. Nuclear Waste Management Semiannual Progress Report October 1982 through March 1983. PNL-4250-3, Pacific Northwest Laboratory, Richland, Washington.
- Felmy, A. R., S. M. Brown, Y. Onishi, R. S. Argo and S. B. Yabusaki. 1984. MEXANS - The Metals Exposure Modeling System. EPA-600/3-84-031 (NTIS #PB84-157155), Environmental Protection Agency, Washington, D.C.
- Felmy, A. R., D. C. Girvin and E. A. Jenne. 1984. MINTEQA: A Computer Program for Calculating Aqueous Geochemical Equilibria. EPA-600/3-84-032 (NTIS #PB84-157148), Environmental Protection Agency, Washington, D.C.
- Langmuir, D. 1978. "Uranium Solution-Mineral Equilibria at Low-Temperature with Applications to Sedimentary Ore Deposits." Geochimica Cosmochimica Acta, 42:547-569.
- Materials Characterization Center. 1981. Materials Characterization Center Test Methods. PNL-3990, Pacific Northwest Laboratory, Richland, Washington.
- McElroy, J. L., and J. A. Powell. 1983. Nuclear Waste Management Semiannual Progress Report April 1983 through September 1983. PNL-4250-4, Pacific Northwest Laboratory, Richland, Washington.
- Rai, D., J. L. Ryan, and M. McCulloch. 1984. "Neptunium (IV) Hydrous Oxide Solubility Under Reducing and Carbonate Conditions." Inorganic Chemistry (in press).
- Robins, R. G. 1966. "Hydrolysis of Uranyl Nitrate Solutions at Elevated Temperatures." Jour. Inorg. Nuclear Chemistry, 28:119-123.

3.0 GEOLOGIC REPOSITORY

The objective of the Geologic Repository Programs at PNL is to support the Office of Civilian Radioactive Waste Management—Geologic Repository Development Project efforts to develop the technology and facilities required for the safe and environmentally acceptable disposal of nuclear waste.

3.0 WASTE ISOLATION

M. R. Kreiter - Program Office Manager

3.1 OFFICE OF NUCLEAR WASTE ISOLATION
(ONWI)3.1.1 Waste Package Program
(DB-30-30-01 - 80597)

D. J. Bradley - Program Manager

The main objective of the Waste Package Program is to help provide the necessary data base on waste package components and multicomponent interactions to qualify a waste package for geologic disposal. Supporting this are the following more specific program objectives: 1) help provide a basis for meeting waste package performance standards; 2) provide input to waste package designers; 3) optimize and select structural barrier materials; 4) develop predictive models for waste package degradation and radionuclide release.

Summary

Based on work conducted during the reporting period, the following conclusions can be made:

- Without irradiation, the general corrosion of cast and wrought low-alloy ferrous materials in Permian Basin brine at 150°C is not particularly severe. It appears that <25 mm (1 in.) of the material would be lost to corrosion in 1000 years, based on linear extrapolation of tests lasting up to 9 months.
- Gamma irradiation at 1×10^5 rad/hr raises the corrosion rate of ferrous materials in Permian Basin brine at 150°C by a factor of ~10. A dose rate of 2×10^3 rad/hr showed a small rate enhancement after a 1-month exposure, none after 3 months or 6 months.

- High-purity iron has shown no advantage over commercial steels or ductile cast iron in the corrosion tests conducted to date.
- The ability of cast mild steel to accommodate plastic deformation is reduced by exposure to the Permian Basin brine environment. Apparently this is because of a strain-aging phenomenon brought about by corrosion-product hydrogen. There is no evidence of a susceptibility to stress-corrosion cracking, which would be potentially more damaging.
- Preliminary fatigue-crack-growth-rate testing of low-alloy steels in Permian Basin brine at 150°C has produced crack-growth rates lower than those found in air at the same temperature and same cyclic loading conditions. This is probably due to crack-tip blunting in the corrosive environment.
- The presence of iron in salt brine causes up to a factor of 10 enhancement in the release of actinides from 76-68 glass. The actinides appear either to be incorporated into precipitates or to form colloids. It appears that hydrolysis of the glass matrix is insensitive to chemical changes brought about by alpha radiolysis when only a thin film of water is available.
- The spent fuel data taken to date suggest that solubility limits alone are not adequate to explain the following observations:
 - a) The leaching characteristics of uranium from both UO_2 and spent fuel in

brine are nearly independent of temperature and time over the ranges studied.

- b) Uranium leached from spent fuel in brine is more than 100 times greater than from UO_2 .
- c) Iron has no apparent effect on the total uranium released in brine, but it causes a substantial reduction in solution concentration of uranium, probably because it lowers the oxidation potential--thereby lowering uranium solubility.
- Americium-241 concentrations in equilibrium with doped glass at $\text{pH} > 7$ are $\sim 10^{-10.5}$ M, regardless of the composition of the equilibrating solution (deionized water, brine, 10X diluted brine). At low pH values (2-4), ^{241}Am solubility limits were $\sim 10^{-5.8}$ M. For ^{237}Np , the equilibrium concentration for $\text{pH} > 7$ was $\sim 10^{-7}$ M for the above solutions, while for ^{239}Pu the concentration was $\sim 10^{-10}$.
- The solubility of anhydrous plutonium oxide in the +4 oxidation state was found significantly higher in 4.0 M NaCl in the neutral-to-basic pH range than in 0.4 M NaCl and 0.4, 4.0 M sodium perchlorate. This is attributed to an alpha radiolysis-generated oxidation potential high enough to convert plutonium to the +6 oxidation state that is kinetically dependent on chloride ion concentration. Chlorine ion complexation is not the cause of the higher plutonium concentrations observed in salt brine.
- Plutonium concentrations in Permian Basin brine resulting from the leaching of spent fuel are similar to those observed from anhydrous plutonium oxide compounds in the +6 oxidation state.
- Alpha radiolysis of salt brines results in a much more oxidizing solution than

does gamma radiolysis. H_2/O_2 ratios after alpha radiolysis are found to be near 10 to 1, whereas they are only about 2 to 1 after gamma radiolysis.

- Chlorine loss from irradiated salt is possible. Preliminary data indicate that this loss is a function of crystal size, salt composition, and temperature.
- The heating of unirradiated Permian Basin salt (190°C for 30 hr) followed by dissolution in deionized water gives a higher rise in pH than does any other combination of heating and/or irradiation. The evolution of as-yet unidentified gases is believed to cause this phenomenon.
- A strong odor of H_2S was noted when crushing the Paradox Basin salt. Analysis of eight samples gave an average value of 37 ppm ($\mu\text{g S}^{2-}/\text{g salt}$) H_2S .
- Results in solution radiolysis product generation following recent advances in the RADIOL computer code have allowed the fitting of gas generation data obtained on this program. The code was verified mathematically after successfully running a benchmark problem that produced results essentially identical to those of a Canadian radiolysis code.

Structural Barriers - R. E. Westerman and S. G. Pitman

General Corrosion Studies. The general corrosion studies to date have been done primarily in flowing brine environments, regardless of the anticipated static, relatively dry conditions expected in a salt repository, as the tests are intended to simulate conservative, worst-case conditions.

The general corrosion tests of low-alloy cast and wrought steels and ductile cast iron are under way in 150°C Permian Basin brine No. 2. The so-called "anoxic" test

utilizes argon-sparged feed brine, containing ~0.3 ppm dissolved oxygen; the "oxic" test utilizes brine sparged with Ar-20% O₂, containing ~1.5 ppm oxygen. Both tests were shut down for analysis of specimen corrosion rates during this reporting period. The results are given in Table 3.1.

The specimens exposed to the oxic environment typically show higher metal penetrations than those under anoxic conditions even though the amount of oxygen admitted to the autoclave is far too small to directly consume metal.

In all cases, the specimens appeared to be in good condition under exposure, as suggested by their uniformly low corrosion rates. The uncleaned samples were all characterized by a black, tightly adherent magnetite scale. The iron and wrought steel specimens showed no signs of nonuniform attack except for a change in surface appearance of the metal in contact with rack insulators of the autoclave. The cast normalized steel showed no increased corrosion around the rack insulators.

A limited-reactant test was completed in which specimens of 1025 cast steel, 1025 wrought steel, ductile cast iron, and high-

purity iron were imbedded in cans of salt, equivalent to dehydrated Brine A,^(a) containing various amounts of moisture. The cans, made of Inconel 625 and welded shut, were held at 150°C for 3 months. Water concentrations in the salt were 2%, 5%, 10%, 19%, and 31% by weight. After 3 months, the cans were opened, the specimens were removed and stripped of their corrosion-product films, and metal penetrations were determined by weight change. Metal penetration as a function of water concentration for all materials is shown in Figure 3.1. The following conclusions can be drawn from the weight change determinations:

- The corrosion rates for all materials were <25 μ /yr (<1 mil/yr), assuming linear-reaction kinetics, at water contents of 10% or less. The corrosion rates increased markedly at the 19% and 31% water levels. (At 31% water, a liquid phase was present in the can: the salt had a "slushy" consistency. At 19%, the salt was "dry" and solid.)

(a) Brine A is distinguished from Permian Basin Brine No. 2 primarily by its high Mg⁺⁺ and K⁺ contents (see Table 3.4).

TABLE 3.1. Corrosion Rates Observed in General Corrosion Studies

Material	Test	Exposure Time, Months	Penetration Rate, μ m/yr (mil/yr)
1025 cast normalized steel	Anoxic	6	5.0 (0.20), 7.0 (0.28)
1025 wrought steel	Anoxic	9	7.6 (0.30), 3.9 (0.15)
High-purity iron	Anoxic	6	5.9 (0.23), 8.6 (0.34)
1025 cast normalized steel	Oxic	6	19.0 (0.74), 21 (0.84)
High-purity iron	Oxic	6	28 (1.1)

FIGURE 3.1. Penetration Rates of All Ferrous Materials, Limited Reactant Test. Three months' exposure to moist brine A-Type salt at 150°C.

- The maximum corrosion rates observed were a factor of 10 to 15 higher than those observed in unirradiated Permian Basin brine No. 2 at the same temperature. This is assumed due to salt-composition effects, as the high-magnesium salts have historically been more corrosive than salts with low levels of magnesium.
- Corrosion rates of the "pure" iron specimens were about the same as those for the other materials.
- Nonuniform corrosion, i.e., pitting attack, was observed on specimens of all materials exposed to salt having water concentrations of 19 and 31%.

The gas present in the can initially containing 19% water was analyzed after the exposure period and was found to consist of 88.6% H_2 , 7.8% He, 1.9% N_2 , 0.6% CO_2 , 0.3% CH_4 , with traces of C_2H_x and C_xH_4 . The gas pressure in the cans was estimated to be ~10 atm. The carbon in the gases is apparently derived from that in the corroding cast iron. The helium is the residue from the helium atmosphere of the welding glove box.

Irradiation-Corrosion Studies.

Two irradiation-corrosion studies are under way with low-alloy cast and wrought steels and ductile case iron in Permian Basin brine No. 2 at 150°C and at two levels of gamma (^{60}Co) irradiation, 1×10^5 rad/hr and 2×10^3 rad/hr. Table 3.2 presents the results of recent specimen penetration rate analyses.

All penetration rate data from the 1×10^5 rad/hr test fall within previously reported bounds. The 2×10^3 rad/hr data are continuing the same trend as the 1- and 3-month data: linear penetration rates are essentially identical to those found in an unirradiated system, and much lower than those found in a system irradiated at a dose rate of 1×10^5 rad/hr. The reference ONWI cast steel (ASTM A 216-77 grade WCA) has now been included in this test.

A 3-month accelerated irradiation-corrosion study of titanium Grade 2 and titanium Grade 12 was conducted using Brine A at 150°C and an irradiation intensity of 1×10^6 rad/hr. The test contained fracture-toughness specimens, Charpy V-notch impact specimens, U-bend specimens and corrosion coupons of titanium Grade 2 and titanium Grade 12 materials. Much corrosion attack was evident, focused primarily on the Charpy specimens, all of the titanium Grade 2 material, and certain rack components made of titanium Grade 2 and Grade 4 materials. Preliminary visual observation has revealed only two areas of attack of the Grade 12 material: the band holding the Charpy specimens in place was broken in two places, without apparent ductility, and the corners and near-hole regions of the Grade 12 fracture toughness specimen.

TABLE 3.2. Irradiation-Corrosion Penetration Rates of Ferrous Materials

Material	Irradiation-Intensity, rad/hr	Exposure Time, Months	Penetration Rate, $\mu\text{m}/\text{yr}$ and mil/yr
1025 cast normalized steel	1×10^5	6	140 (5.5), 79 (3.1)
High-purity iron	1×10^5	6	69 (2.7), 125 (4.9)
Ductile cast iron	1×10^5	9	78 (3.1), 118 (4.7)
1025 cast steel	1×10^5	10	113 (4.5), 94 (3.7)
1025 wrought steel	1×10^5	10	107 (4.2), 59 (2.3)
2-1/2% Cr, 1% Mo cast steel	1×10^5	10	69 (2.7)
1025 cast normalized steel	2×10^3	6	14 (0.57)
High-purity iron	2×10^3	5	28 (1.1), 27 (1.0)
1025 wrought steel	2×10^3	6	13 (0.50)
Ductile cast iron	2×10^3	6	13 (0.52), 18 (0.70)

Some reaction product was lifted from a Charpy specimen and examined by X-ray diffraction for identification of compounds. The major constituents of the reaction product were found to be TiO_2 and TiH_2 . The attack appears to be associated chiefly with hydriding, as shown by the peculiar exfoliated appearance. Hydrogen analyses of selected corrosion coupons are under way. Two titanium bolt-loaded fracture specimens, one of Grade 2 and one of Grade 12, were exposed in the test. Their examination revealed that no crack extension occurred during the test, in which the precracked specimens were loaded to a stress intensity of ~ 20 ksi/inches. Charpy V-notch fracture specimens also were exposed; the titanium Grade 2 specimens were too degraded to test, but the Grade 12 ones will be tested in impact and in slow bend to determine whether mechanical properties were at all degraded during exposure.

Though the test was accelerated by means of high radiation intensity, (about 10 times higher than expected with a titanium overpack design) and though the Grade 12 materials showed more stability than the Grade 2, the susceptibility of titanium alloys to hydrogen attack under irradiation-corrosion conditions was clearly demonstrated.

Enviromechanical Studies

Recent efforts have emphasized the elevated-temperature slow-strain-rate (SSR) testing of cast 1025-equivalent steel (ASTM A27 grade 60-30) and the corrosion-fatigue testing of wrought and cast 1025 steel plate. In an SSR test, a specimen is loaded in the expected service environment and strained to failure. More than one low displacement rate is often used so that strain rate effects can be investigated.

The straining of any metal in tension increases the surface area, which continuously exposes unoxidized material. Deformation mechanisms accommodate the strain in the metal, and slip planes emerging at the surface provide sites for environment-metal interaction. Stress-corrosion cracking (SCC) is often influenced by strain rate. At high strain rates, the time to failure is so fast that the influence of the environment on the metal is minimal; at very low strain rates, damage from the environment is limited by continual repassivation of the oxide film. Intermediate loading rates often cause the lowest ductility; interaction between the metal and the environment occurs as the passivating film is broken.

In SSR tests, the susceptibility of metals to SCC is indicated by three phenomena:

- loss of ductility relative to an inert environment
- ductility diminution at particular slow-strain rates relative to other strain rates
- fractographic evidence of embrittlement.

Loss of ductility and the dependence of ductility on strain rate are the most readily observed signs of SCC; however, strengthening or embrittlement mechanisms also may cause these phenomena to occur. When loss of ductility occurs, the fracture surfaces are examined to determine the mode of failure. If fractographic evidence of embrittlement is not present, the ductility diminution cannot be attributed to SCC.

Slow-strain-rate tests have been done both in air and in Permian Basin brine No. 2 sparged with argon, 20% argon-80% oxygen, and pure oxygen to achieve three different oxygen levels (about 0.3, 1.0, and 2.0 ppm, respectively) in the test environment. In

addition, some of the tests in oxygen-sparged brine used a higher flow rate (110 mL/hr rather than the usual 35 mL/hr) to ensure that oxidic conditions existed at the specimen. The intent of these tests was to determine any effects of the solution oxygen content on the enviromechanical behavior of the cast steel specimens. Two strain rates were used-- 2×10^{-7} in./in.-sec and 1×10^{-4} in./in.-sec; the temperature was 150°C. The following conclusions were reached:

- The ductility of the steel diminished substantially in brine at 2×10^{-7} in./in.-sec compared to tests in air or brine at 1×10^{-4} in./in.-sec.
- Over the range studied, variation in dissolved oxygen concentrations caused no significant change in SSR behavior.
- The load-displacement records of all the specimens were similar up to the maximum load; after this point, however, the deformation behavior varied considerably. Those specimens strained in brine at the lowest strain rate (2×10^{-7} in./in.-sec) fractured soon after the maximum load was reached, while the other specimens showed considerable ductility before fracture. A possible explanation is strain-aging, caused by corrosion-product hydrogen in the steel specimen.

A facility for performing SSR testing of materials in brine under irradiated, hydrothermal conditions is now operating. For the first test, a specimen of ONWI reference steel is being tested at a strain rate of 2×10^{-7} in./in.-sec in Permian Basin brine No. 2 at 90°C and an irradiation intensity of 2×10^5 rad/hr.

Two corrosion-fatigue tests of wrought 1025 steel in Permian Basin brine No. 2 at 150°C have been completed. In both tests,

crack-growth rates were lower than those found in an air environment. This retardation may be caused by corrosive crack-tip blunting, crack closure effects from corrosion products, or by anodic polarization from contact with the Inconel load train. A specimen of reference cast steel has now been electrically isolated, and a test is proceeding at 1 Hz in 150°C Permian Basin brine No. 2.

Source Term Evaluation - G. L. McVay and L. R. Pederson

Glass Interactions. Release characteristics of ^{239}Pu and ^{241}Am from actinide-doped PNL 76-68 glass have been investigated at 90°C, both with and without the presence of ductile iron. These tests were conducted in Permian Basin brine No. 1 as well as deionized water for comparison. Results were similar for both actinides. The presence of iron in brine greatly increases the actinide release (factors of 7 to 10). Most of the actinide, however, ends up on the filter or container walls. Iron causes precipitates to form (primarily iron hydroxide and iron silicate), which sorb actinides and end up either on container walls or as colloids that are removed by filtration. The same experiments in deionized water result in a smaller effect of the iron on actinide removal (about a factor of 2).

Leaching experiments were performed using 76-68 glass (supplied by the Materials Characterization Center (MCC)) in contact with a 250- μ -thick deionized water film, which was also in contact with a ^{238}Pu alpha source. This arrangement allowed the effects of alpha radiolysis of water to be evaluated in the absence of structural damage from alpha radiation, which would have occurred in ^{238}Pu -doped glasses. These experiments com-

plement earlier studies on the effects of gamma radiolysis on glass leaching carried out in deionized water and in brines. These earlier studies have shown that radiolysis effects are most apparent at low temperatures. Present experiments were carried out at room temperature for 24 hr. Short leaching times were necessary to avoid saturating the thin water film. No effect of alpha radiolysis on glass leaching was observed, as determined by depth profiling using secondary ion mass spectrometry (SIMS). It is preliminarily concluded that hydrolysis of the glass matrix is insensitive to chemical changes brought about by alpha radiolysis, as observed when only a very thin film of water is available. Alpha radiolysis effects on actinide solubilities and release characteristics require further examination, however.

Spent Fuel Interactions. The spent fuel experiments conducted last year were on unclad spent fuel and contained ductile iron for interactive effects. Additionally, experiments involving UO_2 were conducted with both ductile iron and oxidized Zircaloy cladding present. The following observations are difficult to explain and require further research:

- Uranium leached from spent fuel in Permian Basin brine No. 1 is more than 100 times greater than UO_2 .
- Iron has no apparent effect on the total uranium released in brine, but it substantially reduces the solution concentration of uranium, probably by lowering the oxidation potential and thereby the uranium solubility.
- Leaching characteristics of uranium from both UO_2 and spent fuel in brine are nearly independent of temperature and time over the ranges studied.

The data imply that solubility limits alone are not adequate to explain the results. It appears that a small portion of the samples (near surface) is more soluble than the bulk and that this soluble phase is larger for spent fuel than for UO_2 --due perhaps to higher temperatures and radiation damage experienced by the spent fuel. Experiments are planned to determine the cause for the large differences in UO_2 and spent fuel leaching. These include oxidizing UO_2 to various degrees prior to leach testing, putting alpha emitters (such as ^{244}Cm) into solutions for UO_2 leach experiments, and conducting long-time experiments on spent fuel in the presence of iron.

Solubility Studies. The solubility limits of ^{241}Am , ^{239}Pu , and ^{237}Np from actinide-doped MCC 76-68 glasses have been evaluated in Permian Basin brine No. 1 at room temperature. The solubilities for ^{241}Am were determined over a pH range of 2-11, while those of ^{239}Pu and ^{237}Np were not pH-controlled and the glass dissolution resulted in pH values of 9. These experiments were not conducted long enough for alpha radiolysis effects to become important at the actinide dopant levels in the glass. Additionally, the experiments did not contain waste-package components (such as steel) and were conducted only at 25°C . Some general conclusions are:

Americium.

- Quantities of americium in colloidal form increase with increasing pH.
- Concentrations of ^{241}Am in equilibrium with doped glass at $\text{pH} > 7$ are about $10^{-10.5}$ M regardless of the equilibrating solution composition (deionized water, brine, 10X diluted brine).
- The same solution concentrations have been approached from both above and be-

low, indicating that concentrations are solubility-limited.

- At low pH values (2-4), ^{241}Am solubility limits were approximately $10^{-5.8}$ M.

Plutonium and Neptunium.

- No significant differences in concentrations were observed among samples contained in brine, 10X diluted brine, or deionized water (concentrations were about 10^{-10} M for plutonium and 10^{-7} M for neptunium).

It was demonstrated last year that alpha radiolysis in Permian Basin brine No. 1 enhances oxidation potential in the brine solutions. Since this can have a large effect on actinide solubility, it has been investigated in simplified systems to gain understanding of the radiolysis phenomenon and effects on actinide solubilities. Some of the results are illustrated in Figure 3.2 for anhydrous plutonium oxide in the +4 oxidation state (initially, at least). Both sodium chloride and perchlorate solutions were used in 0.4 and 4.0 M concentrations. As the figure shows, solubilities at various

FIGURE 3.2. Comparison of $\text{Pu}(\text{OH})_4$ Solubility Data 110 Days in 0.4 M and 4.0 M NaCl and NaClO_4 Solutions at 25°C

pH values are nearly the same for all solutions except the concentrated NaCl solution, the only one where the Eh increased significantly. These samples were all comprised of ^{239}Pu , which has a low activity compared to the ^{244}Cm -doped brines in which alpha radiolysis research was previously done. The concentrated sodium chloride brine resulted in significantly higher (about a factor of 100) plutonium solubilities in the neutral-to-basic pH range. This effect is attributed to the alpha radiolysis-generated higher oxidation potential. Apparently, the sodium is not participating in the radiolysis effect as evidenced by comparison of solutions in Figure 3.2. The concentrated chlorine, however, seems to be required to generate high oxidation potentials with alpha radiolysis under these experimental conditions. These high oxidation potentials can be generated with relatively low alpha activity, about 40 times lower than that of the ^{244}Cm -doped studies.

The fact that 4 M NaCl solution generated sufficient oxidation potential with ^{239}Pu radiolysis to transform the plutonium from a +4 to a +6 oxidation state is illustrated in Figure 3.3. In this figure, the curve for 4 M NaCl from Figure 3.2 is reproduced, which utilizes plutonium in the +4 state as starting material. Additionally, plutonium in the +6 state is used as starting material in 8 M NaNO_3 solution, and the same plutonium solubility results. This illustrates that the plutonium is being oxidized to the +6 state in 4 M NaCl and that complexation with chlorine is not the cause of the higher plutonium solution concentration. For comparative purposes, the plutonium solution concentrations in Permian Basin brine No. 1 from spent fuel static leach tests are also included in Figure 3.3. As can be seen, the

FIGURE 3.3. Illustration of Pu Oxidation (+4 to +6) due to Radiolysis and Illustration of the Lack of Cl Complexation

value is close to those observed from anhydrous plutonium oxide compounds in the +6 state. It appears that alpha radiolysis plays a dominant role in plutonium (and probably other actinides as well) solubility in concentrated sodium chloride brines, even at relatively low alpha activity levels.

Colloid Investigations. Americium-doped MCC 76-68 glass has been leached in room-temperature Permian Basin brine No. 1 for 100 days and analyzed for ^{241}Am -containing colloids. A relatively large number of colloids were formed: about half were larger than $0.45\ \mu$ with the remaining half distributed on progressively smaller sized filters down to $18\ \text{\AA}$. It was found that colloid formation is progressively favored as solutions become more basic.

Investigations of colloid generation in the presence of iron have been conducted utilizing actinide-doped 76-68 glass. This is more realistic and is complementary to previous experiments in which nonradioactive colloids were generated and actinide sorption characteristics were evaluated. The

results indicate that large quantities of actinide-bearing colloids are generated in the presence of iron. They are primarily pseudo-colloids consisting of iron silicate and iron hydroxide precipitates, with an estimated 20% of the actinides tied up as true colloids consisting of actinide compounds such as hydroxides. The current research was conducted in 90°C brine with ^{239}Pu and ^{241}Am doped 76-68 glass.

Brine Radiolysis. Gamma radiolysis of a magnesium-rich Permian brine produced a gas pressure-versus-dose curve essentially the same as the Permian Basin brine No. 1 itself. Thus, substitution of magnesium for some of the sodium had no effect. The magnesium-rich brine was prepared by adding MgCl_2 to Permian Basin brine No. 1. After standing for a few days, the magnesium and sodium concentrations in solution were 45 and 59 g/L, respectively. This compares to the original sodium concentration of 127 g/L in brine No. 1.

An error was discovered in the calibration of the mass spectrometer being used to analyze gas compositions. When this error is corrected, H_2/O_2 ratios after gamma radiolysis of the concentrated brine solutions are roughly two to one rather than about three to one as reported earlier.

It is becoming clear that alpha radiolysis of salt brines results in a much more oxidizing solution than does gamma radiolysis. H_2/O_2 ratios after alpha radiolysis are found to be near ten to one, whereas they are only about two to one after gamma radiolysis. If this ratio were exactly two to one, then the redox potential of the solution should be unchanged by irradiations. The few Eh measurements made on gamma-irradiated solutions show this to be nearly the case. Eh values of alpha-irradiated

salt brines, however, are about 1.2 volts compared with about 0.3 to 0.4 volts for the unirradiated brine.

Crystalline Salt Radiolysis. Efforts are continuing to evaluate the influence of gamma irradiation and heating of crystalline salt on the expected chemical environment of a high-level waste package in a salt repository. Specifically, rock salts from the Palo Duro Basin (G. Friemel Core Hole No. 1, Cycle 4, and Zeeck Core Hole No. 1, Cycle 5) and Paradox Basin (GD-1 Core Hole, Cycle 6) plus Harshaw single-crystal sodium chloride are being irradiated at dose rates of 2×10^3 , 4×10^4 , 6×10^5 , 2×10^6 , and 7×10^6 rad/hr. Irradiation temperatures are ambient and 150°C, while total doses extend upwards to 1×10^{10} rad.

The brine chemistry expected from the dissolution of irradiated salt will depend at least partially upon the fate of the free chlorine created by radiolysis. If chlorine can be lost from the crystals, excess sodium metal will remain, which will produce sodium hydroxide on contact with water, resulting in a basic solution. The reactivity of gaseous chlorine is also a concern. Past experiments have shown that no chlorine appears to be lost from room-temperature-irradiated salts during irradiation. When crystals ($>0.1 \text{ cm}^3$) of sodium chloride and rock salt were crushed and/or annealed, some loss of chlorine was evident, however. Results are given in Figure 3.4 for salts irradiated to 5×10^9 rad. When sodium chloride crystals were crushed to ~200 mesh, a definite odor of chlorine was detectable, as has been reported in other studies. On dissolution, the solution pH increased while the hypochlorite ion concentration decreased compared to that obtained for uncrushed sodium chloride, indicating chlorine loss.

FIGURE 3.4. Solution pH Versus Annealing Temperature for Cycle No. 4 Permian Basin Rock Salt and Harshaw NaCl Irradiated to 5×10^9 rad at Room Temperature. The salts were dissolved after irradiation, crushing, and/or annealing (0.10 g salt/1.00 mL water). The combination of crushing and annealing was most effective in liberating chlorine from the rock salt.

Upon heating, defects were largely annealed. The finding that the solution pH after heating to $>350^\circ\text{C}$ was nearly neutral indicates that the loss of chlorine was a small fraction of the total amount present.

Crushing natural rock salt crystals at room temperature to ~300 mesh did not appear to release chlorine to the extent found with sodium chloride. However, crushing and annealing together appeared to be important. On heating crushed rock salt to 200°C followed by dissolution, the solution pH was as great as 10.8 ± 0.3 (for 0.1 g salt in 1.0 mL water). Further heating to 400°C , which totally eliminated the color centers, gave a solution pH value upon dissolution of 9.6 ± 0.3 . This final pH is a measure of the excess sodium remaining in the crystal (which is related to the amount of chlorine irreversibly lost) plus any other salt decomposition reactions which liberate acidic gases. Preliminary data indicate that this

loss is a function of crystal size, salt composition, and temperature.

Additional experiments heating irradiated and unirradiated salts to 300°C have been carried out to determine the kinetics of chlorine and other gaseous product desorption. At least three different processes are apparent when irradiated rock salts are heated above about 150°C :

1. Free chlorine is evolved from the crystals.
2. Radiation-induced defects (sodium colloids and free chlorine) begin to recombine, reducing the density of defects.
3. Other unidentified gas(es) evolve, causing the remaining salt upon dissolution to become even more basic.

Although not completely separable, the effects of these processes can be seen in the titration curves of Figure 3.5. In this figure, 1.00 g of irradiated and/or annealed Palo Duro Basin rock salt, or 1.00 g of unaltered Palo Duro Basin rock salt (G. Friemel Core Hole No. 1, Cycle 4) was dissolved in 25.0 mL deionized water. Under continuous sparging with nitrogen, the solution was titrated against $9.90 \pm 0.05 \times 10^{-2} \text{ M HCl}$, using an automated endpoint titrator. From a least-squares fit of hydrogen-ion activity indicated by the pH electrode versus equivalents of acid added, the quantity of base per gram of salt can be calculated. The amount of base contained per gram salt calculated from the data in Figure 3.5 and initial solution pH are given in Table 3.3.

The greatest amount of base was found for the irradiated-but-unheated sample, despite the relatively modest pH upon dissolution. Past work has shown that this behavior is due to formation of the hypochlorite ion

FIGURE 3.5. Titration Curves for 1.00-g Permian Rock Salt (G. Friemel Core Hole No. 1, Cycle 4, Lower San Andres). Heating of irradiated salt causes some defects to recombine, seen by a reduction in the amount of base present. The increase in pH from heating unirradiated salt is due to evolution of unidentified gases (perhaps HCl and H₂S), while the increase in pH from heating irradiated salt may additionally be due to escape of free chlorine.

TABLE 3.3. Heating and Irradiation Effects in Permian Rock Salt^(a)

Irradiated ^(b)	No	No	Yes	Yes
Heated ^(c)	No	Yes	Yes	No
pH ^(d)	7.7 ± 0.3	9.7 ± 0.3	8.6 ± 0.3	8.2 ± 0.3
Base, μ equiv/g	2.9 ± 0.3	7.7 ± 0.6	15.9 ± 0.9	22.2 ± 1.1

(a) G. Friemel Core Hole No. 1, Cycle 4, Lower San Andres unit salt.

(b) 5×10^9 rad at 7×10^6 rad/hr and 60°C.

(c) 30 hr at 190°C.

(d) 1.00 g salt dissolved in 25.0 mL deionized water.

in solution, the salt of a weak acid, which effectively buffers the solution. Processes 1, 2, and 3 listed above could all contribute to the observed results when the irradiated salt was heated. Process 2, recombination of defects, must have occurred since the total amount of base measured was reduced with respect to the irradiated but unheated case; however, processes 1 and 3 are less easily distinguished. Only process 3 could have contributed to results found when the unirradiated salt was heated, since free chlorine should not be present. Thus, it is likely that the increase in solution pH when the irradiated salt was heated is at least partially attributable to process 3.

Brine Chemistry. Tests have been completed to determine the intrusion brine chemistry for Permian Basin Cycle 5 salt and for Paradox Basin Gibson Dome salt. The technique used in this determination was identical to that used for Permian Basin Cycle 4 intrusion brine (Permian Basin brine No. 1). Starting material for the determination of Permian Basin Cycle 5 intrusion brine composition was prepared by crushing and homogenizing salt from a 1/4 core from the Zeeck #1 hole (2582.4 to 2693.9 ft).

Starting material for the determination of the Paradox Basin intrusion brine composition was prepared by crushing and homogenizing a 1/4 core from the Gibson Dome (3150.2 to 3358.0 ft).

Initial intrusion brine compositions for Permian Cycle 5 salt and Paradox Basin salt, along with Permian Basin brine No. 1 (Cycle 4), are presented in Table 3.4. The table also includes Permian Basin brine No. 2 and WIPP Brines A and B for comparison.

The Permian Basin Cycle 5 intrusion brine is very similar to Permian Basin brine No. 1, the Cycle 4 intrusion brine composition. The Paradox Basin intrusion brine composition is somewhat different, being lower in Ca^{2+} and higher in Mg^{2+} and K^{+} .

A very strong H_2S odor was observed during crushing of the Paradox Basin salt core. No H_2S odor was detected during crushing of the Permian Basin salt cores. Because of the obvious presence of H_2S in the Paradox salt cores several small uncrushed samples were saved for H_2S analysis. The results of these determinations, carried out on eight solid samples ranging from 8.5 to 22 g, range from 11 to 80 ppm S^{2-} with an average value of 37 ppm ($\mu\text{g S}^{2-}/\text{g salt}$). Because of loss through volatilization this should be considered a minimum value for S^{2-} in the salt. H_2S is an important corrosion agent in oil-field brines, and its presence in relatively high concentrations in the Paradox Basin samples has important implications for the durability of waste package materials, particularly iron-based materials, in this salt.

Modeling - W. L. Kuhn and S. A. Simonson

Overpack Corrosion Modeling. A simplified corrosion model has been proposed that relates corrosion rates of various ferrous alloys in a brine to the gamma-irradiation rate of the brine. The analysis was based in part on the rates of generation and re-consumption of oxidizing and reducing radiolysis products, as predicted by an approximate steady-state radiolysis model. Since then a more comprehensive and accurate radiolysis analysis has been perfected; thus future versions of the irradiation-corrosion model should be on more solid footing and

TABLE 3.4. Compositions of Various Saturated Salt Brines at 25°C

Ion	Permian Basin ^(b) Cycle 5	Permian Basin ^(c) Cycle 4 (Brine No. 1)	Permian Basin ^(d) Cycle 4 (Brine No. 2)	Paradox Basin ^(e) Cycle 6	WIPP A ^(f)	WIPP B ^(f)
Na ⁺	114,000 ^(a) ± 4,800	127,000 ± 3,000	123,000	121,400 ± 4,800	42,000	115,000
K ⁺	45 ± 4	40 ± 2	39	670 ± 50	30,000	15
Ca ²⁺	1,460 ± 10	1,580 ± 40	1,100	820 ± 9	600	900
Mg ²⁺	104 ± 4	132 ± 23	122	750 ± 20	35,000	10
Sr ²⁺	52 ± 2	34 ± 1	35	31 ± 1	5	15
Zn ²⁺	2 ± 0.4	8 ± 2	8			
Cl ⁻	185,000 ± 1,000	191,300 ± 600	191,000	181,300 ± 3,500	190,000	175,000
SO ₄ ²⁻	3,700 ± 100	3,260 ± 100	1,910	3,500 ± 0	3,500	3,500
HCO ₃ ⁻	30 ± 0	28 ± 15	23	47 ± 8	700	700
Br ⁻	<20	27 ± 6	24	<20	400	400
BO ₃ ³⁻	<10	<10	<10	<10	1,200	1,200
S ²⁻				>37		

(a) ppm by weight.

(b) Zeeck Core Hole No. 1.

(c) G. Friemel Core Hole No. 1.

(d) Permian Basin No. 2 is based on the composition of the supernatant fluid resulting from heating Permian Basin brine No. 1 to 150°C.

(e) Gibson Dome Core Hole No. 1.

(f) Molecke 1983.

less vulnerable to questions regarding radiolysis calculations.

Recent improvements in the computer code RADIOL have made it possible to predict results for experimentally relevant time scales without using excessive computer time. Therefore, the need for the approximate method of computing the concentrations of the radiolytically produced species has been eliminated. A benchmark problem, i.e., a test of the code after the changes were made, has been successfully run and verified with virtually identical results from the Canadian code Maksima-Chemist. Now that the code is mathematically sound, work to improve the brine-specific input data can continue unhindered by constraints of the code.

Brine-specific evaluation has begun by taking the hydrogen gas-generation data of

Gray's radiolysis experiment for a 5-M NaCl brine (Gray 1983) and fitting to it a theoretical equation of hydrogen gas generation, Equation 1, by the method of least squares, with the results shown in Figure 3.6.

$$[H_2] = \frac{f_n G(H_2) D}{k_1 [OH^\bullet]} \left(1 - \exp \left(- \left[\frac{k_1 [OH^\bullet]}{1 + n} \right] t \right) \right) \quad (1)$$

where:

n = dimensionless factor to account for the solubility of hydrogen in the brine

$G(H_2)$ = radiation yield of hydrogen from water (= 0.45 molecules/100 eV)

D = dose rate, eV/sec-L

$[H_2]$ = moles H_2 /L of gas phase

f = conversion factor for units

FIGURE 3.6. Plot of Hydrogen Pressure Versus Time (Gray), with a Functional Fit to the Data by the Method of Least Squares

$[\text{OH}^\bullet]$ = concentration of OH radical in solution

k_1 = rate constant ($\text{molar}^{-1}\text{s}^{-1}$) for the reaction:

From a simple analysis of the parameters D and $\text{OH}^\bullet$, the least-squares fit adjustments are obtained for the dose rate D , and the rate constant k_2 , which determines the $\text{OH}^\bullet$ concentration through the scavenging reaction of the $\text{OH}^\bullet$ radical, as given by Equation 2:

D and $\text{OH}^\bullet$ are potentially the least reliable parameters in Equation 1; $\text{OH}^\bullet$ depends on k_2

through Equation 2, such that actually it is D and k_2 that must be fitted. The fitted values are:

$$D = 3.5 \times 10^6 \text{ eV/sec-L}$$

$$k_2 = 7.5 \times 10^6 \text{ molar}^{-1}\text{s}^{-1}$$

The above values were then used as part of the input data for RADIOL and the code was run to experimentally relevant times; 18 hr or 65,000 seconds was appropriate for simulation of the autoclave fluid residence time typical of irradiation corrosion experiments to date on this program. Results from the computer run are given in Figure 3.7. After about 10,000 seconds the code predicts a 2 to 1 ratio of hydrogen to oxygen such as seen experimentally (Gray 1983). The values obtained from RADIOL, at

FIGURE 3.7. Plot of the Concentration of Radiolytically Produced Species Versus Time as Predicted by RADIAL at a Dose Rate of 3.5 Mrads/hr and Initial Oxygen Concentration of 1.5 ppm

an appropriate time, can be used as input to an algorithm that predicts the diffusion of oxidants across a protective layer of the iron.

A caveat to these results is the exclusion of bromine and sulfate, which have been shown to affect the gas-generation rate (Gray 1983); they have not been included in our calculations due to a lack of reaction information concerning these anions. The effect of iron in solution has also been excluded from the calculation, but it will be included in future computer runs.

References

- Gray, W. J. "Gamma Radiolysis of Groundwaters Found Near Potential Radioactive Waste Repositories." Proceedings of Second International Symposium on Ceramics in Nuclear Waste Management, Chicago, Illinois, April 24-27, 1983.
- Molecke, M. A. 1983. A Comparison of Brines Relevant to Nuclear Waste Experimentation. SAND83-0516, Sandia National Laboratories, Albuquerque, New Mexico.

3.1.2 Verification, Benchmark and Validation Support (DB-30-10-01 - 80748)

C. R. Cole - Program Manager

The objective of this program is to assist the Office of Nuclear Waste Isolation (ONWI) in the process of verifying and benchmarking performance analysis codes which will then be used to perform the comprehensive analysis required to site, design, and license a repository in salt.

Background

Efforts this year consist of work in the following areas:

- Providing ONWI with input for their code documentation and verification and benchmarking reports for the hydrologic codes that were verified and benchmarked last fiscal year.
- Defining and setting up salt site-specific heat and contaminant transport verification and benchmark problems, performing any updates to the codes selected for testing, performing the verification and benchmarking runs and documenting this process with a formal report.
- Providing support to ONWI in their efforts to update their Performance Assessment Plan and their Verification and Validation Plan, and preparing a draft report dealing with statistical and uncertainty methods.

Technical Progress

The new documentation report for the FE3DGW hydrologic code has been reviewed, and a complete user's manual has been prepared. Chapters 1, 2, 3 and 5 of the new CFEST documentation report have been reviewed, and a new user's manual is being developed. The need for a quality assurance

procedure for performing and documenting a complex geohydrologic flow and/or transport code was perceived as the numerous verification and benchmark problems were being developed and run. This procedure has been developed as part of this effort and is now being formally documented.

Nuclear Regulatory Commission baseline and benchmark problems and the INTRACOIN problems, along with other available analytical solutions for geohydrologic transport, were reviewed. The results of this review were documented in a letter report to ONWI ("Nuclide Transport Baseline and Benchmark Problem Specifications for SCOPE (BAIRN), CFEST, LAYFLO, MMT and SWENT") to provide input for the final selection of contaminant transport verification and benchmark problems. Assessment codes selected for transport verification and benchmarking have been obtained, made operational on the PNL VAX 11/780 computer, and run on the test problems supplied with the code. Assembly of the input for the transport model baseline (verification) and benchmark problems is in progress.

Selection of codes for modeling heat transport is in progress. The Department of Transportation code has been obtained from ONWI and made operational on the VAX. Canister, room, repository and regional scale temperature benchmark problems are being defined. The SWENT code is being utilized to develop a regional-scale thermal benchmark problem and initial runs have been completed.

A modification of the CFEST code has been completed which allows the adjoint inverse hydrologic problem to be solved. This modification, which will allow limited uncertainty and sensitivity studies to be performed, is now being tested. Results of

this work will provide valuable insight and support in providing input to ONWI for updating their Performance Assessment Plan as it relates to statistical and uncertainty methodology. It will also help in making improvements in their Verification and Validation Plan.

3.1.3 Site and Assessment Support

(DB-30-30-01 - 80847)

F. L. Thompson - Program Manager

The main objective of this program is to provide ONWI with support for their in-house site and system assessments for salt sites that are being considered for a nuclear waste repository. Supporting this are the following more specific objectives: 1) assist in the preparation of reports required for each site, 2) apply selected computer models to each site to provide a better understanding of the important long-term geologic and hydrologic phenomena at each site, and 3) perform sensitivity/uncertainty analyses on selected performance assessment results to help define data needs and thereby optimize ONWI's future data collection efforts.

Overview and Summary

Seven salt sites are being considered by the Department of Energy for nuclear waste repository locations. The suitability of each proposed site will be assessed in three reports--the Environmental Assessment (EA), the Site Characterization Plan (SCP), and the Safety Analysis Report (SAR)--to be prepared for each site. One task of this program will include general assistance in the preparation of these reports. The other four tasks will involve the use of computer simulation to 1) provide a better understanding of the long-term geologic and hydrologic phenomena important at the various salt sites and 2) provide guidance to ongoing site characterization efforts by defining additional data needs.

The sites under consideration include:

1) Deaf Smith County and 2) Swisher County, both in the Palo Duro Basin in northern Texas; 3) Davis Canyon and 4) Lavender Canyon, both in Gibson Dome in Utah; 5) Richton Dome and 6) Cyprus Dome, both in Mississippi; and 7) Vacherie Dome in Louisiana. Our computer modeling efforts in FY 1984 focus on the two sites at the Palo Duro Basin in Texas. Future activities will focus on the Utah and Gulf Coast sites.

During the reporting period, environmental assessment contributions were completed for each of the seven sites. In addition, a topical report (Petrie 1984) was drafted that addresses the potential for future climatic events to affect the integrity of a repository located at each site.

Investigations regarding long-term geologic and hydrologic processes at the Palo Duro sites were initiated through 1) preliminary development of a Geologic Simulation Model for the region and 2) preliminary regional modeling of the basin hydrology.

Progress in the area of sensitivity/uncertainty analysis included testing of initial changes made by ONWI in a performance assessment code.

Technical progress for the first half of FY 1984 is discussed here under the four topics: 1) environmental assessment contributions, 2) geologic simulation, 3) computer simulation of flow and transport processes, and 4) test and demonstration of adjoint-analysis upgrade.

Environmental Assessment Contributions

We provided ONWI with input for three sections--climate, tectonics, and erosion--of their Environmental Assessment for each site. A topical report was drafted that

focuses on the climate at each site; specifically, it addresses the potential for future (i.e., within the next 10,000 years) climatic events to affect the integrity of a repository located at the site. The report assesses what effect a new glacial period would have on isolation at each site.

Geologic Simulation

A Geologic Simulation Model (GSM) will be developed under this program for each site, to aid in evaluating geologic factors that could affect the integrity of a salt-site repository. An important advantage to computer simulation of geologic changes is the capability to account for interactions among disruptive phenomena and their cumulative effect on ground-water flow. Geologic factors to be accounted for in the model include climate, tectonics, salt dissolution, and geomorphology.

Preliminary development of the GSM for the Palo Duro Basin was accomplished in the first half of FY 1984. In this first version of the Palo Duro GSM, a representative cross-section of the region is being used. Figure 3.8 shows the cross-section and its location with respect to the study area. In the GSM the cross-section will be represented by a finite-element grid, shown in Figure 3.9. Characteristics of each finite element (e.g., permeability, node locations) will vary with time as a function of geologic changes. At each time step a steady-state solution will be found for ground-water flow using a finite element solution. During important geologic events, marker particles will be released from the repository and moved according to ground-water velocities calculated for the time step. In this way the paths and final destinations of repository releases can be tracked,

and the effect of geologic events on their travel paths can be estimated.

The GSM will simulate the following geologic phenomena:

- Tectonic events/salt movements. Two types of tectonic events are modeled: general uplift or subsidence, and localized faulting. General uplift/subsidence is handled by changing the elevation of all nodes in the finite element grid. Local faulting is accounted for by the creation of a new set of narrow elements with appropriate permeability values. The permeability of some of the narrow elements will change with time to reflect the movement of salt "healing" the fault rupture.
- Geomorphic processes. Only deposition and erosion are included in this version of the GSM. Each process is accounted for by changing the elevation of surface nodes in the affected area.
- Salt dissolution. Salt dissolution will be simulated by changing the position of the nodes associated with the moving dissolution front. Lateral erosion of the escarpment, resulting from collapse into the new salt cavities, will be accounted for by changing the positions of appropriate nodes.
- Climate. The GSM predicts potential future climatic states for the North American continent based on the effect of the earth's orbital variations, on the latitudinal distribution of insolation, and on random, superimposed perturbations of insolation related primarily to volcanic ash loading of the atmosphere. On the time scale of the model runs, surface insolation is assumed to dominate the other natural variables driving the temporal variations in the North American climate.

FIGURE 3.8. East-West Cross-Section of Major Depositional Systems in Palo Duro Basin (after Stone and Webster Engineering Corp. 1983)

FIGURE 3.9. GSM Finite-Element Grid

Computer Simulation of Flow and Transport Processes

Our main objective in the Palo Duro computer simulation is to better understand the flow and transport processes in the immediate vicinity of each of the two proposed repository locations, within Deaf Smith County and Swisher County (i.e., through "near-field modeling"). This will improve our understanding of the so-called "disturbed zone" and the important phenomena affecting it.

To obtain the boundary conditions for our local, or county-size, modeling, however, we must simulate a larger area (i.e., perform "regional modeling"). Figure 3.10 shows the study area that we have selected for our regional modeling as well as the finite-element grid that was used for our initial simulations. The figure locates the two proposed repository sites.

The computer codes that we are using to simulate flow and transport processes are the FE3DGW (Finite-Element, 3-Dimensional, Ground-Water) code and the CFEST (Coupled

Flow, Energy, and Solute Transport) code. Both are three-dimensional, saturated-flow computer models.

In the first half of FY 1984, work focused on updating our formation-surface data base, which is an important source of input data for the FE3DGW and CFEST simulations. The data describe the surface (with respect to mean sea level) of each geologic formation in the study area. These data were obtained from two sources: 1) isopach (formation-thickness) contours contained in the literature and 2) well logs compiled by Stone and Webster Engineering Corporation. Data gaps for each formation were filled in by kriging the available data.

Kriging is a statistically based interpolator of irregularly spaced data. Thus it provides an estimate of surface elevations in locations where data are unavailable. In addition, it provides an estimate of the uncertainty associated with the formation-elevation estimate for each node point. Figure 3.11 shows the thickness of one formation found in the study area, as calculated from our updated data base.

FIGURE 3.10. Regional Model Study Area

Initial FE3DGW simulations of the regional model were also completed in the first half of FY 1984. We are presently refining the model grid and making adjustments in hydraulic conductivity distributions to obtain a better match with available potentiometric data.

Test and Demonstration of Adjoint-Analysis Upgrade

This task will support ONWI's efforts to address sensitivity and uncertainty questions regarding performance assessment results. Sensitivity/uncertainty analysis includes parameter uncertainty (defining error bars around the values selected for each parameter), model sensitivity (defining the effect of a change in model input on model output), and model-output uncertainty (defining the uncertainty in model predictions of variables such as travel time or radionuclide flux).

ONWI is upgrading the CFEST (Coupled Flow, Energy, and Solute Transport) code, one of the hydrologic performance assessment codes, to include the capability to perform adjoint analysis. This capability will allow the code to be used to estimate both parameter uncertainty (i.e., by performing a stochastic inverse) and model sensitivity. Defining the model sensitivity (the effect of a change in model input on model output) will significantly streamline the effort involved in calibrating the model to known data.

This task is to check, test, and demonstrate the use of the CFEST enhancement using our data for the Palo Duro Basin. The CFEST code was modified by ONWI during the first half of FY 1984 to include the capability to calculate adjoints. The initial changes were then checked by PNL. Additional modifications for developing a full adjoint inverse are under way.

FIGURE 3.11. Smoothed Thickness of Ogallala Formation

Reference

Stone and Webster Engineering Corporation.
1983. Area Geological Characterization
Report for the Palo Duro and Dalhart
Basins, Texas. DOE/CH/10140-1, prepared
for Office of Civilian Radioactive Waste
Management, U.S. Department of Energy,
Washington, D.C., Figure 4-6, p. 201.

3.1.4 Disequilibrium Dating Salt Geologies (AP-05-15-15 - TD1792)

J. C. Laul - Program Manager

The objective of this program is to establish migration rates of natural uranium and its chain member radionuclides based on their equilibrium/disequilibrium ratios at working depth intervals in ground waters and cores of salt dome sites that are being considered as potential high-level nuclear waste repositories.

Summary

The following are some conclusions from this work:

- Retardation factors of the various radionuclides relative to radium in the ^{238}U and ^{232}Th chains are extremely high (from 20 to 10^4), which means that the long-lived radionuclides of thorium and uranium are not very soluble in brine water. Sorption and desorption appear to be important mechanisms in explaining the observed distribution between dissolved and attached phases.
- Based on the noted enrichment of $^{234}\text{U}/^{238}\text{U}$, the brine waters from the Sawyer well, Mansfield well and J. Friemel well, are one million years old or more.
- The activity ratio of $^{234}\text{U}/^{230}\text{Th}$ is nearly unity in all zones, indicating that ^{234}U , like ^{232}Th , is in the +4 state instead of the +6 state. The +4 state of uranium suggests a reducing environment in the system.

- Concentrations of these radionuclides are extremely low and far below their solubility limits. Carbonate and dolomite zones are more effective in retaining radionuclides than is the granite wash zone.

Technical Progress - M. R. Smith,
P. O. Jackson, C. W. Thomas, and
D. M. Robertson

The following samples were collected from Zone 6 (7300 to 7326 ft) and Zone 7 (5825 to 5926 ft) of J. Friemel well No. 1, Amarillo, Texas. Tracer level was below detection limit, and brine water was quite clean. There was no precipitation during collection, waiting period, and pumping of brine water. Large swimming pool filters were used, and filtered brine water was pumped through an 8-in. large-volume sampler.

Details are as follows:

1. Sixty gallons of brine water were pumped through 8-in.-dia filters (six 0.30- μm filters operated in parallel) and two 1/4-in.-thick $\text{Al}_2\text{O}_3\text{-BaSO}_4$ adsorption beds (8-in.-dia). Radioactive tracers (^{233}U , ^{133}Ba , ^{234}Th and ^{232}Th) were added before pumping. The outflow rate was 1 to 2 gal/min.
2. To check precision of the data, Step 1 was repeated with the first sample. Again 60 gal of brine water were pumped through 8-in. 0.3- μm filters and two 1/4-in.-thick $\text{Al}_2\text{O}_3\text{-BaSO}_4$ adsorption beds. Tracers were added.
3. Next 300 gal of brine water were pumped through a large swimming pool filter which was connected to 8-in.-dia filters (six 0.30- μm filters) and two 1/4-in. Al_2O_3 beds and two 1/4-in. $\text{Al}_2\text{O}_3\text{-BaSO}_4$ beds (8 in.). The purpose of this experiment was to hold uranium and thorium

radionuclides on the Al_2O_3 - BaSO_4 beds.

No tracers were added.

In addition, 10 gal each of filtered ($0.3\ \mu\text{m}$) and unfiltered waters were collected, and both waters were acidified with HCl , for the analysis of radionuclides.

The adsorption beds from both zones were dried and counted in an 80-g can (about 30% of the total adsorption bed) on a low-energy photon detector (LEPD). We could measure only ^{226}Ra , ^{224}Ra , and ^{228}Ra isotopes instrumentally. As in the past, the rest of the radionuclides, such as ^{238}U , ^{235}U , ^{234}U , ^{232}Th , ^{234}Th , ^{230}Th , ^{210}Pb , ^{210}Bi and ^{210}Po , are too low to be measured instrumentally even in the Al_2O_3 beds with the larger samples. These radionuclides from Zone 6 have been measured through chemical separations from two 4-L aliquots taken from the 5-gal jerry cans. These radionuclides from Zone 7 are now being measured.

3.2 BASALT WASTE ISOLATION PROJECT (BWIP)

3.2.1 Hydrologic Working Group

(DB-30-10-01 - 80750)

D. A. Zimmerman - Program Manager

This effort supports a variety of activities each of which contributes important knowledge about the greater Pasco Basin ground-water flow system. Previously known as the "Modeling Task Force" because of its focus on the development of the Expanded Pasco Basin Ground-Water Model, the Working Group's primary goal is to contribute to the characterization of the ground-water flow system of the Pasco Basin. Two major objectives resulting from this goal are: 1) to further the development of the Expanded Pasco Basin Ground-Water model and 2) to establish a potentiometric baseline suitable for regional numerical modeling and a "near-field" potentiometric baseline in the vicinity of the reference repository location prior to the start of the large-scale pump tests. The Working Group is comprised of representatives from the USGS, RHO, and PNL.

Overview

In October the Hydrologic Working Group changed the focus of its overall objective from resolving differences between numerical models to that of developing an understanding of the ground-water flow system of the Pasco Basin. This requires knowledge of both the current state of the ground-water system and how the system is changing with time. The numerical modeling effort is designed to determine the general ground-water flow patterns on a regional scale and to provide important information for interpreting data and characterizing the flow system in the vicinity of the reference repository location. The potentiometric baselining effort is designed to establish a consensus defining the past, current, and possible future states of the ground-water flow system for the regional and local areas of interest with respect to the interpreted potentiometric surfaces for each geologic formation. This knowledge is essential for calibrating the regional model and is required in order to properly analyze the data from the large-scale aquifer tests. The results from the large-scale aquifer tests will support characterization of the local flow system around the reference repository location.

Technical Progress

In support of the modeling effort, the following activities are ongoing: the Expanded Pasco Basin Groundwater Model has been implemented on the VAX computer system using the new U.S. Geological Survey's (USGS) modular finite-difference ground-water flow code. Soil property data (water-holding capacity and depth) obtained from the Soil Conservation Service (SCS) has been

transformed to digital form in support of new recharge calculations. About 20% of the model area has not been surveyed by the SCS; soil property data in these areas is being synthetically generated by matching the soil classifications to the variables that directly influence the soil's water-holding capacity. These variables include elevation, slope, aspect, vegetative cover, and rainfall, all of which are available in the unsurveyed areas. Figure 3.12 shows the current status of the color-coded soil-classification distribution map for the greater Pasco Basin. Stratigraphic maps (Myers et al. 1979) for major geologic formations within the greater Pasco Basin have been digitized, and a computer code for displaying the stratigraphy has been developed. The code will be used to visually check the correctness of the structural geometry used in the ground-water model. This method of displaying model input data is shown in Figure 3.13.

In support of the potentiometric baselining task, a set of maps was prepared showing water-level changes for the unconfined aquifer on the Hanford Site from 1950 to 1975. These maps provide a way to track the aquifer's response to changes in waste-disposal practices that have occurred. Water-level measurements from boreholes drilled into basalt by BWIP, those measured by PNL for the Hanford's alluvial aquifer, and those measured by the USGS across the model region have been compiled into a single data base. Currently, these data are being plotted by formation and time interval so that contoured potentiometric surfaces can be generated and areas requiring more data can be identified.

Kriging is also being used as a tool to augment the interpretation process and for identifying sites where adequate information

is lacking. Many boreholes registered in the USGS data base have no geologic identification. For these boreholes, the revised structural maps of the major formations are being used to determine which formations these boreholes penetrate so that additional candidate monitoring points can be identified. A field data review of the techniques used during drilling and testing is being undertaken to evaluate the applicability of the data and interpretations and to determine the limitations on use of the reported data values. This work is focusing on what effect variable-temperature, variable-density fluids have on the observed heads.

Future Activities

On completion of the soil-property aggregation task, the USGS recharge code will be run and the runoff portion of the model will be calibrated using data from subbasins within the model area. Computer runs will then be made to identify the "nominal" base case data set which will serve as a starting point for the planned sensitivity runs. Interpretation of head data will continue, and specific sites for additional monitoring wells will be identified. The feasibility of using the method of adjoints in connection with the analysis and interpretation of the large-scale pump tests will be investigated. LANDSAT multi-spectral scanner data for 1983 will be used to determine the amount and distribution of irrigated crop land for the model region.

Reference

- Myers, C. W., et al. 1979. Geologic Studies of the Columbia Plateau--A Status Report. RHO-BWI-ST-4, Rockwell Hanford Operations, Richland, Washington.

84C217

FIGURE 3.12. Current Status of Color-Coded Soil Classifications for the Greater Pasco Basin

FIGURE 3.13. Three-Dimensional Plot of Stratigraphy Underlying Hanford Illustrates Method for Displaying Spatial Data

3.2.2 Development of the pH Sensor and Reference Electrode

(DB-30-10-01 - 80752)

M. J. Danielson - Program Manager

O. H. Koski - Major Contributor

The objective of this task for FY 1984 is to develop a pH sensor and reference electrode compatible with the Dickson rocking autoclave that will provide, by fiscal year end, Eh-pH monitoring capabilities for the hydrothermal waste-barrier-rock interaction studies up to 300°C and 300 bars. The Eh monitor was completed in FY 1983.

Summary

Significant improvements have been made in construction and operation of the pH sensors. The pH electrodes are found to give

good pH response from 100 to 300°C, but only after they are "seasoned" at 300°C.

Several designs for an improved reference electrode have been developed. Evaluation will begin in the second half of the fiscal year.

pH Sensor

The pH is the most important variable in water chemistry. This program is to develop pH sensors suitable for use in the Dickson rocking autoclave at temperatures to 300°C and 300 bars pressure.

An improved mechanical/electrical sealing system for the pH electrode is shown in Figure 3.14. The electrical termination is moved away from the pressure seal to prevent

FIGURE 3.14. PNL pH Electrode

any solution leaks from shunting the electrical signal. Several internal reference fills have been examined (silver, gold, copper/copper dioxide), but all are revers-

ible to oxygen once the sensor is "seasoned." Excellent pH response is found from 100 to 300°C. Reversibility to oxygen is extremely important since it greatly simplifies calibration. The pH can be estimated by comparing the measured potential to that predicted from a table of thermodynamic data. One area of difficulty deals with making the sensors reversible to oxygen. The tubes require "seasoning" at 300°C for 24 to 48 hr before becoming reversible to oxygen, but then the sensors can be used at temperatures as low as 100°C. Storage at ambient conditions results in the tubes losing their reversible response to oxygen after a few days so that another 300°C treatment is needed.

Reference Electrode

Both pH and Eh electrodes require a stable reference electrode. All previous high-temperature reference electrode designs have leaked electrolyte excessively into the outside environment. Due to the small volume of the gold bag in the Dickson rocking autoclave, this leakage would seriously contaminate the rock-water interaction experiment. An example of a low-leakage reference electrode is shown in Figure 3.15.

FIGURE 3.15. PNL Micro-Porous Reference Electrode

3.2.3 Hydrothermal Materials Testing in the 325 Building Hot Cell Test Facility (DB-30-10-01 - 80752)

D. G. Coles - Program Manager

The objectives of the hydrothermal waste barrier-rock interactions studies are two-fold. The first is to acquire the necessary data for quantifying the performance of

waste package components, both individually and together, in an environment appropriate to a repository located in basalt. The second is to evaluate and integrate these site specific data with the BWIP waste package design effort. Testing with fully radioactive waste forms can be accomplished only in a hot-cell facility.

Background

The Pacific Northwest Laboratory (PNL) and Westinghouse Hanford Company (WHC), under the direction of the Basalt Waste Isolation Project (BWIP), are conducting hydrothermal testing of waste barrier-rock interactions using both tracer and fully radioactive waste forms. This project utilizes an existing PNL hydrothermal testing facility (Bldg. 325, Lab 48) for evaluating tracer-doped waste forms and a new BWIP-funded facility (Bldg. 325, Lab 201) that WHC built for testing fully radioactive waste forms. PNL has the lead responsibility for operating the tracer-testing facility while WHC has the lead responsibility for operating the fully radioactive testing facility. Staff for both organizations work together in either facility. PNL and BWIP plan the testing and PNL is responsible for the initial interpretation of all data from both facilities. WHC is responsible for the analysis of both the fluid and solid samples obtained from all tests. This team approach to conducting a large and complicated testing effort allows the skills and facilities from each organization to be efficiently applied to a common task.

Summary

The initial tests were performed in the tracer-testing facility and included a ^{237}Np , ^{239}Pu -doped glass waste form. These tests were previously described by Coles

(1983). Their purpose was twofold. They provided experience in the hydrothermal testing of radioactive waste forms, including the analysis of the fluid and solid samples. They also yielded important baseline data on the behavior of neptunium and plutonium under basalt-repository hydrothermal conditions for comparison to later tracer and fully radioactive tests.

The radiochemical solution analysis data obtained from the initial tests on the neptunium and plutonium-doped glasses are presented. A chemical, physical and mineralogical analysis of the post-run solids is not yet available so that a complete interpretation of the test results cannot be made at this time. In addition, further related tests, not yet concluded, will also contribute to an understanding of the variables investigated.

Essentially, the preliminary conclusion from this work is that neptunium and plutonium show higher concentrations when basalt is present compared to the test with no basalt present. In addition, a significant filtration effect was observed, indicating that neptunium and plutonium are associated mostly with filterable particulates and colloids rather than being in true solution. The increase in the amounts of neptunium and plutonium in solution was about a factor of ten.

Effect of Basalt on Release of ^{237}Np and ^{239}Pu from Borosilicate Glass Under Hydrothermal Conditions

The basalt sample used in these tests was a reference BWIP sample obtained from an outcrop of the Umtanum flow in the entablature section of that flow. Its preparation for testing has been described by Myers

et al. (1983). Although that report states that RUE-1 reference basalt, -60 to +115 mesh fraction, was used exclusively in the hydrothermal testing program, the following material was used in our testing activities. The basalt (designated RUE-2) was crushed and then was sieved to less than 120 and greater than 230 mesh (125 and 62 μm , respectively). The preparation of the synthetic basalt ground water used in these tests has been described previously by Jones (1982) and Myers et al. (1983). A ^{237}Np , ^{239}Pu -doped glass sample with a PNL 76-68 composition was used. This glass was chosen for study because it is readily available, it has been previously characterized, and its composition has been extensively studied by many laboratories.

Because only a limited amount of the doped-glass sample was available, and it contained more than a sufficient amount of activity, the glass was mixed with about the same weight of undoped MCC 76-68 glass. The undoped glass was obtained as a monolith which was crushed, sieved, and cleaned in a manner identical to the doped glass. The mixed glasses were then thoroughly blended by gently inverting their containers. The proportions of the two glasses in these final samples were 50.0% cold glass and 50.0% Np , Pu -doped glass. Major element compositions were very similar for the tracer glass and the MCC glass.

The general BWIP philosophy for defining the parameters used in these tests has been described by Myers et al. (1983). All tests were conducted under hydrothermal conditions using crushed glass and crushed basalt and synthetic basalt ground water. The common

(a) Value at start of test. Reduced as run progressed due to periodic withdrawal of fluid samples.

experimental parameters used for the experiments are as follows: temperature, 200°C; pressure, 30 MPa; solution-to-solid ratio (by weight), 10 to 1;^(a) run duration, 3 months.

The 200°C temperature relates to repository conditions early in its history, but waste-package breaching is more likely to occur after the temperature has decreased. However, reactions are sufficiently slow at lower temperatures that only limited fluid changes would occur over the short duration of these tests. The 200°C temperature constitutes reasonable acceleration conditions for the reactions so that fluid changes and reaction products can be observed and measured within a 3-month test. Testing under accelerated conditions has been discussed in more detail by Myers et al. (1983), Apted and Myers (1983), and Coles and Apted (1983).

The testing matrix was simply a hydrothermal test of ^{237}Np , ^{239}Pu -doped glass with and without basalt present. The objectives of these tests were to assess the effect that basalt had on the steady-state fluid concentration of each tracer, as well as overall fluid composition, and to assess its effect on the formation of secondary minerals and the dissolution behavior of the glass. These tests were designed to provide baseline data on tracer solubility and secondary mineral formation for comparison to subsequent tests that included canister material and tests that included fully radioactive waste-forms where radiolysis of the solution was expected.

Dickson rocking autoclaves were used in this study. Their operation and the analytical procedures used for both fluid and solid samples have been described by Myers et al. (1983).

Samples were collected in plastic syringes and moved immediately into an argon-atmosphere box where the pH was measured. Samples were then filtered and split. Radiochemical analysis provided the ^{237}Np and ^{239}Pu data. Figure 3.16 shows the concentration of ^{237}Np from glass reacted with only synthetic ground water. The fluid concentrations for the unfiltered, 4000-Å filtered, and 18-Å filtered samples are shown. The ^{237}Np rose to about 0.05 mg/L at the beginning of the test. No 18-Å filtered fluid was analyzed until about 800 hr of run time had elapsed. At about 300 hr run time, an apparent steady-state solution concentration was reached and, with some fluctuations, the concentration remained at ~0.002 mg/L throughout the remainder of the test. When analyzed, the 18-Å filtered solution was at or below the detection limit of about 7×10^{-4} mg/L. This indicates that colloids probably accounted for the bulk of

FIGURE 3.16. Concentration of ^{237}Np from Run B-48-03 (glass only) 200°C, 30 MPa. Filtration effect.

the neptunium in the fluid. The fluid seems to have stabilized with respect to neptunium early in the test.

Figure 3.17 shows the effect of adding basalt to the glass. The filtration effect was much more pronounced, which indicates that little neptunium was in true solution and that it was associated mostly with filterable particles and some colloids. Figure 3.18 illustrates the 4000-Å filtered solution ^{237}Np concentrations for the glass only and glass plus basalt test. It can be observed that basalt tended to increase the amount of neptunium in the fluid. Figure 3.19 presents the plutonium concentration data from glass reacted with synthetic ground water. The unfiltered fluid shows a plutonium concentration higher than the 4000-Å filtered and 18-Å filtered fluids for the duration of the test.

FIGURE 3.17. Concentration of ^{237}Np from Run B-48-04 (glass + basalt) 200°C, 30 MPa. Filtration effect.

FIGURE 3.18. Comparison of ^{237}Np Concentrations from Runs B-48-03 (glass only) and B-48-04 (glass + basalt) 200°C, 30 MPa. 4000-Å filtered fluids.

FIGURE 3.19. Concentration of ^{239}Pu from Run B-48-03 (glass only) 200°C, 30 MPa. Filtration effect.

Very early in the test, colloidal plutonium appears to have increased and then decreased. No 18-Å filtered samples were analyzed for plutonium during this period. When the 18-Å fluids were analyzed, plutonium, like neptunium, was at or below the detection limit, indicating that very little plutonium existed in true solution. The fluid appears to have been dominated by particulate and, to a lesser extent, colloiddally associated plutonium. Figure 3.20 shows that when basalt was added, the filtration effect on plutonium concentration in solution became dramatic. Little or no plutonium existed in the true solution, at least 100 times more plutonium existed as a colloid, and nearly ten times more than that was associated with particulate material. The final (quenched) 4000-Å filtered sample shows that plutonium content decreased while the unfiltered, quenched sample increased in

FIGURE 3.20. Concentration of ^{239}Pu from Run B-48-04 (glass + basalt) 200°C, 30 MPa. Filtration effect.

plutonium content, indicating that quenching promoted the formation of even more plutonium-bearing particulates.

Figure 3.21 illustrates the plutonium concentrations in the 4000-Å filtered solutions from the glass-only and glass-plus-basalt tests. As was the case for neptunium, basalt increased the amount of the colloiddally associated plutonium, which effectively increased plutonium in the fluid by an order of magnitude in contrast to glass reacted alone.

Figure 3.22 sums the observations for the behavior of actinides released from glass with and without basalt present. In both cases, the presence of basalt increased the amount of actinides in the fluid by about an order of magnitude. Neptunium was about an order of magnitude higher in concentration than plutonium. However, neptunium was also an order of magnitude higher in the glass sample (i.e., 2.0 mg $^{237}\text{Np/g}$ glass and

FIGURE 3.21. Comparison of ^{239}Pu Concentrations from Runs B-48-03 (glass only) and B-48-04 (glass + basalt) 200°C, 30 MPa. 4000-Å filtered fluids.

FIGURE 3.22. Fluid Concentrations for Both ^{237}Np and ^{239}Pu from Runs B-48-03 (glass only) and B-48-04 (glass + basalt) Comparing Concentrations of Both Actinides. 200°C, 30 MPa. 4000-Å filtered fluids.

0.2 mg ^{239}Pu /g glass), so that the difference in the fluid may reflect the glass composition. This may indicate that the actinides were released from the glass by glass dissolution and that once released, they immediately became associated with particulates and colloids. These fluid concentration values cannot be cited as indicative of solution solubility because the formation of solubility-limiting phases has not been observed.

The analyses of the solid material sampled at the end of runs B-48-03 and B-48-04 have not been completed, so that the interpretation of the test results is limited to the fluid data. Any conclusions from the data on fluids must be considered provisional until the data are available from analyses of solids.

In summary, the preliminary conclusion is that neptunium and plutonium show higher concentrations when basalt is present compared to the test with no basalt present. In addition, a significant filtration effect was observed, indicating that neptunium and plutonium are associated mostly with filterable particulates and colloids rather than being in true solution. The increase in the amounts of neptunium and plutonium in solution was by about a factor of ten.

Future Activities

During the latter half of FY 1984, and beyond, another series of tracer tests using the Laboratory 48 facility will be started. These tests will include an investigation of the effect of varying ratios of solids; 1-year-duration tests; tests parallel to hot-cell tests to assess the effects of radiolysis; tests with stepwise decreases in temperature to assess the rate at which the fluid composition changes to a new steady-state value; tests with methane to assess the effect methane has on fluid chemistry; tests with monoliths of solids to assess surface reactions; tests at low temperatures (100 to 150°C) in 125-cc Ti Parr bombs using a roller oven will be compared to parallel tests in rocking autoclaves to assess whether Parr bombs, sequentially sacrificed, will give the same fluid data as the rocking vessels at low temperature, thus potentially expanding our experimental capability for low temperatures; tests with magnetite instead of basalt to assess the effect that the reaction of magnetite to hematite has on Eh and, if steel alters to magnetite, use this material as an "aged-canister" or accelerated test method; undoped glass plus package materials will be reacted with solutions containing excess radiotracers in

order to approach solid-state solution concentration values from the saturated direction instead of the undersaturated direction. Although other tests will be conducted in the tracer facility, those enumerated are currently planned.

The fully-radioactive testing began in early FY 1984. Further tests are being planned, but many will parallel the tracer experiments to assess the effect of radiolysis. Others will include actual spent fuel. Unfortunately, little parallel testing can be done on spent fuel because its complex composition makes it difficult to simulate in tracer-level formulations.

The tests described here are intended to provide data relevant to choosing a design for a waste package in a basalt repository. The aim is to understand the effects that various parameters and waste-package components have on the solubility of key radionuclides under repository-simulated conditions and to obtain data valuable to the various BWIP modeling efforts for predicting the long-term behavior and radionuclide release rates from a waste package located in a basalt repository. The experimental program is designed for flexibility to accommodate the needs of the BWIP as it evolves and to adjust experimental directions as the nature of waste-package components and rock interactions, under hydrothermal conditions, are better understood.

References

- Apted, M. J., and J. Myers. 1983. Comparison of the Hydrothermal Stability of Simulated Spent Fuel and Borosilicate Glass in a Basaltic Environment. RHO-BW-ST-38 P, Rockwell Hanford Operations, Richland, Washington.

Coles, D. G. 1983. The Effect of Basalt on the Release of ^{99}Tc , ^{237}Np , and ^{239}Pu from Borosilicate Glass Under Hydrothermal Conditions. SD-BWI-TI-190, Rockwell Hanford Operations, Richland, Washington.

Coles, D. G., and M. J. Apted. 1983. Description of the Experimental Approach and Procedures Used by the Basalt Waste Isolation Project in Conducting Hydrothermal Tests on ^{99}Tc -Doped Borosilicate Glass. SD-BWI-TI-127, Rockwell Hanford Operations, Richland, Washington.

Coles, D. G., and M. J. Apted. 1983. "The Behavior of ^{99}Tc in Doped-Glass/Basalt Hydrothermal Interaction Tests." PNL-SA-11456 (Pacific Northwest Laboratory Report) and RHO-BW-SA-3190 (Rockwell Hanford Operations Report). To be published in the Proceedings of the November 1983 Materials Research Society Symposium D, Scientific Basis for Nuclear Waste Management VII, edited by G. L. McVay.

Jones, T. E. 1982. Reference Material Chemistry, Synthetic Groundwater Formation. RHO-BW-ST-37 P, Rockwell Hanford Operations, Richland, Washington.

Myers, J., et al. 1983. Hydrothermal Reaction of Simulated Waste Forms with Barrier Materials Under Conditions Expected in a Nuclear Waste Repository in Basalt. SD-BW-TI-141, Rockwell Hanford Operations, Richland, Washington.

3.2.4 Radiation Effects

(DB-30-10-01 - 80752)

G. L. McVay - Program Manager

The objective of this research is to investigate the interaction of ionizing radiation with the near-field environment of the waste package throughout the period of geologic isolation in Columbia River basalt.

Summary

Gamma radiolysis of basalt ground water containing methane causes the methane to be partially converted to hydrogen and higher molecular weight hydrocarbons, most notably

a polyethylene-like substance that occurs as a milky-looking suspension of fine particles in the water.

Radiolysis of Basalt Ground Water Containing Methane

Grande Ronde basalt ground water samples containing about 700 ppm methane have been gamma-irradiated at 65° and 150°C to doses between 37 and 380 Mrad at dose rates in the range of 0.023 to 5.3 Mrad/hr. The radiolytic products generated have not varied appreciably. In general, the methane is partially converted to hydrogen and higher hydrocarbons, most notably a polyethylene-like substance that occurs as a milky-looking suspension of fine particles in the water. The colors of these suspensions have varied from nearly white through pale yellow to orange. Molecular weights of all polymer samples measured ranged from around 100 to nearly 50,000 and averaged from 2000 to 3000. Their molecular structure is characterized as primarily a highly branched aliphatic hydrocarbon although they do contain 1 to 5% oxygen which IR spectroscopy reveals to be alcoholic or carbonyl.

A few samples have been irradiated with basalt, bentonite or iron present. Experimental difficulties have hampered interpretation of results, but effects of these waste package materials do not appear to be large. Additional testing is required to determine whether the basalt and bentonite have much effect other than to sorb some of the intermediate-weight hydrocarbons.

Since most of the irradiation tests were conducted with both gas and liquid phases present, the question arose as to whether the observed reaction took place predomi-

nantly in the gas or the liquid phase. A few tests performed with only the gas phase present showed it to be the liquid.

Alpha-radiolysis experiments using ^{238}Pu have been started on Grande Ronde basalt ground water and on deionized water, both containing about 700 ppm methane. Aside from the observation that the total gas pressure remains essentially constant during irradiation, just as in gamma-radiolysis, there are no results to report yet.

Computer modeling efforts have consisted of setting up two codes, MAKSIM and RADIOL, and running a few test cases. Conversion of the appropriate fraction of the methane into hydrogen and higher hydrocarbons was successfully modeled. However, there was no provision in the model to account for the very high-molecular-weight polymers. Therefore, the hydrocarbons in the model were all of the intermediate-weight kind, which, of course, does not correspond to experiment. One might put the high-molecular-weight polymers in the model by using guesses for rate constants, but the chances of successfully modeling molecular structure and how it might change with conditions seem remote. Modeling efforts, therefore, have been curtailed in favor of a more extensive experimental program.

3.2.5 Structural Barrier Materials (DB-30-10-01 - 80752)

R. E. Westerman - Program Manager

The Structural Barrier Materials Task has as its objective the characterization and recommendation of metallic materials for use as structural barrier components in high-level nuclear waste packages for a Hanford basalt repository medium.

Summary

The Structural Barrier Materials Study being performed at PNL for the Basalt Waste Isolation Project has as its objective the characterization and recommendation of metallic materials that have the ability to contain nuclear waste for time periods of 300 to 1000 years in a repository constructed in basalt. During this period the package materials will be subjected to corrosion by the elevated-temperature ground waters that have been modified by radiation emanating from the waste contained within the packages.

Material degradation by means of general (uniform) corrosion was determined in autoclave studies with and without the imposition of gamma irradiation. The corrosion rates of iron-base alloys were increased by

the presence of 3×10^5 rad/hr irradiation under the 250°C test conditions, and the corrosion rates of the materials increased at 150°C compared to 250°C under unirradiated conditions. Cast low-alloy steel containing a small amount (2-1/2%) of chromium demonstrated the best resistance to corrosion. All ferrous materials showed some degree of nonuniform attack by the end of the tests (20 months maximum).

General Corrosion

The corrosion rates of six candidate iron-base materials have been determined in synthetic Grande Ronde Basalt ground water at 250°C for time periods up to 20 months. The corrosion rates of five of the materials are plotted in Figure 3.23. The sixth material, 9% Cr-1% Mo steel, was under test for

FIGURE 3.23. Corrosion of Iron-Base Alloys Exposed to Synthetic Grande Ronde Basalt Ground Water at 250°C

only one exposure period, 5 months, and the data from the ten specimens analyzed were not plotted on the figure in order to keep the presentation as simple as possible. (They exhibited corrosion rates similar to the 1020 wrought steel specimens.) Data from the five materials exposed at 150°C are plotted in Figure 3.24. In both figures the bulk of the data is enclosed in cross-hatched scatter bands for ease of visualization of overall magnitudes and trends.

The corrosion rates observed at 250°C (Figure 3.23) showed a sharp decrease after a 1-month exposure. From 3 months to 12 months the corrosion rates were reasonably uniform among the materials tested, and the corrosion rates observed were low, i.e., $<8 \mu\text{m/yr}$ ($<0.3 \text{ mil/yr}$). Also, there was little sign of nonuniform attack, such as pitting corrosion. Between 12 and

17 months, however, pitting attack became evident, notably on specimens of the normally well-behaved 1-1/4% Cr-1/2% Mo material. The pits were numerous on these specimens, averaging 1 to 2/cm², and were nonuniformly distributed over the specimen surfaces. They were typically 50-100 μm (2-4 mil) deep, and 500-1000 μm (20-40 mil) in diameter, though the size variation was great. A similar phenomenon was observed at 17 and 20 months exposure in the 150°C test (Figure 3.24), in that all specimens showed significant evidence of nonuniform attack, manifesting itself primarily in formation of arrays of shallow pits. Prior to this observation, four other specimens had shown evidence of pitting attack at 150°C: three 1020 wrought steel specimens, after exposures of 2 to 5 months, and a 1-1/4% Cr-1/2% Mo specimen after 12 months exposure.

FIGURE 3.24. Corrosion of Iron-Base Alloys Exposed to Synthetic Grande Ronde Basalt Ground Water at 150°C

The corrosion rates observed at 150°C were somewhat higher, in general, than those observed at 250°C. Interestingly, at 20 months specimens exposed to 150°C water showed much more evidence of pitting attack than specimens exposed at 250°C. Obviously, susceptibility of the candidate alloys to pitting attack is of much greater concern at this time than the modest penetration rates associated with general corrosion.

If this concern about pitting attack can be put aside, the corrosion data presented in Figures 3.23 and 3.24 suggest that ferrous materials offer promise as waste package structural barrier elements in a repository constructed in basalt for time periods up to 1000 years. It should be pointed out that the present experiments were performed at much higher oxygen (dissolved oxygen in ground water) levels than those anticipated in the repository. Of course, possible effects of radiation and the possible interaction of environmental and mechanical stresses, as in stress corrosion cracking, are not addressed in these nonirradiated general corrosion test results.

Irradiation-Corrosion

The corrosion rates of four candidate iron-base materials have been determined in 250°C synthetic Grande Ronde basalt ground water at an irradiation intensity of 3×10^5 rad/hr. The rates obtained are plotted in Figure 3.25 based on a linear kinetics assumption. Presently available data obtained from the nonirradiated tests performed in an otherwise equivalent environment are included for comparison. In general, irradiation appears to enhance the corrosion rate somewhat, compared to the unirradiated situation. However, the amount

of scatter in the data and the presence of nonuniform attack make quantitative comparison difficult. The irradiated-system corrosion rates show an increase progressing from the 1-month to the 3-month exposure. The ductile iron sample showing the highest corrosion rate after a 3-month exposure exhibited nonuniform corrosion, which was not apparent in other samples. This attack consisted of an array of closely spaced shallow pits covering about two-thirds of one sample surface. The 6-month corrosion rate data are somewhat higher than those of the nonirradiated system, but they are much lower than the 3-month irradiated-system rates.

Between the 1-month and 3-month data points, the autoclave operated in the vapor phase for several days, apparently because of a reduced back pressure and slightly elevated temperature. It is possible that this operational anomaly had a bearing on the increased corrosion rates observed. Also, the 3-month specimens selected for penetration determinations were taken from a region of the specimen holder where the most serious corrosion was observed, namely, the region near the autoclave inlet, whereas the other specimens were taken from positions uniformly spaced along the holder. At 10 months exposure, a specimen from the bottom of the specimen holder was found to be covered with basalt particles from the basalt-chip bed lying just below the holder. This specimen, of 1025 cast steel, exhibited extremely severe pitting, apparently exacerbated by the crevice-corrosion conditions created by the presence of the particles. (This specimen data point lies above the scatter band in Figure 3.25.) In general, apart from the instances noted, the position of a specimen in the holder was not found to exert a significant effect on its observed corrosion rate.

FIGURE 3.25. Corrosion of Iron-Base Alloys Exposed to Synthetic Hanford Grande Ropde Basalt Ground Water at 250°C and ^{60}Co γ -Irradiation Intensity of 3×10^5 rad/hr

There appears to be a general increase in corrosion rate after 10 months exposure. Particularly notable was the relatively severe pitting corrosion exhibited by a specimen of 2-1/2% Cr-1% Mo alloy at 16 months exposure. Some pits were as deep as 400 μm (16 mil) on this specimen. Conclusions cannot be drawn at present about anticipated nonuniform attack of containers made from these iron-base alloys, as expected conditions at the container surface include contact with a basalt-bentonite packing mixture and a much lower concentration of oxygen in the ground water. Should future testing under more relevant repository conditions continue to reveal extensive nonuniform attack, tests will have to be devised and

conducted that will provide data on pit-deepening kinetics as a function of time, temperature, and water chemistry. It should be noted that evidence of pitting does not necessarily signify the need to reject a particular material, as the pit depth may remain constant with time once a maximum depth is attained.

Surface Layer Composition

The composition of the surface layers on the corrosion coupons was investigated by means of X-ray diffraction. The layers were found to be extremely nonuniform, and to consist of a mixture of iron corrosion products along with materials derived primarily

from the silicon/calcium/aluminum-rich aqueous phase. In general, the coupons from the 250°C tests had surface layers consisting primarily of analcime ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$), nontronite ($(\text{Fe,Al})\text{Si}_2\text{O}_5(\text{OH}) \cdot \text{nH}_2\text{O}$), and magnetite (Fe_3O_4). Nonidentifiable layer-type minerals close to nontronite in diffraction characteristics were frequently present. The presence of irradiation eliminated the analcime, and the nontronite-type materials predominated. At 150°C the surface layers consisted primarily of zeolites (for example, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3.3\text{--}5.3\text{SiO}_2 \cdot 4.3\text{--}5.7\text{H}_2\text{O}$), nontronite and related minerals, and magnetite. No hematite, Fe_2O_3 , was observed on the specimens. Aside from the obvious analcime-zeolite temperature dependence, no other significant correlation was observed, e.g., between alloy composition and surface film composition, or between exposure time and surface film composition.

Conclusions

1. Unirradiated corrosion data, based on the assumption of general (uniform) attack, indicate that the rates obtained at 150°C are somewhat higher than those obtained at 250°C; and rates obtained under 3×10^5 rad/hr irradiated conditions are somewhat higher than those obtained under unirradiated conditions, at 250°C. The scatter in the data and the presence of pitting attack make a quantitative comparison difficult.
2. Based on general (uniform) corrosion rates, iron-base alloys appear to exhibit acceptably low corrosion rates under conditions expected to be conservatively severe relative to anticipated waste package environments in nuclear waste repositories constructed in basalt. Additional testing under conditions more

closely simulating the waste package environment is required, and the kinetics of any observed nonuniform corrosion will require special attention.

3.3 NEVADA NUCLEAR WASTE SITE INVESTIGATIONS

Structural Barriers (DB-30-20-01 - TD1691)
R. E. Westerman - Program Manager

The objective of the Structural Barriers Program is the characterization of metals considered potentially useful as structural barrier materials in high-level nuclear waste packages intended for a Nevada tuff repository.

Summary

The material currently being considered for waste package structural barrier applications in a tuff rock repository is 304L stainless steel. As general corrosion is not considered to be a serious issue, the current program at PNL is addressing the stress-corrosion-cracking (SCC) resistance of this material. U-bend specimens of 304 and 304L stainless steels are undergoing exposure to tuff rock and tuffaceous ground water under irradiated elevated-temperature test conditions, and specimens of the same material are undergoing slow-strain-rate tests in unirradiated hydrothermal ground water environments. Some U-bend specimens of sensitized 304 have failed in test, and slow-strain-rate tests of the same material have revealed susceptibility to stress-corrosion cracking.

U-Bend Irradiation-Corrosion Tests

The irradiation-corrosion tests are performed in two autoclaves in the ^{60}Co

irradiation facility. The autoclaves are operated at 50°C and 90°C, and at irradiation intensities of 6×10^5 and 3×10^5 rad/hr, respectively. Each autoclave is divided into three zones, water and rock (bottom), rock and vapor (middle), and vapor only (top). Each zone contains duplicate U-bend specimens of 304 and 304L stainless steel, in both the solution annealed (15 min at 1050°C, air cool) and solution annealed and sensitized (600°C for 24 hr) conditions. The U-bend specimens are mounted on an alumina rod with alumina spacers, and are insulated from the autoclave by means of a 1-in.-wide strip of 20-mil mica sheet located at the end (nonstressed portion) of the U-bend specimens. With the rack in place, rock chips are added to cover the desired number (16) of specimens, i.e., two-thirds of the total number (24) in the autoclave. At this time the autoclave is closed and sealed in the usual manner. Sponsor-supplied J-13 well water is added to the autoclave to a measured level to cover the desired one-third of the specimens. A temporary Tygon sight tube connected to the inlet fitting at the bottom of the autoclave is used to check the water level. Prior to insertion into the appropriate irradiation-facility access tube, the autoclave is operated at full temperature for one to two days to verify the temperature profile. One thermocouple projecting into each of the zones is used for this purpose. Adjustment of the positions of heaters and insulation is usually required before a satisfactory temperature profile is achieved. At this time, the sight tube is replaced with the 0.125-in. Inconel feed tubing and the autoclave is inserted into the access tube of the irradiation facility. Each day during the exposure period, the autoclaves are refreshed with 240 mL of air, measured as it

escapes from the exit line after being forced through the system from a compressed air supply. The inlet line is closed off at the end of the air-refreshment procedure and the outlet line is immersed in a water trap.

In all cases, the Topopah Springs tuff rock was used in a nominally 1/4-in. major-dimension particle size. The fines that resulted from the crushing operation were not discarded, but were included with the larger particles in the autoclave tests.

The vendor-supplied composition and mechanical properties of the 60-mL stainless steel sheet used in the manufacture of the U-bend specimens are presented in Table 3.5.

The U-bend specimens in both the 50°C and the 90°C study have been examined after 3 months exposure. In the 50°C study, two specimen failures have been recorded: one after 1 month of exposure and one after 3 months of exposure. Both failures occurred in the vapor-only region of the autoclave, and both were specimens of sensitized 304 material.

The 90°C study had problems during its first month of operation. It was pulled from the irradiation facility and dismantled four times because of line plugging, i.e., because refreshment air could not be forced into the system, or because of indications of aberrant temperature profile. Each time the autoclave was found to be dry. These problems have been solved, and the test is now progressing well. After one month of exposure, two specimens of sensitized 304 material were found to have failed, both in the water-plus-rock region of the autoclave. Two additional failures of the same material were found at the 2-month-exposure inspection, one in the vapor-only and one in the vapor-rock region of the autoclave.

Metallographic examination of the specimens failing after 1 month in both the 50°C

TABLE 3.5. Compositions of Steel Sheet Used in U-Bend Specimens

304L STAINLESS STEEL										
Alloying Element, %										
N	C	Mn	P	S	Si	Cr	Ni	Mo	Cu	Co
0.082	0.017	1.70	0.019	0.018	0.57	18.42	8.66	0.19	0.21	0.09
YS:40.5 ksi (279 MPa)										
TS:84.2 ksi (581 MPa)										
El:53.0%										

304 STAINLESS STEEL										
Alloying Element, %										
N	C	Mn	P	S	Si	Cr	Ni	Mo	Cu	Co
0.025	0.063	1.35	0.026	0.018	0.45	18.33	9.37	0.10	0.19	0.08
YS:44.2 ksi (304 MPa)										
TS:90.4 ksi (624 MPa)										
El:55.5%										

and the 90°C tests revealed only intergranular stress-corrosion cracking.

Other than the failures noted, the specimens appeared to be in good condition, with no evidence of pitting or other forms of nonuniform attack.

Slow-Strain-Rate (SSR) Tests

In addition to the U-bend tests described, the stress-corrosion-cracking resistance of 304 and 304L stainless steels was investigated by means of SSR tests. These tests were performed in air-sparged flowing J-13 well water, with a layer of crushed Topopah Springs tuff rock in the bottom of the autoclave. The water was pumped into the bottom of the autoclave at ~35 mL/hr on a once-through basis, as in the case of the general corrosion studies. Control tests were done in air.

The compositions of the 304 and 304L steel plate stock used in the studies are

presented in Table 3.6 along with vendor-supplied mechanical properties.

The 304 material was tested in the mill-annealed condition and the solution-annealed and sensitized condition [1922°F (1050°C) for 15 min, water quenched, followed by 932°F (600°C) for 24 hr with air cool]. The 304L material was slow-strain-rate tested in two conditions: solution-annealed [1922°F (1050°C) for 15 min, water-quenched], and solution-annealed with a post-annealing sensitization treatment [932°F (600°C) for 10 hr, followed by air cooling].

The results of the 304 stainless steel tests are presented in Table 3.7. The mill-annealed specimens had slightly lower ductility in the ground water at the low strain rate than in air; however, the changes in ductility were slight and do not indicate a susceptibility to SCC.

Specimens of 304 stainless steel that were solution-annealed and sensitized failed by intergranular crack propagation, and the

TABLE 3.6. Compositions of Steel Plate Used in Slow-Strain-Rate Tests

<u>304L STAINLESS STEEL</u>										
<u>Alloying Element, %</u>										
<u>N</u>	<u>C</u>	<u>Mn</u>	<u>P</u>	<u>S</u>	<u>Si</u>	<u>Cr</u>	<u>Ni</u>	<u>Mo</u>	<u>Cu</u>	<u>Co</u>
0.0480	0.054	1.44	0.019	0.009	0.39	18.07	8.20	--	--	--
YS:47.3 ksi (326 MPa)										
TS:89.4 ksi (617 MPa)										
El:57.3%										

<u>304 STAINLESS STEEL</u>										
<u>Alloying Element, %</u>										
<u>N</u>	<u>C</u>	<u>Mn</u>	<u>P</u>	<u>S</u>	<u>Si</u>	<u>Cr</u>	<u>Ni</u>	<u>Mo</u>	<u>Cu</u>	<u>Co</u>
--	0.024	1.65	0.031	0.012	0.42	18.12	9.52	--	--	--
YS:42.4 ksi (292 MPa)										
TS:81.1 ksi (559 MPa)										
El:58.5%										

TABLE 3.7. Results of Slow-Strain-Rate Tests of 304 Stainless Steel at 150°C

<u>Specimen Number</u>	<u>Environment</u>	<u>Strain Rate/sec</u>	<u>Reduction of Area, %</u>	<u>Elongation, %</u>	<u>Yield Strength, ksi</u>	<u>Ultimate Strength, ksi</u>
<u>Mill-Annealed Specimens</u>						
P405	Air	10 ⁻⁴	80.2	48.0	37.4	74.4
P406	Air	2 x 10 ⁻⁷	76.5	45.0	35.9	76.6
P397	J-13(a)	10 ⁻⁴	77.9	47.0	36.1	75.3
P404	J-13	10 ⁻⁴	79.6	46.0	36.3	74.9
P401	J-13	2 x 10 ⁻⁷	75.7	50.0	33.5	77.5
P402	J-13	2 x 10 ⁻⁷	76.4	47.0	35.1	77.0
<u>Solution-Annealed and Sensitized Specimens</u>						
P413	Air	10 ⁻⁴	72.2	50.6	21.9	68.0
P415	Air	10 ⁻⁴	66.5	51.5	26.0	68.8
P407	J-13	10 ⁻⁴	75.5	53.5	23.5	68.8
P408	J-13	10 ⁻⁴	74.9	51.0	23.5	69.0
P414	J-13	2 x 10 ⁻⁷	50.9	(b)	22.0	70.1
P416	J-13	2 x 10 ⁻⁷	26.4	(c)	20.7	64.5

(a) Air-sparged J-13 well water.

(b) Not determined.

(c) Broke at gage mark.

ductility was significantly reduced at low (2×10^{-7} /sec) strain rates in J-13 well water at 150°C. Cracks were found along the gage section of these specimens, and the fracture surface showed clear evidence of intergranular fracture.

Results of testing 304L stainless steel are summarized in Table 3.8. It is apparent that neither the solution-annealed nor the solution-annealed and sensitized specimens were susceptible to SCC under these test conditions.

Conclusions

1. The 304 stainless steel U-bend specimens, in a sensitized condition, showed a high

degree of susceptibility to SCC in an irradiated environment of J-13 well water at 50°C and 90°C. Solution-annealed 304 stainless steel, and 304L stainless steel, in both solution-annealed and solution-annealed and sensitized conditions, showed resistance to such failure after 3 months of exposure.

2. The 304 stainless steel, in a sensitized condition, showed susceptibility to intergranular cracking in slow-strain-rate tests in an environment of 150°C J-13 well water at a strain rate of 2×10^{-7} /sec. Mill-annealed 304, and 304L in both solution-annealed and solution-annealed and sensitized conditions, showed no susceptibility to SCC.

TABLE 3.8. Results of Slow-Strain-Rate Tests of 304L Stainless Steel at 150°C

Specimen Number	Environment	Strain Rate/sec	Reduction of Area, %	Elongation, %	Yield Strength, ksi	Ultimate Strength, ksi
<u>Solution-Annealed Specimens</u>						
P234	J-13 ^(a)	10^{-4}	80.5	54.0	25.8	68.4
P235	J-13	10^{-4}	78.4	52.0	27.1	68.2
P233	J-13	2×10^{-7}	68.7	48.0	28.4	67.7
P236	J-13	2×10^{-7}	72.9	46.3	26.7	68.2
<u>Solution-Annealed and Sensitized Specimens</u>						
P243	Air	10^{-4}	73.7	49.0	29.4	68.6
P239	J-13	10^{-4}	72.2	49.6	(b)	(b)
P240	J-13	10^{-4}	74.8	51.6	29.6	69.1
P241	J-13	2×10^{-7}	76.0	49.0	26.6	68.8
P244	J-13	2×10^{-7}	70.4	48.0	27.2	68.8

- (a) Air-sparged J-13 well water.
(b) Not determined.

4.0 SUPPORTING STUDIES

The objectives of the Waste Management Supporting Studies are to do the following: 1) focus technical analysis on the independent assessment of the information base upon which to make decisions to implement waste management systems and technologies of interest, 2) review on-going technology base activities, both domestic and foreign, 3) provide support to DOE's Office of Civilian Radioactive Waste Management, 4) conduct environmental impact studies and analyses, and 5) provide R&D support to the Low-Level Lead Site Program Office at Idaho and to the Consolidated Fuel Reprocessing Program at Oak Ridge.

4.0 SUPPORTING STUDIES

J. V. Robinson, L. T. Lakey and K. M. Harmon -
Program Office Managers

4.1 HANFORD DEFENSE WASTE STUDIES PREPARA-
TION OF ENGINEERING AND ENVIRONMENTAL
IMPACT DATA FOR DISPOSAL OF HANFORD
DEFENSE WASTES (AR-05-10-02 - 80754)
I. C. Nelson - Program Manager

The objective is to assist DOE-RL in developing and assessing methods for the disposal of existing and future Hanford radioactive defense wastes.

Activities During Report Period

Work performed during this reporting period is summarized as follows:

- Review of Rockwell engineering packages
- Performance assessment
- Impact analysis
- DOE-HQ review

Engineering Data Packages

Engineering data packages were received from Rockwell on schedule December 1, 1983. The data packages were reviewed by PNL staff and comments were provided during formal review meetings with DOE-RL and Rockwell staff.

Revisions of the Rockwell engineering data packages were received on February 25 and 28, 1984. The revised data were used to perform recalculations of environmental analyses in support of the preliminary draft of the Hanford Defense Waste Draft Environmental Impact Statement (HDW-DEIS). Because of the extensive revisions submitted, the review of these data packages is expected to continue throughout the next reporting

period. Clarification of various portions of the data was and continues to be sought by PNL technical staff. This effort is expected to continue as environmental analyses are being completed.

Performance Assessment

A concentrated effort was made to review, compile, and analyze performance assessment data for onsite waste disposal systems. The effort was made in response to DOE-RL's concern, whether Table II of proposed EPA standard 40 CFR 191, which describes the limits of radionuclide releases, can be met for 10,000 years if onsite disposal would be implemented.

Briefing materials were prepared for DOE-RL in January and February and for a DOE-HQ staff visit to Hanford during early March.

Impact Analysis

Analyses of environmental impacts from the disposal of Hanford defense waste continue. Efforts focused on:

- dose assessments (workers and population)
- potential occupational accidents during disposal operations (radiological and nonradiological)
- socioeconomic impacts
- transportation impacts
- postdisposal impact scenarios
- cost analyses.

The data are expected to be included in appendices to the HDW DEIS.

DOE-HQ Review

A briefing on Hanford waste engineering and environmental analyses disposal options was provided during a DOE-HQ visit to the Hanford Site in December.

4.2 HANFORD DEFENSE WASTE STUDIES PREPARATION OF AN ENVIRONMENTAL IMPACT STATEMENT FOR DISPOSAL OF HANFORD DEFENSE WASTES (AR-05-10-02 - 80381)

I. C. Nelson - Program Manager

The objective is to assist DOE-RL in the preparation of a draft and a final Environmental Impact Statement for existing and future Hanford radioactive defense wastes.

Activities During Reporting Period

Work performed during this reporting period is summarized as follows:

- Revision of the EIS Implementation Plan continued.
- EIS work plan was prepared.
- Drafts for technical peer review plan for the HDW-DEIS were prepared.
- Draft chapters for the preliminary draft EIS (DEIS) were prepared.
- Presentation was made to the PNL Senior Overview Committee.
- Staff prepared for and participated in DOE-HQ Hanford Site visit.
- Staff prepared for and participated in meetings with DOE-HQ.

EIS Implementation Plan

The EIS Implementation Plan (IP) was revised as requested by DOE-RL (August 22, 1983, Revision 1). The revised IP was reviewed by DOE-RL and formally submitted by

PNL after the revision via the Nuclear Waste Technology Program Office (NWTPO).

Most of the requested changes addressed refinements of the proposed engineering actions (as described in Section 3.0, Scope) to be considered for analysis in the EIS.

HDW-EIS Work Plan

The work plan for preparation of the HDW-EIS was revised and forwarded to DOE via the PNL NWTPO on January 19. Major milestones identified in the work plan were as follows:

Publication of the availability of the Draft EIS in the Federal Register	November 30, 1984
--	-------------------

Public Hearing on Draft EIS	Mid-January 1985
-----------------------------	------------------

Issuance of the Final EIS	August 1, 1985
---------------------------	----------------

Issuance of the Record of Decision	September 15, 1985
------------------------------------	--------------------

Technical Peer Review Plan

Drafts of the HDW-EIS Technical Peer Review Plan have been submitted to DOE-RL. The plan addresses technical reviews to be conducted by DOE-RL, DOE-HQ, staff from certain DOE field offices and contractors, a scientific advisory group, and the National Academy of Sciences.

The reviews are expected to provide enhanced technical credibility to the EIS analysis and to ensure compatibility with other national waste management program elements. The plan is expected to be closely coordinated with DOE-RL's external affairs activities that are intended to solicit public comment.

Preliminary Draft EIS

A preliminary draft of the Hanford Defense Waste DEIS was reviewed within PNL and resubmitted to the chapter preparers for revisions. Concentrated efforts were under way to prepare and revise EIS chapters and appendices. The preliminary draft will be submitted for review by DOE-RL and Rockwell on April 20, prior to formal submittal to DOE-RL on May 15, 1984.

Review by Senior Overview Committee

An overview was provided on March 22 on the status of the HDW EIS Program as well as major technical issues associated with the program. Written guidance has been provided by the Senior Overview Committee.

DOE-HQ Briefing

A briefing on the status of the HDW-EIS Program was provided to DOE-HQ and DOE-RL at DOE-HQ/Germantown on January 31, 1984, and at DOE-RL/Richland on March 6-9, 1984.

4.3 COVER TECHNOLOGY EVALUATION FOR URANIUM MILL TAILINGS (AH-10-15 - 80379)

J. N. Hartley - Program Manager

The objective of this program is to monitor the earthen and asphalt radon barriers on the Grand Junction tailings pile to obtain information on the long-term performance of the barriers for use in designing the remedial action of UMTRA sites.

Summary

- Six papers were prepared and were presented at the Sixth Annual Symposium on Management of Uranium Mill Tailings, Low Level Waste, and Hazardous Waste.

- One paper was prepared and presented at the Annual AIME meeting.
- The surface stabilization research summary report was completed and sent to Weston for incorporation into the overall UMTRAP Technology Summary.
- A trip was made to Grand Junction in December to perform maintenance on the data loggers and to install additional moisture blocks and thermocouples in the earthen covers.
- Grand Junction weather data and alpha nuclear tube data from the Grand Junction column tests were received. They will be used to assist in model verification and analysis of accumulated Grand Junction data from the field tests.
- A contract was awarded in Grand Junction, Colorado, to provide maintenance of the data loggers and make weekly radon flux measurements on the earthen covers.
- Radon flux measurements made on the earthen covers during March 1984 were not significantly different from those measured during February 1982. Three of the four covers were still under the Environmental Protection Agency limit of 20 pCi-m-2sec-1.

Program Management - J. N. Hartley

Six papers, listed below, were prepared and presented at the Fort Collins meeting held February 1-3, 1984:

- "Radon Barrier Field Test Monitoring at Grand Junction, Colorado" by H. D. Freeman, J. N. Hartley and G. W. Gee.
- "Predicting Radon Fluxes from Uranium Mill Tailings Piles" by H. D. Freeman and J. N. Hartley.

- "Asphalt Emulsion Radon Barrier Systems for Uranium Mill Tailings - An Overview of the Technology" by E. G. Baker, J. N. Hartley and H. D. Freeman.
- "Predicting Long-Term Moisture in Earthen Covers" by G. W. Gee, K. K. Nielson and V. C. Rogers.
- "Long-Term Stabilization of Uranium Mill Tailings: Effects of Rock Material on Vegetation and Soil Moisture" by P. A. Beedlow.
- "Uranium Mill Tailings Remedial Action Project (UMTRAP) Surface Stabilization (Rock/Soil/Vegetation Aspects) Research Summary" by J. N. Hartley and P. A. Beedlow.

A paper entitled "Uranium Mill Tailings Management: Cover Systems, Contaminant Migration and Long-Term Stability," authored by J. N. Hartley, G. W. Gee and M. G. Foley, was prepared and presented at the Annual AIME (American Institute of Mining, Metallurgical and Petroleum Engineers) meeting in Los Angeles, California, February 26-March 1.

The topical report on long-term stability (Milestone 201B), Revegetation and Rock Cover for Stabilization of Inactive Uranium Mill Tailing Disposal Sites: Final Report by P. A. Beedlow, is currently in the final stages. The asphalt technology report, Asphalt Emulsion Radon Barrier Systems for Uranium Mill Tailings - An Overview of the Technology, was completed and distributed. A report entitled Long-Term Protection of Uranium Mill Tailings (PNL-4984) by P. A. Beedlow and J. N. Hartley was completed and is being distributed in April 1984.

Site Visits - H. D. Freeman

A trip was made to Grand Junction by H. D. Freeman, December 14-17, 1983, to

perform maintenance on the data loggers at the site and to install a barometric pressure sensor in the weather station. In addition, several new moisture blocks and thermocouples were installed near the surface of the uncompacted adobe earthen cover to monitor moisture and temperature changes. Personnel from Bendix were contacted during the visit to discuss transfer of the alpha tube data from the column tests to PNL.

A contract was awarded in Grand Junction, Colorado, to have data logger maintenance and weekly radon flux measurements performed on the earthen cover field tests. The 24-hr radon flux measurements are being made on one location on each earthen cover, using 15-in.-dia activated-carbon canisters. To date, four sets of measurements have been made, and their results are shown in Table 4.1.

The fifth column in Table 4.1 lists the average radon fluxes measured in February 1982 on the earthen covers. These are presented for comparison with the measurements made at a single location on each earthen cover this month. It appears that the measurement sites are fairly representative of the entire cover, based on the February 1982 measurements. The exception is the uncompacted adobe cover, which has always shown a wide variability in fluxes over the years.

Data Analysis - H. D. Freeman

The data logger data from Grand Junction collected over the last 2 years is being edited and reformatted for plotting. The plotted data will allow us to select the most reliable data for model verification. Data from the first quarter of 1983 show some moisture cycling in the top 2 ft of the covers and at depth in the tailings. The

TABLE 4.1. Radon Flux Measurements, pCi-m-2sec-1, Made on the Earthen Covers During March 1984

Location	March 4	March 13	March 19	March 26	Feb. 1982
Mancos shale	1.4	1.3	0.8	1.2	1.4
Bentonite clay	15.5	17.6	12.3	13.8	11.1
Compacted adobe	9.2	11.0	8.8	9.7	10.0
Uncompacted adobe	54.1	69.1	46.0	37.8	24.7

moisture cycling in the tailings is most likely due to fluctuations in the tailings water table.

Weather data for Grand Junction, Colorado, was received from the National Oceanic and Atmospheric Administration and was placed on a PNL computer. These data will be used to correlate the matrix potential and temperature measurements made in the earthen and asphalt covers over the last 2 years. The alpha nuclear tube data collected by Bendix in the column tests was received on computer tapes. The data is currently being transferred to a PNL computer for further analysis. The data may be used in model verification and in correlation with the weather data for a better understanding of the transport of radon.

4.4 SPECIAL WASTE-FORM LYSIMETERS - ARID (AP-05-20-15 - 80749)

M. J. Graham - Program Manager

The primary objective of this task is to conduct waste-form leaching tests in a field facility to determine typical source terms generated by commercial solidified low-level waste. The solidification agents to be tested are cement and polyvinyl styrene. Through field and laboratory research, the chemical and physical processes will be identified that control the concentration of radionuclides in the soil solution surrounding the waste in an arid climate. Methods for representing source-term boundary conditions in radionuclide transport models will be determined.

Summary

The Special Waste-Form Lysimeters - Arid Task was begun in FY 1983 and is scheduled to be completed in FY 1988. A similar task is ongoing at the Savannah River Laboratory for a humid climate. A field lysimeter facility, consisting of ten lysimeters around a central instrument caisson, has been constructed in which to perform the field testing. Waste samples have been emplaced in the facility, which became fully operational at the end of the second quarter of FY 1984. Two of the lysimeters remain open due to the failure of two of the polymer samples to solidify. Efforts are under way to obtain bitumen samples for these lysimeters.

All laboratory-scale solidified samples for the leach tests have been prepared by Brookhaven National Laboratory (BNL). The leach tests are proceeding on schedule. PNL has completed the organic analyses of one of the liquid-waste samples.

The geochemical computer code used on this program has also been selected and deficiencies in the thermodynamic data base identified. Work to upgrade the model to better suit the needs of this task is scheduled for this fiscal year.

Lysimeter Study

The Special Waste-Form Lysimeters Study is designed to quantify the release and

migration of radionuclides from solidified commercial low-level waste. A field test facility has been built to contain selected waste forms in specially constructed lysimeters. Solidified low-level waste samples have been emplaced in the facility: four Portland cement samples from the Dresden Station reactor in Illinois; two polymer samples, also from Dresden; and two masonry cement samples from the Beaver Valley reactor in Pennsylvania. Two polymer samples failed to solidify; therefore, two of the lysimeters remain open. Efforts are under way to obtain commercial waste samples solidified with bitumen.

The waste forms will be characterized by standard laboratory tests such as MCC-1 and the IAEA leach test to obtain estimates of radionuclide release. Solubility studies will also be conducted to determine the amount of contaminant available for transport after release. Data collected from this research will be used to relate laboratory measurements of waste-form characteristics to the release and migration rates observed in the field. Results obtained for this arid site facility will be compared with those from the humid site located at Savannah River Laboratory.

The field test facility is now completely operational. Figure 4.1 shows the cut-away and top view of the facility. The commercial waste samples were removed from the 55-gal drums and placed in the 10-ft-deep, 6-ft-dia, closed-bottom lysimeters. The central caisson (Figure 4.1) provides access to the individual lysimeters for selective sampling and to the instrumentation. Suction candles (ceramic cups) placed in the bottom and around the waste will be used to periodically collect soil water samples for chemical analysis. Moisture content and soil temperature are being monitored on a

FIGURE 4.1. Engineering Drawing of Special Waste-Form Lysimeter Test Facility

12-hr interval. The data are sent over a phone line to a computer; a backup cassette tape data-storage system is also in place. Radiological analyses will be performed in situ and through selective sampling. This will provide the Low-Level Waste Management Program direct field results regarding leaching and migration rates from actual commercial solidified waste.

PNL has completed the organic analyses of the liquid-waste sample from the Beaver Valley Power Station. A variety of organic chelating agents were identified in the hydrophilic organic fraction of the sample. Two of the chelating agents, ethylenediaminetetraacetic acid (EDTA) and citric acid, are typically used in the decontamination

operations at nuclear facilities. EDTA is present in the sample at 11.2 ppm and citric acid is present at 7.1 ppm. A third compound, ethylenediaminetriacetic acid (ED3A), is the most abundant of the chelating agents at 22.5 ppm. ED3A is presumably a degradation product of EDTA via chemical diagenesis. Seven chelator fragments have been identified in the waste sample. Like ED3A, they appear to be degradation products of EDTA. The analytical procedures and results of these organic analyses are contained in a letter report. Work is under way to conduct similar analyses on the remaining liquid-waste samples received from BNL.

In addition to the field monitoring, which is the central purpose of the task, a series of laboratory testing and geochemical modeling exercises is planned. These tests will help to predict expected leach rates and help to interpret the field data. The ion speciation-solubility and mass transfer geochemical code MINTEQ will be used to model the waste stream, waste form, and any column effluent and batch solutions. Specifically, the goals of the laboratory and modeling work will be to identify which mechanisms are controlling the release of radioactivity from the waste form.

4.5 TRANSPORT ASSESSMENT - ARID

(AR-05-15-15 - 80033)

G. W. Gee - Program Manager

The mission of this program is to provide the required technology for use in monitoring radionuclide transport through geohydrologic systems. This technology will assist in the assessment of the safety of buried solid low-level radioactive waste.

Summary

- Field Data Collection

Monitoring of soil moisture and atmospheric variables affecting surface-moisture flux continued for the second year at the grass-transpiration site. Additional measurements of evapotranspiration were continued at the Buried Waste Test Facility (BWTF) site using weighing lysimeters.

- Transpiration Modeling

Modeling efforts have been directed at evaluating the different drainage rates from two typical soil types found on the Hanford Site. Progress to date indicates the drainage of 5 cm or more from the sandy soils and 2 cm or less from a silt loam under bare surface conditions. The same simulations are being run with a grass vegetation cover.

- Program Management

Two topical reports were published and distributed. The first report, PNL-4747, summarized the technology needs, model verification, and measurement efforts associated with unsaturated zone transport during FY 1978 to FY 1983. The second report, PNL-4896, contains results of model validation studies used to simulate water balance experiments conducted at the BWTF. Two additional reports which document the measurements and modeling of the grass site water balance and the weighing lysimeter experimental design and example test results were prepared and accepted for open literature publication.

Field Data Collection - R. R. Kirkham

Monitoring of soil water content and meteorological variables at the field transpiration site continues for the second year. Above-normal levels of precipitation have continued with the exception of January 1984, which was only 24% of normal. The primary neutron moisture probe failed, forcing the use of a backup probe for 2 months. The collection of moisture profile data continued during this time, with the conversion of data dependent upon calibration of the backup probe. An infiltration test was initiated to determine field values of saturated and unsaturated conductivities. Saturated conductivity for undisturbed surface soils was measured at 8.0 E-4 cm/sec . Saturated conductivities of sandy subsurface soils increased to 6.8 E-1 cm/sec . Measurements to determine unsaturated conductivities of field soils are continuing at this time.

Transport Model Comparison - R. R. Kirkham, G. W. Gee, T. L. Jones

Model simulations have been made comparing effects of hydraulic properties of a sand and a silt loam soil on the annual water balance (drainage) estimates for the field transpiration site. Six years of simulation runs have been completed using bare soils. These simulations use 4 years of 1982 and 2 years of 1983 meteorologic data as input. Precipitation for 1982 is slightly above normal and is well above normal for 1983, the third wettest year on record. Both simulations were started at a uniform soil water potential of 100 cm. The silt loam soil stores significantly more water than does the sand at a water poten-

tial of 100 cm as expected. The silt loam soil drains rapidly during the first year to ~500 cm of head with a yearly drainage rate of 1.5 cm of water below 3.5 m depth at the end of the simulation. The sand soil has very little stored water at 100 cm of head; hence the drainage rate is very low until the stored soil water increases and a new equilibrium potential of ~60 cm is reached. At this potential the yearly drainage rate is ~14 cm of water below the 3.5-m depth at the end of the 6-year simulation period (Figure 4.2).

Program Management - G. W. Gee, R. R. Kirkham

The program report, PNL-4747, Assessment of Unsaturated Zone Transport for Shallow Land Burial of Radioactive Waste: Summary Report of Technology Needs, Model Verification, and Measurement Efforts (FY 1978-FY 1983), was distributed in January 1984. This document provides an overview of shallow-land burial site design and addresses the specific results of research activities conducted by PNL related to radionuclide transport under arid, shallow-land burial conditions. The report Water Balance at an Arid Site: A Model Validation Study of Bare Soil Evaporation (PNL-4896) was distributed in March 1984. The model validation tests consisted of using unsaturated water-flow models to simulate water-balance experiments conducted at the BWTF. The paper "Measurement of Unsaturated Flow Below the Root-Zone at an Arid Site" was completed and presented at the National Water Well Association, Conference on Characterization and Monitoring of Vadose (Unsaturated) Zone. Also, a manuscript describing the weighing-lysimeter facility at the BWTF, was submitted to and

FIGURE 4.2. Simulated Annual Drainage Values (in cm H₂O) for 6-Year Simulation of Climatic Data for Two Soil Types (silt loam and sand) at the Hanford Site. Each drainage value represents annual drainage as affected by the previous year's climate and soil-water storage.

accepted by the Soil Science Society of America for journal publication and will be published sometime in 1984.

4.6 KRYPTON-85 COSTS AND HEALTH IMPACTS ASSESSMENT (AS-15-05 - 80841)

P. J. Mellinger - Program Manager

Major Contributors: L. W. Brackenbush,
J. E. Tanner and E. S. Gilbert

The objective of this study is to develop documentation on the need, or lack thereof, for ⁸⁵Kr recovery and storage as opposed to routine release of the radionuclide. The benefits will be based upon cost and dose averted.

Technical Progress

Phase 1 of this program is to develop a ⁸⁵Kr health risk assessment for the Barnwell Nuclear Fuel Plant. Krypton-85 recovery and immobilization systems were theoretically incorporated into the Barnwell Nuclear Fuel Plant (BNFP) to evaluate their potential elevation of radiation-induced health effects to occupationally exposed individuals. This risk was then compared to the potential rise of public risk if all the krypton was routinely released to the environment.

Cryogenic distillation and fluorocarbon absorption are alternative technologies considered for supplying a gaseous ^{85}Kr product stream to a facility for immobilization by ion-implantation sputtering. Operation and maintenance activity requirements for these systems are analyzed and radiation doses calculated.

The occupational doses from fluorocarbon absorption activities are estimated to be about 20% those from cryogenic distillation. Occupational doses that may be incurred from operating and maintaining the immobilization system are estimated to be about twice as high as those for cryogenic distillation.

The average occupationally exposed worker is estimated to receive about 500 mrem/yr from ^{85}Kr recovery and immobilization activities. This dose is considerably higher than that estimated for the maximum individual (0.02 mrem/yr) and that for the average member of the 50-mile population (0.003 mrem/yr).

Lifetime health-risk estimates based on several models discussed in a National Academy of Sciences report (NAS 1980), referred to here as BEIR III, have been considered. Here we consider only the estimates based on the linear-quadratic relative risk model. To obtain estimates for the number of cancers expected in each case studied, we reduced the BEIR III 10-rad estimates of risk in proportion to the estimated ^{85}Kr dose and then multiplied by the number of individuals at risk to obtain the expected number of cancer deaths induced by the radiation received in a single year of plant operation. These estimates are then multiplied by 30 to obtain estimates of the cancers expected to result from 30 years of plant operation.

It is emphasized that these estimates are based on the assumption that at the levels

being compared, risks are proportional to dose. Data from animal experiments indicate that exposures at low dose rates (~ 10 rad/day) convey less risk (per rad) than do exposures at high dose rates (~ 50 rad/min) (NAS 1980). Unfortunately, there are no data adequate to allow comparisons of effects resulting from exposures at rates of ~ 500 mrem/year with effects resulting from exposures at rates of ~ 0.003 mrem/year, the situation of interest here. The possibility that there are no risks from any of the three situations cannot be ruled out.

Given the uncertainties in the models used to generate these numbers (0.02 - 0.027 radiation-induced cancers expected in the occupational work force and 0.017 cancers in the general population), the differences in total risks for the three situations cannot be considered meaningful. Certainly there is no compelling reason to conclude that risks from ^{85}Kr routinely released to the environment are greater than those from the other two situations considered.

The second phase of this program is to compare and evaluate differences in the ways the EPA and PNL calculate radiation dose and human health effects. An estimate of the present-value cost of constructing and operating a fuel reprocessing plant employing the process alternatives described in Phase I will be made.

Reference

NAS. 1980. The Effects on Populations of Exposure to Low Levels of Ionizing Radiation (BEIR III). Report of the Advisory Committee on the Biological Effects of Ionizing Radiation, National Academy of Sciences, National Research Council, Washington, D.C.

4.7 KRYPTON ION IMPLANTATION

(AS-25-05 - 86116)

The objective of this program is to develop the process of implanting krypton in a sputter-deposited metal matrix for the ultimate storage of krypton-85. Pilot-scale demonstration of the process, using nonradioactive krypton, and small laboratory-scale tests using krypton-85 will be conducted.

Summary

The need for reliable, easily maintainable power supplies combined with current-control circuits for the krypton implantation process makes it advisable to evaluate several engineering approaches. The major effort in seeking the best way to control electrical arcs in the process has focused on the high-voltage target power supply circuit. Three approaches are being evaluated: one developed by PNL and two by commercial manufacturers. The two commercial power supplies have been received and are being installed in the RTL building for testing.

Several metal alloy systems in addition to the nickel-lanthanum-krypton are being evaluated for improved mechanical properties. Four bench-scale experiments were performed using graded targets designed to produce a compositional variation along the longitudinal axis of the cylindrical substrate from ~3 to 20 at% rare earth (RE) metal for both copper and nickel RE alloys. The krypton content was found to initially increase slowly with the RE metal, then increase almost linearly with the RE metal in the range of 3-11% RE before leveling off. Copper-yttrium had the best mechanical stability of the four deposits. The maximum krypton content of 6.9 at% occurred at an yttrium concentration of 16.5 at%.

A cross-hatched pattern of grooves machined into one-third of the substrate wall area reduced crack propagation. Increasing the substrate temperature from 20 to 90°C for the nickel-lanthanum-krypton alloy appeared to increase rather than decrease the deposit stress. The krypton trapping rate was not significantly reduced by the higher substrate temperature.

Equipment Development

One of the critical components in krypton ion implantation is a high-voltage target power supply/integrated control circuit capable of interrupting the output power by promptly dropping the target voltage to zero and restoring the target voltage. The interruption and restoration of the target voltage must be done without losing control of the process. This not only requires a properly designed power supply/current limiter combination but also the necessary logic in the overall process control program. A description and the relative merits for three target power supply/limiter combinations approaches were given in the prior issue of this report (PNL-4250-4, p. 6.9). Plans for evaluating these units are proceeding. The PNL series-tube multilimiter combination approach has been successfully tested on a 2400 V-10 amp sputtering load. Both commercial supplies, the series-tube limiter and the solid-state shunt type supply were completed and witnessed-tested at the factory. Presently they are being installed in the RTL Building for test and evaluation.

Supporting Research

The primary purpose of the supporting research is to improve upon the mechanical

stability of the metal-krypton deposits. Several metal alloy systems in addition to the nickel-lanthanum-krypton are being screened for improved mechanical properties. A second purpose is to refine the design of the experimental apparatus used for deposition, to improve system reliability and to increase the length of time that the apparatus can be run without shutting down for cleaning or repair. This improved reliability is necessary for producing thick deposits. Because system failure can result from mechanical failure (spallation) of the deposited material, and vice versa, improvement of deposit materials-properties and improvement of hardware reliability are interrelated.

Relatively poor mechanical properties can be expected from any material that contains concentrations of entrapped inert gas of several percent or more. The brittleness and high compressive stress in the metal-krypton deposits present no problem in thin (<1 mm) deposits. However, as deposit thickness increases, the accumulated (total) stress increases and can eventually cause fracturing and spallation of the deposits. While the $\text{Ni}_{80}\text{La}_{10}\text{Kr}_{10}$ used previously in this program had satisfactory gas-trapping and gas release characteristics, its poor mechanical properties necessitated study of other nickel-lanthanum alloy compositions and of other transition metal-rare earth alloy systems for improved mechanical stability.

This study is being performed using a bench-scale sputter-deposition system that employs a 3.8-cm ID substrate (260 cm^2 surface area) similar in design to the system used for the 11-Cf ^{85}Kr /nickel-lanthanum deposition experiment. A line drawing of the bench-scale deposition system is given in Figure 4.3. Composite metal sputtering

targets were fabricated to produce deposits of nickel-yttrium-krypton, copper-yttrium-krypton, and copper-lanthanum-krypton, as well as to produce additional nickel-lanthanum-krypton deposits. In all cases the target composition is graded, i.e., the rare earth content varies along the axis of the cylindrical target (Figure 4.3), allowing a spectrum of deposit compositions to be produced in a single run. A new target design was employed here (except in the case of nickel-yttrium) to allow production of deposits thicker than 3 mm in the bench-scale system. In addition to effects of alloy composition, effects of substrate surface topography and substrate temperature on deposit integrity were also studied.

To date, four different bench-scale experiments were performed, as described in Table 4.2. In all cases, the Kr^+ ion implantation energy was 225 eV. Because previous work had shown that a thick (6 mm), stable nickel-yttrium-krypton deposit could be made, the first bench-scale experiment was mainly to determine the influence of yttrium content on the entrapped krypton concentration. In that experiment, the graded composite target produced a deposit varying in yttrium content from 3 to 17 at%. As in a previous experiment with nickel-lanthanum, the krypton content was found to initially increase very slowly with yttrium content, then increase almost linearly with yttrium in the range of 3 to 11% yttrium. The krypton content leveled off abruptly in the range of 11 to 13% yttrium, reaching a value of 6.5-7.0 at% krypton here. For higher yttrium content the krypton content remained constant or declined slightly.

The relatively thick (3 mm) copper-yttrium-krypton deposit had the best mechanical stability of the four deposits described in Table 4.2. Its yttrium content

FIGURE 4.3. Bench-Scale (260-cm^2 substrate surface area) Krypton Trapping Unit

TABLE 4.2. Description of Bench-Scale Deposition Experiments Performed Through March 1984

Run No.	Target Compos.	Deposit Metal Compos. Range, at%	Deposit Kr Conc. Range, at%	Substrate Surface Condition	Substrate Temp., °C	Deposit Thickness, mm
GT-126	Ni-Y	3-17% Y	0.7-7.3%	(c)	20	0.5
GT-129	Cu-Y	3-16.5% Y	0.8-6.9%	(d)	20	2.5-3
GT-130	Cu-La	(a)	(a)	(d)	20	0.5-0.8
GT-131	Ni-La	(a)	(a)	(d)	90	(b)

(a) Composition not yet measured.

(b) Deposit spalled during deposition.

(c) Cylindrically grooved and smooth-walled regions.

(d) Cross-hatched (grooved) and smooth-walled regions.

varied from 3 to 16.5 at%, with the maximum krypton concentration (6.9 at%) occurring in the 16.5 at% yttrium region of the deposit. A somewhat higher krypton content could apparently be attained in alloys containing more yttrium. This experiment indicated that grooving the substrate wall can reduce crack propagation in the thick, brittle deposit. A cross-hatched pattern of grooves (1.5 mm deep x 1.5 mm wide) with 6-mm spacing was machined into one-third of the substrate wall, and the remaining wall was left smooth. While several large cracks traversed the deposit covering the smooth wall, no cracks were found in the cross-hatched deposit. The deep grooves may help accommodate compressive strain in the thick deposit and thereby reduce the tendency to spall.

In the course of the copper-lanthanum-krypton deposition (done in several separate runs), modifications were made to the apparatus to try to decrease unwanted deposit buildup in the anode and upper-lid regions of the chamber. Such accumulations cause electrical shorts in the chamber, requiring disassembly and cleaning of the apparatus before the deposit has reached the desired thickness. One change involved replacing

the original nickel anode by a tantalum one, operable at a higher temperature, to increase the re-evaporation rate of deposited material. The sputtering target also was modified by affixing a nonerodable alumina ring to its top, to prevent the gradual buildup of deposit above the target.

While the anode modification appeared to work well, the target modification caused excessive arcing and was not successful. The equipment modification required that the deposition chamber be opened and exposed to air several times; thus the copper-lanthanum-krypton was deposited in several short runs, resulting in several interfaces within the deposit. Failure of the deposit because of debonding at an interface occurred in the fourth run; hence the intrinsic mechanical stability of the copper-lanthanum-krypton could not be fairly tested in this experiment. Measurement of the krypton flow rate (trapping rate) during deposition suggested that the krypton content should be about the same as in a nickel-lanthanum-krypton deposit. However, detailed measurement of krypton content as compared to lanthanum content has not yet been performed.

The nickel-lanthanum-krypton alloy was deposited on a substrate held at 90°C rather

than at the usual 20°C. The objective was to determine whether a higher substrate temperature would allow greater relaxation (stress relief), and thus thicker deposits to be produced. Unfortunately, deposit began spalling from the substrate (and from itself) before the total thickness had reached 0.5 mm; hence the higher temperature must increase the deposit stress. However, the krypton trapping rate at this temperature was nearly as high as at 20°C.

4.8 INTERNATIONAL PROGRAM SUPPORT

(AP-05-20-10; AP-05-25-10; AP-05-10-02)

K. M. Harmon and L. T. Lakey -
Program Managers

The objective is to provide a center for the collection, organization, assembly, evaluation, and dissemination of information on international programs; provide technical assistance to DOE in planning, coordinating and evaluating INFEX (International Information Exchange) activities; conduct special studies identified by DOE.

Progress During Reporting Period

- PNL-3594 Rev. 4, International Nuclear Fuel Cycle Fact Book, was completed and issued to DOE recipients. Early in FY 1980, PNL published this document to fill a need for summarizing foreign programs concerned with the back end of the fuel cycle. The book also included information concerning foreign fuel cycle facilities, organizations and personnel.

Work has also continued on other studies of foreign fuel cycle activities:

- PNL-4938, The International Program to Study Subseabed Disposal of High-Level Radioactive Wastes, was completed and issued. A summary of the rationale, activities and status of the subseabed disposal program was prepared by E. M. Carlin, K. R. Hinga and J. A. Knauss under a subcontract with the University of Rhode Island.
- The second draft of PNL-4981, A Summary of Nuclear Fuel Reprocessing Activities Around the World, by P. J. Mellinger, L. T. Lakey, and K. M. Harmon, was completed.
- A draft of PNL-5078, "Foreign Programs for the Storage of Spent Nuclear Power Plant Fuels and High-Level Wastes," was completed.
- A paper, "Survey of Foreign Terminal Radioactive Waste Storage Programs," was prepared for the Civilian Radioactive Waste Management Information Meeting in December 1983 and has been included in the published proceedings.
- PNL-3774 Rev. 4, INFEX Guide: Summary of DOE Plans and Activities, was completed and issued.

Copies of these documents, when issued, are available to the public through the National Technical Information Service.

5.0 RECENT WASTE MANAGEMENT PUBLICATIONS

5.0 RECENT WASTE MANAGEMENT PUBLICATIONS

- Allen, R. P., L. K. Fetrow and M. W. McCoy. 1983. "PNL Size Reduction and Decontamination Facilities and Capabilities." CONF-830650-4, FRG/US Workshop on Size Reduction and Decontamination Facilities, Karlsruhe, Federal Republic of Germany, June 27, 1983.
- Ames, L. L. (PNL), P. F. Salter (Rockwell), J. E. McGarrah and B. A. Walker (PNL). 1984. "Selenate-Selenium Sorption on a Columbia River Basalt (Umtanum Basalt, Washington, U.S.A.)." Chem. Geol., 43:287-302.
- Andrews, W. B., J. M. Alzheimer, W. B. Jackson and R. H. Jones. 1983. "Transportation Packaging for Processed Transuranic Waste." CONF-820705-14, Joint ASME/ANS Nuclear Engineering Conference, Portland, Oregon, July 25, 1982.
- Baer, D. R., L. R. Pederson and G. L. McVay. 1983. "Glass Reactivity in Aqueous Solutions." CONF-831171-14, Proceedings of American Vacuum Society Meeting, Boston, Massachusetts, November 1983.
- Barner, J. O. 1984. LWR Spent Fuel Approved Testing Materials for Radionuclide Release Studies. PNL-4686, Pacific Northwest Laboratory, Richland, Washington.
- Barner, J. O., J. L. Daniel and R. K. Marshall. 1983. Zeolite Vittrification Demonstration Program Characterization of Radioactive Vittrified Zeolite Materials. PNL-4856, Pacific Northwest Laboratory, Richland, Washington.
- Barner, J. O., W. J. Gray, G. L. McVay and J. W. Shade. 1983. Interactive Leach Tests of UO₂ and Spent Fuel with Waste Package Components in Salt Brine. PNL-4898, Pacific Northwest Laboratory, Richland, Washington.
- Bradley, D. J., D. G. Coles, F. N. Hodges, G. L. McVay and R. E. Westerman. 1983. Nuclear Waste Package Materials Testing Report: Basaltic and Tuffaceous Environments. PNL-4452, Pacific Northwest Laboratory, Richland, Washington.
- Brodzinski, R. L. 1983. Instrumentation and Assay Procedures for Verification of the Radionuclide Content of Low-Level Waste Packages. PNL-4848, Pacific Northwest Laboratory, Richland, Washington.
- Burger, L. L., and R. D. Scheele. 1983. Status of Radioiodine Control for Nuclear Fuel Reprocessing Plants. PNL-4689, Pacific Northwest Laboratory, Richland, Washington.
- Burkholder, H. C., and J. L. McElroy. 1983. "Commercial Waste Treatment Technology and Programs." Transactions of the American Nuclear Society, 44:100-101.
- Carlin, E. M., K. R. Hinga and J. A. Knauss (Graduate School of Oceanography, University of Rhode Island). 1984. International Program to Study Subseabed Disposal of High-Level Radioactive Wastes. PNL-4938, Pacific Northwest Laboratory, Richland, Washington.
- Cass, A., G. S. Campbell and T. L. Jones. 1984. "Enhancement of Thermal Water Vapor Diffusion in Soil." Soil Science Society of America Journal, 48(1):25-32.
- Cataldo, D. A., R. E. Wildung and T. R. Garland. 1983. "Root Absorption and Transport Behavior of Technetium in Soybean." Plant Physiology, 73:849-852.
- Chick, L. A., and W. M. Bowen. 1983. "Nuclear Waste Glass Development by Statistically Designed Mixture Studies." Proceedings of the American Ceramic Society Pacific Coast Regional Meeting, San Diego, California, October 3, 1983.
- Chick, L. A., and L. R. Pederson. 1983. "The Relationship Between Reaction Layer Thickness and Leach Rate for Nuclear Waste Glasses." Scientific Basis for Nuclear Waste Management, Vol. VII, pp. 635-642, G. L. McVay, ed., Materials Research Society. Elsevier Science Publishing Company, New York, New York.
- Coles, D. G., and M. J. Apted. 1983. "The Behavior of ⁹⁹Tc in Doped-Glass/Basalt Hydrothermal Interaction Tests." Scientific Basis for Nuclear Waste Management, Vol. VII, pp. 129-136, G. L. McVay, ed., Materials Research Society. Elsevier Science Publishing Company, New York, New York.

- Danielson, M. J., O. H. Koski (PNL) and J. Myers (Rockwell). 1984. "Development of High Temperature and Pressure Eh and pH Sensing Instruments." Scientific Basis for Nuclear Waste Management, Vol. VII, pp. 153-160, G. L. McVay, ed., Materials Research Society. Elsevier Science Publishing Company, New York, New York.
- Deutsch, W. J., and R. J. Serne. 1983. "Uranium Mobility in the Natural Environment--Evidence from Sedimentary Roll-Front Deposits." CONF-830375, Conference on Geochemical Behavior of Disposed Radioactive Waste.
- Devary, J. L. (PNL), W. V. Harper (ONWI), J. F. Sykes (University of Waterloo) and J. L. Wilson (INTERA). 1984. "Far Field Flow Uncertainty Analysis for the Palo Duro Basin." Scientific Basis for Nuclear Waste Management, Vol. VII, pp. 397-404, G. L. McVay, ed., Materials Research Society. Elsevier Science Publishing Company, New York, New York.
- Devary, J. L. 1983. "Kriging Analysis for a Candidate Nuclear Waste Repository." CONF-830899, Proceedings of the American Statistical Association.
- Devary, J. L. 1983. Permian Potentiometric Analysis. PNL-4738, Pacific Northwest Laboratory, Richland, Washington.
- Divine, J. R., and W. M. Bowen. 1984. "Corrosion of Carbon Steel in Oxidizing Caustic Solutions." Corrosion/84, Paper No. 190, Presented at Corrosion/84 Conference, April 2-6, 1984, New Orleans, Louisiana.
- Divine, J. R., W. M. Bowen, S. A. McPartland, R. P. Elmore and D. W. Engel. 1983. Double Shell Slurry Low Temperature Corrosion Tests. PNL-4727, Pacific Northwest Laboratory, Richland, Washington.
- Dodson, M. E., R. J. Serne and G. W. Gee. 1983. "Effects of Crystalline Fe and Mn Oxides on Contaminant Migration Through Soil Liners." CONF-840245-2, Proceedings of Sixth Annual Symposium on Management of Uranium Mill Tailings, Low-Level Waste, and Hazardous Waste, Fort Collins, Colorado, February 1, 1984.
- DuBois, R. D. (PNL), L. H. Toburen (PNL) and M. E. Rudd (University of Nebraska). 1984. "Multiple Ionization of Rare Gases by H^+ and He^+ Impact." Physical Review A, 29(1):70-76.
- Ethridge, L. J. (compiler). 1983. Savannah River Plant Defense Waste Vittrification Studies During FY 1982. Summary Report. PNL-4834, Pacific Northwest Laboratory, Richland, Washington.
- FitzPatrick, V. F., D. R. Brown, J. L. Buelt, S. E. King, B. A. Napier, K. H. Oma, D. J. Silveira and C. L. Timmerman. 1983. "In-Situ Vittrification of Trans-uranic Wastes: Systems Evaluation and Applications Assessment." Proceedings of DOE Low-Level Waste Management Program Meeting, Denver, Colorado.
- Gee, G. W., D. Rai and J. R. Serne. 1983. "Mobility of Radionuclides in Soils." In Chemical Mobility and Reactivity in Soil Systems, D. W. Nelson, ed., Soil Science Society of America Special Publication No. 11, pp. 203-228.
- Gilbert, E. R., et al. 1983. "Methodology for Computing Limiting Temperature to Control UO_2 Oxidation." Proceedings of the American Nuclear Society Winter Meeting, San Francisco, California, November 1, 1983.
- Grambow, B. E., and D. M. Strachan. 1984. "Leach Testing of Nuclear Waste Glasses Under Near-Saturation Conditions." Scientific Basis for Nuclear Waste Management, Vol. VII, pp. 623-634, G. L. McVay, ed., Materials Research Society. Elsevier Science Publishing Company, New York, New York.
- Gray, W. J. 1984. "Gamma Radiolysis Effects on Grande Ronde Basalt Groundwater." Scientific Basis for Nuclear Waste Management, Vol. VII, pp. 147-152, G. L. McVay, ed., Materials Research Society. Elsevier Science Publishing Company, New York, New York.
- Gray, W. J. "Gamma Radiolysis of Groundwaters Found Near Potential Radioactive Waste Repositories." Proceedings of Second International Symposium on Ceramics in Nuclear Waste Management, Chicago, Illinois, April 24-27, 1983.
- Gray, W. J., G. L. McVay, J. O. Barner, J. W. Shade (PNL) and R. W. Cote (ONWI). 1984. "Evaluation of Spent Fuel as a Waste Form in a Salt Repository." Scientific Basis for Nuclear Waste Management, Vol. VII, G. L. McVay, ed. Elsevier Science Publishing Company, Inc., New York, New York.

- Gray, W. J., and J. W. Shade. 1983. "Effects of Zircaloy Cladding and Potential Canister Materials on Leach Rates of Spent Fuel." Proceedings of Second International Symposium on Ceramics in Nuclear Waste Management, Chicago, Illinois, April 24-27, 1983.
- Johnson, A. B., Jr. 1983. "U.S. Wet Storage/Dry Storage Integrity Programs." Paper presented at IAEA BEFAST Working Group, Vienna, Austria, October 1983.
- Johnson, A. B., Jr., and B. M. Cole. 1983. "Spent Fuel Dry Storage Experience and Future Needs." Proceedings of the Civilian Radioactive Waste Management Information Meeting, Washington, D.C., December 14-16, 1983.
- Johnson, A. B., Jr., and E. R. Gilbert. 1984. "Current Status of Fuel Degradation Studies in Dry Storage." Proceedings of the Seminar on Spent Fuel Storage Technology, Washington, D.C., January 10-13, 1984.
- Kalkwarf, D. R., and W. B. Silker. 1983. "Diffusion Coefficients of Radon in Candidate Soils for Covering Uranium Mill Tailings." Proceedings of the Sixth Annual Symposium on Management of Uranium Mill Tailings, Low-Level Waste, and Hazardous Waste, Fort Collins, Colorado, February 1, 1984.
- Kennedy, W. E., Jr., and F. M. Mann. 1983. "Potential Low-Level Waste Disposal Limits for Fusion Radionuclides." CONF-831047, Proceedings of the American Nuclear Society Winter Meeting, October 30, 1983.
- Knowlton, D. E., and W. F. Bonner. 1983. "Status, Direction, and Critical Issues of Waste Treatment Technology." 18th Intersociety Energy Conversion Engineering Conference, August 21-26, 1983, pp. 2254-2259.
- Krupka, K. M., E. A. Jenne and W. J. Deutsch. 1983. Validation of the WATEQ4 Geochemical Model for Uranium. PNL-4333, Pacific Northwest Laboratory, Richland, Washington.
- Kuhn, W. L., R. D. Peters and S. A. Simonson. 1983. "Development of a Leach Model for a Commercial Nuclear Waste Glass." Nuclear Technology, 63:82-89.
- Leonhart, L. S., G. E. Wukelic, H. P. Foote and S. C. Blair. 1983. "Monitoring Land and Water Uses in the Columbia Plateau Using Remote-Sensing Computer Analysis and Integration Techniques." CONF-830847, Energy Resource Management '83, San Francisco, California.
- Laul, J. C. (PNL), R. J. Walker (State University of New York), C. K. Shearer, J. J. Papike and S. B. Simon (South Dakota School of Mines). 1984. "Chemical Migration by Contact Metamorphism Between Pegmatite and Country Rocks: Natural Analogs for Radionuclide Migration." Scientific Basis for Nuclear Waste Management, Vol. VII, pp. 951-958, G. L. McVay, ed., Materials Research Society. Elsevier Science Publishing Company, New York, New York.
- Libby, R. A., and G. M. Holter. 1983. "Decay Heat and Age of Spent Fuel in Commercial Power Reactor Inventories." Waste Management '84, R. G. Post, ed., University of Arizona, Tucson, Arizona, March 11-15, 1984.
- Lokken, R. O., and D. M. Strachan. "Long-Term Leaching of Two Simulated Waste Glasses." Proceedings of Second International Symposium on Ceramics in Nuclear Waste Management, Chicago, Illinois, April 24-27, 1983.
- McKee, R. W., H. K. Elder, R. F. McCallum, D. J. Silveira, J. L. Swanson and L. E. Wiles. 1983. Systems Study of the Feasibility of High-Level Nuclear-Waste Fractionation for Thermal-Stress Control in a Geologic Repository. PNL-4530-Vols. 1&2, Pacific Northwest Laboratory, Richland, Washington.
- McVay, G. L. 1983. "Radiation Effects on Nuclear Waste Storage Materials." Second International Conference on Radiation Effects in Insulators, Albuquerque, New Mexico, May 30-June 3, 1983.
- McVay, G. L., ed. 1984. Scientific Basis for Nuclear Waste Management. Materials Research Society, Elsevier Science Publishing Company, New York, New York.
- McVay, G. L., D. J. Bradley (PNL) and J. F. Kircher (ONWI). 1983. "Elemental Release From Glass and Spent Fuel." The Technology of High-Level Nuclear Waste Disposal, P. L. Hofmann and J. J. Breslin, eds., pp. 171-202 (DOE/TIC-4621, Vol. 1).
- McVay, G. L., and C. Q. Buckwalter. 1983. "The Effect of Iron on Waste Glass Leaching." J. Amer. Cer. Soc., 66(3):170-174.

- McVay, G. L., L. C. Olsen and L. R. Pederson. 1983. "Surface Change Effects on Glass/Water Interactions." Proceedings of Second International Symposium on Ceramics in Nuclear Waste Management, Chicago, Illinois, April 24-27, 1983.
- McVay, G. L., and G. R. Robinson. 1983. Effects of Tuff Waste Package Components on Release from 76-68 Simulated Waste Glass. PNL-4897, Pacific Northwest Laboratory, Richland, Washington.
- Montgomery, D. R., and J. F. Nesbitt. 1983. Review and Evaluation of Metallic TRU Nuclear Waste Consolidation Methods. PNL-4754, Pacific Northwest Laboratory, Richland, Washington.
- Myers, J. (Rockwell), G. C. Ulmer, D. E. Grandstaff, R. Brozdowski (Temple University), M. J. Danielson and O. H. Koski (PNL). 1984. "Developments in the Monitoring and Control of Eh and pH Conditions in Hydrothermal Experiments." American Chemical Society Symposium Series, No. 246, Geochemical Behavior of Disposed Radioactive Waste, G. S. Barney, J. D. Navratil and W. W. Schulz, eds.
- Nelson, J. L., R. E. Westerman and F. S. Gerber. 1984. "Irradiation-Corrosion Evaluation of Metals for Nuclear Waste Package Applications in Grande Ronde Basalt Groundwater." Scientific Basis for Nuclear Waste Management, Vol. VII, pp. 121-128, G. L. McVay, ed., Materials Research Society. Elsevier Science Publishing Company, New York, New York.
- Newman, D. F. 1984. "Current Status of DOE's Research, Development and Demonstration Program on Spent Fuel Storage." Proceedings of the Spent Fuel Storage Seminar, Washington, D.C., January 11-13, 1984.
- Newman, D. F., and B. M. Cole. 1984. "Implementation of DOE's Spent Fuel Program: A First Anniversary Report." Waste Management '84, R. G. Post, ed., University of Arizona, Tucson, Arizona.
- Oma, K. H., D. R. Brown, J. L. Buelt, V. F. FitzPatrick, K. A. Hawley, G. B. Mellinger, B. A. Napier, D. J. Silveira, S. L. Stein and C. L. Timmerman. 1983. In-Situ Vitrification of Transuranic Wastes: Systems Evaluation and Applications Assessment. PNL-4800, Pacific Northwest Laboratory, Richland, Washington.
- Oma, K. H., R. K. Farnsworth and C. L. Timmerman. 1984. "Characterization and Treatment of Gaseous Effluents from In Situ Vitrification." Radioactive Waste Management and the Nuclear Fuel Cycle, 4(4):319-341.
- Pederson, L. R., F. N. Hodges, G. L. McVay, D. Rai (PNL) and D. E. Clark (ONWI). 1984. "The Expected Environment for Waste Packages in a Salt Repository." Scientific Basis for Nuclear Waste Management, Vol. VII, G. L. McVay, ed., Elsevier Science Publishing Company, New York, New York.
- Pederson, L. R., and G. L. McVay. 1983. "Effect of Gamma Radiolysis on Waste Glass Leaching in Brines." Proceedings of Second International Symposium on Ceramics in Nuclear Waste Management, Chicago, Illinois, April 24-27, 1983.
- Pederson, L. R., and G. L. McVay. 1983. "Influence of Gamma Irradiation on Leaching of Simulated Nuclear Waste Glass: Temperature and Dose Rate Dependence in Deaerated Water." The Journal of the American Ceramic Society, 66(12):863-867.
- Pederson, L. R. (PNL), and L. R. Vanselow (Rockwell). 1983. "Thermal Dissolution of Aluminum Oxide Layers on Tungsten and Molybdenum (111) and on Tungsten (110) in the Presence of Electric Fields." Surface Science, 135:553-564.
- Peterson, S. R., A. R. Felmy, R. J. Serne and G. W. Gee. 1983. "Geochemical Modeling of Uranium Mill Tailings: A Case Study." Annual Geochemistry Review, Washington, D.C.
- Petrie, G. M., S. C. Sneider and R. A. Craig. 1984. "Description of the Scope (Simplified Codes for Performance Evaluation) System for Use in Exploratory Analysis of Radionuclide Transport in a Geologic Medium." Scientific Basis for Nuclear Waste Management, Vol. VII, pp. 975-978, G. L. McVay, ed., Materials Research Society. Elsevier Science Publishing Company, New York, New York.
- Phillips, M. W., K. Chyi and J. W. Shade. 1983. "Supercaline SPC-8a-5: Characterization and Hydrothermal Stability in the Presence of Basalt." In Proceedings of Toledo Glass and Ceramics Symposium, pp. 101-131, University of Toledo, Toledo, Ohio.

- Primak, W. (Argonne National Laboratory), and F. P. Roberts (PNL). 1984. "Stored Energy in a Radioactive Waste Borosilicate Glass: Its Frequency Factor and Kinetics and Its Source." Nuclear Science and Engineering, 86:191-205.
- Rai, D., and J. L. Ryan. 1984. "Solubility Constraint: An Important Consideration in Safety Assessment of Nuclear Waste Disposal." Scientific Basis for Nuclear Waste Management, Vol. VII, pp. 805-816, G. L. McVay, ed., Materials Research Society. Elsevier Science Publishing Company, Inc., New York, New York.
- Rai, D., R. G. Strickert, D. A. Moore and J. L. Ryan. 1983. "Am(III) Hydrolysis Constants and Solubility of Am(III) Hydroxide." Radiochimica Acta, 33:201-206.
- Rickard, W. H., and L. J. Kirby. 1983. "Tritium in a Deciduous Forest Adjacent to a Commercial Shallow Land Burial Site: Implications for Monitoring to Detect Radionuclide Migration." Proceedings of Fifth Annual Participants Information Meeting of DOE Low-Level Waste Management Program, Denver, Colorado, August 30, 1983.
- Ryan, J. L., and D. Rai. 1983. "The Solubility of Uranium(IV) Hydrous Oxide in Sodium Hydroxide Solutions Under Reducing Conditions." Polyhedron, 2(9):947-952.
- Scheele, R. D., L. L. Burger and C. L. Matsuzaki. 1983. Methyl Iodide Sorption by Reduced Silver Mordenite. PNL-4489, Pacific Northwest Laboratory, Richland, Washington.
- Scheele, R. D., L. L. Burger and K. D. Wiemers. 1984. "Leach Resistance of Iodine Compounds in Portland Cement." American Chemical Society Symposium Series, No. 246, Geochemical Behavior of Disposed Radioactive Waste, G. S. Barney, J. D. Navratil and W. W. Schulz, eds.
- Schneider, K. J. 1984. "Low-Cost Concepts for Dry Transfer of Spent Fuel and Waste Between Storage and Transportation Casks." Waste Management '84, R. G. Post, ed., University of Arizona, Tucson, Arizona, March 11-15, 1984.
- Shade, J. W., L. L. Ames and J. E. McGarrah. 1983. "Actinide and Technetium Sorption on Iron-Silicate and Dispersed Clay Colloids." American Chemical Society Symposium Series, No. 246, Geochemical Behavior of Disposed Radioactive Waste, G. S. Barney, J. D. Navratil and W. W. Schulz, eds.
- Shade, J. W., C. Q. Buckwalter and L. R. Pederson. 1983. "Waste Glass/Metal Interaction in Brines." Proceedings of Second International Symposium on Ceramics in Nuclear Waste Management, Chicago, Illinois, April 24-27, 1983.
- Shade, J. W., and R. W. Clark. 1983. "Temperature Dependence and SA/V x Time Limits on Forward Reaction Leach Rates of MCC 76-68 Waste Glass." American Chemical Society Symposium Series, No. 246, Geochemical Behavior of Disposed Radioactive Waste, G. S. Barney, J. D. Navratil and W. W. Schulz, eds.
- Shade, J. W., L. R. Pederson and G. L. McVay. 1983. "Waste Glass/Metal Interactions in Brines." Proceedings of Second International Symposium on Ceramics in Nuclear Waste Management, Chicago, Illinois, April 24-27, 1983.
- Simonson, S. A., and W. L. Kuhn. 1984. "Predicting Amounts of Radiolytically Produced Species in Brine Solutions." Scientific Basis for Nuclear Waste Management, Vol. VII, G. L. McVay, ed., Elsevier Science Publishing Company, Inc., New York, New York.
- Stein, S. L., J. E. Tanner, B. L. Murphy, J. C. Gillings, R. T. Hadley, O. M. Lyso, R. L. Gilchrist and D. W. Murphy. 1983. U.S. Army Facility for the Consolidation of Low-Level Radioactive Waste. PNL-4640, Pacific Northwest Laboratory, Richland, Washington.
- Strachan, D. M. 1983. "Effect of Flow Rate on the Leaching of Nuclear Waste Glass." Proceedings of Second International Symposium on Ceramics in Nuclear Waste Management, Chicago, Illinois, April 24-27, 1983.
- Strachan, D. M. 1983. "Results from Long-Term Use of the MCC-1 Static Leach Test Method." Nuclear and Chemical Waste Management, 4(2):177-188.
- Strachan, D. M. (PNL), and B. Grambow (Hahn-Meitner Institut). 1983. "Leach Testing of Waste Glasses Under Near-Saturation Conditions." Proceedings of Second International Symposium on Ceramics in Nuclear Waste Management, Chicago, Illinois, April 24-27, 1983.

- Strachan, D. M., and K. M. Krupka. 1983. "Solubility Interpretations of Leach Tests on Nuclear Waste Glass." American Chemical Society Symposium Series, No. 246, Geochemical Behavior of Disposed Radioactive Waste, G. S. Barney, J. D. Navratil and W. W. Schulz, eds.
- Strickert, R. G. 1983. "Importance of Actinide Solubility and Speciation in Nuclear Waste Repository Assessment." Proceedings of Workshop on Standardization of Methods for Measuring Migration of Radionuclides in Geomedia, Berlin, Federal Republic of Germany.
- Strickert, R. G., D. Rai and R. W. Fulton. 1984. "Effect of Aging on the Solubility and Crystallinity of Np(IV) Hydrrous Oxide." American Chemical Society Symposium Series, No. 246, Geochemical Behavior of Disposed Radioactive Waste, G. S. Barney, J. D. Navratil and W. W. Schulz, eds.
- Thomas, J. M., L. L. Eberhardt and J. R. Skalski. 1983. "Survey of Statistical and Sampling Needs for Environmental Monitoring of Commercial Low-Level Radioactive Waste Disposal Facilities." Proceedings of the Fifth Annual Participants Information Meeting of DOE Low-Level Waste Management Program, August 30, 1983.
- Timmerman, C. L., and R. O. Lokken. 1983. "Characterization of Vitrified Soil Produced by In Situ Vitrification." Proceedings of Second International Symposium on Ceramics in Nuclear Waste Management, Chicago, Illinois, April 24-27, 1983.
- Wald, J. W., and W. J. Weber. 1983. "Effects of Self-Radiation Damage on the Leachability of Actinide-Host Phases." Proceedings of Second International Symposium on Ceramics in Nuclear Waste Management, Chicago, Illinois, April 24-27, 1983.
- Weber, W. J. 1983. "Damage Ingrowth and Recovery in Alpha-Irradiated CaF_2 , SrF_2 , and BaF_2 ." Radiation Effects, 70:217-230.
- Weber, W. J. 1983. "Radiation-Induced Swelling and Amorphization in $\text{Ca}_2\text{Nd}_8(\text{SiO}_4)_6\text{O}_2$." Radiation Effects, 77:295-308.
- Weber, W. J. 1983. "A Review of the Current Status of Radiation Effects in Solid Nuclear Waste Forms." Scientific Basis for Nuclear Waste Management, VI, D. G. Brookins, ed., Elsevier Science Publishing Co., New York, New York, pp. 407-414.
- Weber, W. J. 1983. "Thermal Recovery of Lattice Defects in Alpha-Irradiated UO_2 Crystals." J. Nucl. Mater., 114:213-221.
- Weber, W. J., L. R. Pederson, W. J. Gray and G. L. McVay. 1984. "Radiation Effects on Nuclear Waste Storage Materials." Nuclear Instruments and Methods in Physics Research, 229[B1](2,3):527-533.
- Westerman, R. E., J. L. Nelson, S. G. Pitman, W. L. Kuhn (PNL) and S. J. Basham and D. P. Moak (UNWI). 1984. "Evaluation of Iron-Base Materials for Waste Package Containers in a Salt Repository." Scientific Basis for Nuclear Waste Management, Vol. VII, pp. 427-436, G. L. McVay, ed., Materials Research Society. Elsevier Science Publishing Company, Inc., New York, New York.
- White, G. D., and E. R. Gilbert. 1983. " UO_2 Oxidation at Low Temperatures in Air." Proceedings of the 36th Annual Pacific Coast Regional Meeting of American Ceramic Society, San Diego, California, October 3-5, 1983.

DISTRIBUTIONNo. of
CopiesOFFSITE

27 DOE Technical Information Center

2 Nuclear Regulatory Commission
7915 Eastern Avenue
Silver Springs, MD 20910
ATTN: R. E. Cunningham
J. RobertsR. D. Smith
Division of Waste Management
Nuclear Regulatory Commission
Washington, DC 20555D. M. Rohrer
Office of Inspection and Enforcement
Nuclear Regulatory Commission
MS359 EW/W
Washington, DC 20555Materials Section Leader
High-Level Waste Licensing Branch
Nuclear Regulatory Commission
Washington, DC 20555W. F. Holcomb
Environmental Protection Agency
Office of Radiation Programs
Washington, DC 20460W. E. Mott
Office of Environment, Safety
and Health
DOE Office for Policy, Safety and
Environment
PE-24
Washington, DC 205454 DOE Terminal Waste Disposal and
Remedial Action
GTN
Washington, DC 20545
ATTN: J. E. Baublitz, NE-24
F. E. Coffman, NE-20
J. A. Coleman, NE-25
D. J. McGoff, NE-233 DOE Office of Defense Waste and
Byproducts Management
GTN
Washington, DC 20545
ATTN: J. E. Dieckhoner, DP-122
J. J. Jicha, DP-123
D. B. Leclaire, DP-12No. of
Copies4 Office of Geologic Repository
Deployment
DOE Office of Civilian Radioactive
Waste Management
RW, GTN
Washington, DC 20545
ATTN: J. W. Bennett, RW-20
C. R. Cooley, RW-24
C. H. George, RW-3
R. Stein, RW-21K. O. Laughon, Sr.
DOE Office of Spent Fuel Management
and Reprocessing Systems
NE-40, GTN
Washington, DC 20545R. H. Bauer
Office of Storage and Systems
Development
DOE Office of Civilian Radioactive
Waste Management
RW-30, Forrestal
Washington, DC 20585S. A. Mann
DOE Chicago Operations Office
9800 South Cass Avenue
Argonne, IL 60439J. O. Neff
DOE National Waste Terminal Storage
Program Office
505 King Avenue
Columbus, OH 43201J. D. Hamric
DOE Idaho Operations Office
550 2nd Street
Idaho Falls, ID 83401Office of the Assistant Manager
for Energy Research and Development
DOE Oak Ridge Operations Office
P.O. Box E
Oak Ridge, TN 378303 Oak Ridge National Laboratory
P.O. Box X
Oak Ridge, TN 37831
ATTN: W. D. Burch
L. J. Mezga
T. H. Row

Distr-2

No. of
Copies

D. T. Oakley
Los Alamos National Laboratory
P.O. Box 1663
Los Alamos, NM 87545

2 DOE Savannah River Operations Office
P.O. Box A
Aiken, SC 29801
ATTN: H. L. Brandt
T. B. Hindman, Jr.

2 Westinghouse Idaho Nuclear Co.
P.O. Box 2800
Idaho Falls, ID 83401
ATTN: M. P. Johnson
File Copy

E. A. Jennrich
EG&G Idaho
P.O. Box 1625
Idaho Falls, ID 83415

S. G. Harbison
DOE San Francisco Operations
1333 Broadway
Oakland, CA 94612

J. McGough
DOE Albuquerque Operations Office
P.O. Box 5400
Albuquerque, NM 87115

2 Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439
ATTN: J. H. Kittel
M. J. Steindler/L. E. Trevorow

7 Battelle Memorial Institute
Office of Nuclear Waste Isolation
505 King Avenue
Columbus, OH 43201
ATTN: S. H. Basham
W. Carbiener
N. E. Carter
S. Goldsmith
J. F. Kircher
W. J. Madia
B. Rawles

L. Smith
Rockwell International
Rocky Flats Plant
P.O. Box 464
Golden, CO 80401

No. of
Copies

2 E. I. du Pont de Nemours Company
Savannah River Laboratory
Aiken, SC 29808
ATTN: J. L. Crandall
E. J. Hennelly

R. Williams
Electric Power Research Institute
3412 Hillview Avenue
P.O. Box 10412
Palo Alto, CA 94304

G. L. Hohmann
Westinghouse Electric Corporation
Advanced Energy Systems Div.
WIPP Library
P.O. Box 40039
Albuquerque, NM 87196

J. L. Knabenschuh
Nuclear Fuels Services, Inc.
P.O. Box 191
West Valley, NY 14171

2 Bechtel National, Inc.
Box 3965
San Francisco, CA 94119
ATTN: J. L. Jardine
W. A. Freeby

J. L. Larocca, Chairman
Energy Research and Development
Authority
Empire State Plaza
Albany, NY 12223

2 Sandia National Laboratories
Albuquerque, NM 87185
ATTN: D. R. Anderson
W. Weart

J. W. Bartlett
The Analytic Sciences Corp.
6 Jacob Way
Reading, MA 01867

R. G. Post
College of Engineering
University of Arizona
Tucson, AZ 85721

L. L. Hench
Dept. of Materials Science and
Engineering
University of Florida
Gainesville, FL 32611

No. of
CopiesONSITE9 DOE Richland Operations Office

E. A. Bracken
M. Dayani
O. J. Elgert
N. T. Karagianes
J. J. Krupar, Jr.
O. L. Olson
H. E. Ransom
M. W. Shupe
J. D. White

10 Rockwell Hanford Operations

J. L. Ash
K. A. Gasper
R. J. Gimera
R. N. Gurley
H. E. McGuire
J. W. Patterson
J. H. Roecker
P. F. Salter
D. D. Wodrich
File Copy

UNC United Nuclear Industries

T. E. Dabrowski

Westinghouse Hanford Company

A. G. Blasewitz

No. of
Copies42 Pacific Northwest Laboratory

W. F. Bonner
D. J. Bradley
T. D. Chikalla
C. R. Cole/F. L. Thompson
R. L. Dillon
D. W. Dragnich
V. F. FitzPatrick/R. A. Brouns/
J. L. Buelt
R. M. Fleischman
G. W. Gee/T. L. Jones
W. A. Glass
C. R. Hann
J. N. Hartley/H. D. Freeman
J. H. Jarrett
M. R. Kreiter
L. T. Lakey
J. M. Latkovich
R. C. Liikala
R. P. Marshall/W. R. Wiley/
D. B. Cearlock
J. L. McElroy
R. W. McKee
J. E. Mendel/M. D. Merz
J. E. Minor/D. H. Siemens
I. C. Nelson/J. G. Stephan
R. E. Nightingale
D. E. Olesen
A. M. Platt
J. A. Powell
J. V. Robinson
G. L. Tingey/G. A. Jensen
R. P. Turcotte/G. L. McVay
C. M. Unruh/E. C. Watson
H. H. Van Tuyl
B. E. Vaughan
R. E. Westerman
E. J. Wheelwright/J. L. Swanson
Technical Information (5)
Publishing Coordination (2)