Distribution Categories:
Nuclear Waste Management (UC-70)
Environmental Control Technology
and Earth Sciences (UC-11)
General Reactor Technology (UC-80)

ANL-84-57

ANL--84-57

DE85 008124

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

NUCLEAR TECHNOLOGY PROGRAMS
QUARTERLY PROGRESS REPORT

April-June 1984

M. J. Steindler

Associate Division Director
for
Nuclear Technology
Programs

Chemical Technology Division

January 1985

MASTER

Previous reports in this series

ANL-84-37	January-March 1984
ANL-84-15	October-December 1983
ANL-83-88	July-September 1983
ANL-83-78	April-June 1983

EBB

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

CONTRIBUTORS

The following is a list of contributors to this report. Included are personnel of the Chemical Technology Division, Argonne National Laboratory, as well as contributors with other affiliations, as indicated.

J. K. Bates	J. E. Kincinas
R. A. Benson	J. Leddin (Co-op student, Lewis University, Romeoville, IL)
G. Buckau (Technical Univ. Munich, Federal Republic of Germany)	R. A. Leonard
E. L. Callis (ANL/Analytical Chemistry Laboratory)	N. M. Levitz
T. F. Cannon	N. Luckner (Technical Univ. Munich, Federal Republic of Germany)
G. L. Chapman	F. J. Martino
R. A. Couture	R. E. Nelson
P. G. Deeken	J. Osudar (Science Applications, Inc., Schaumburg, IL)
J. E. Fagan	D. J. Raue
D. F. Fischer	L. N. Ruppert
T. J. Gerding	M. G. Seitz
D. G. Graczyk (ANL/Analytical Chemistry Laboratory)	M. Smith (Student res. participant, Providence Coll., Providence, RI)
R. R. Heinrich (ANL/Analytical Chemistry Laboratory)	M. J. Steindler
J. C. Hoh	N. C. Sturchio
R. W. Kessie	G. F. Vandegrift
J. I. Kim (Technical Univ. Munich, Federal Republic of Germany)	C. G. Wach

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
SUMMARY	1
I. MODIFICATION OF BACKFILL MATERIALS UNDER REPOSITORY CONDITIONS	4
A. Introduction	4
B. Methods and Materials	4
C. Results	5
D. Discussion	9
II. TRACE-ELEMENT TRANSPORT IN LITHIC MATERIAL BY FLUID FLOW	11
A. Chemical Studies of Active Geothermal Systems	11
1. Introduction	11
2. Oxygen Isotope Data	11
3. Inductively Coupled Plasma Emission Spectroscopy Data	17
4. Uranium Analysis of Water Samples	22
5. Further Work	22
B. Chemical State of Iron in Surfaces of Altered Basalt	22
1. Laboratory Work	23
2. X-Ray Photoemission Spectroscopy Technique	23
3. Sample and Preparation	24
4. Experimental Results	24
C. Americium Complexation with Groundwater Colloids	26
1. Groundwaters and Previous Results	27
2. Characterization of Colloids in Groundwaters	28
3. Analyses of the Separated Particles and Groundwaters	31
III. REACTION OF GLASS WITH WATER	34
A. Nevada Nuclear Waste Storage Investigations Test Development	34
1. Test 1 Development	34
2. Parametric Testing	37
3. Test 2 Development	43
4. Quality Assurance Plan	45
B. Gamma Radiation Testing	45
1. SRL Glass Preparation	46
2. PNL Glass Preparation	46
3. Oven and Vessel Preparation	46

TABLE OF CONTENTS (contd)

	<u>Page</u>
C. Glass Hydration Studies	47
1. Background	47
2. Instrumentation	48
3. Experiment	49
4. Conclusions	59
IV. TRU REMOVAL FROM HIGH-LEVEL WASTE	61
A. Introduction	61
B. Progress	61
1. Experimental Verifications of Flowsheets for TRU Removal from DSW	61
2. TRU Removal from Complexant Concentrate Waste Solution	62
V. LIGHT WATER BREEDER REACTOR PROOF-OF-BREEDING ANALYTICAL SUPPORT PROJECT	63
A. Full-Scale Shear Facility	63
B. Dual Dissolver System	63
C. Scrap and Waste Disposal	65
1. Waste Packaging	65
2. In-Cell Installations	65
3. Procedures	66
D. Computer System and Data Management	66
1. Hardware System	67
2. Software Systems	67
3. Summary	67
E. Error Analysis	68
F. Analytical Operations	69
1. Mass Spectrometer	69
2. Analytical Hot Cell	70
3. Laboratory M-150	70
4. Alpha/Gamma Counting	70
G. M-Wing Hot Cell Facility	71
1. Manipulators	71
2. ICSAM Project	71
3. Cell M-4	72
H. Radiation Monitoring Systems	72
I. Fissile Material Inventory	73

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
I-1.	X-Ray Diffraction of Purified Montmorillonite Unaltered and Altered	8
II-1.	Portions of the Binding Energy Spectra for Electrons from the Interior Surface of Pomona Flow Basalt	26
II-2.	Geometry and Radii of Rotation of Sealed Tubes in the Type 80 Ti Rotor	29
III-1.	A Reaction Product Formed on the Surface of SRL Defense Waste Glass During Parametric Test No. P-II-3	41
III-2.	Energy Dispersive X-Ray Spectrum of the Reaction Product Shown in Fig. III-1	41
III-3.	A Second Reaction Product Formed on the Surface of SRL Defense Waste Glass During Parametric Test No. P-II-3	42
III-4.	Energy Dispersive X-Ray Spectrum of a Calcium-Rich Precipitate from the Surface of Test No. P-II-4	42

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
I-1.	Thermal Alteration of Bentonite by Water Vapor	6
I-2.	Exchangeable Ions in Bentonite	8
II-1.	Oxygen Isotope Data for Mineral Separates from Yellowstone Samples	12
II-2.	Oxygen Isotope Data for Mineral Separates from Marysville Samples	15
II-3.	ICPAES Analyses of Bulk Vitrophyre and Pumiceous Tuff Separates from Flow Breccia of Biscuit Basin Flow, Yellowstone Drill Holes Y7 and Y8	18
II-4.	ICPAES Analyses of Matrix Separates from Flow Breccia of Biscuit Basin Flow, Yellowstone Drill Holes Y7 and Y8	20
II-5.	ICPAES Analyses of Mineral and Xenolith Separates from Flow Breccia of Biscuit Basin Flow, Yellowstone Drill Holes Y7 and Y8	21
II-6.	Uranium Concentrations in Thermal Water from Yellowstone Drill Hole Y7	22
II-7.	Pomona Flow Basalt Average Whole Rock Analyses	25
II-8.	Wells from Which Groundwaters from Columbia River Basalt Were Obtained	27
II-9.	Speed, Time, and Calculated Size Above Which All Particles Are Cleared during the Centrifugation Run	29
III-1.	Description of Prototype T1 Testing	35
III-2.	Results of Prototype T1 Testing	36
III-3.	Test Matrix for Parametric Testing	39
III-4.	Results of Parametric Testing	40
III-5.	Conditions and Results of Analog Pretreatment Tests	44
III-6.	Water Composition in Blank Silicone Gasket Test No. TF-66	47
III-7.	Analysis of Pretreated J-13 Water To Be Used in Irradiation and Phase II Testing	48

LIST OF TABLES (contd)

<u>No.</u>	<u>Title</u>	<u>Page</u>
III-8.	Tests of Glass Standards	50
III-9.	Composition of SRL 131 Defense Waste Glass	55
III-10.	Results of Reaction of Samples at 202°C	56
III-11.	Results of Analyses of Glass Samples	57

NUCLEAR TECHNOLOGY PROGRAMS
QUARTERLY PROGRESS REPORT

April-June 1984

ABSTRACT

Reduction of the ability of bentonite to retard groundwater flow after its exposure to moisture at high temperatures has been evaluated. A decrease in swelling capacity of bentonite after reaction with water vapor at high temperature has been observed, and an increase in sand-bentonite permeability results. Studies of the redistribution of elements in lithic materials during hydrothermal alteration and of the thermal history of active geothermal systems are under way. Iron in basalt near surfaces exposed to water can reduce and immobilize actinide elements in groundwaters; the chemical state of iron in altered rock is examined. The influence of colloids on the chemical behavior of americium in groundwaters is investigated. Parametric tests to aid the interpretation of a waste form performance test are in progress. The behavior in a radiation field of waste glasses doped with uranium, neptunium, plutonium, and americium is under investigation. The hydration of defense waste glass has been examined. Extraction processes for separating transuranic elements from high-level wastes are being investigated, and conceptual flowsheets have been developed. A demonstration of operational readiness for the destructive analyses of irradiated fuel rods has been accomplished. All systems and procedures were subjected to qualification tests, and a full-length, irradiated, experimental rod has been processed.

SUMMARY

Modification of Backfill Materials under Repository Conditions

Wyoming (sodic) bentonite swells in water at room temperature to specific volumes typically over $35 \text{ cm}^3/\text{g}$, but after reaction with absorbed water vapor at 250°C for seven days, swelling capacities as low as $4 \text{ cm}^3/\text{g}$ were observed. Large reductions in swelling capacity were also observed after reaction at 150 and 200°C . The change in swelling capacity is pronounced over a limited range of low water/clay ratios. Reaction with water causes an irreversible change in hydration behavior of the montmorillonite lattice, expansion in excess liquid at room temperature being limited to a maximum basal spacing of $19 \text{ \AA}$, compared with over $100 \text{ \AA}$ for unreacted montmorillonite. The change causes very large increases in permeability of sand-bentonite mixtures. Exposure of bentonite to moisture at high temperatures would reduce its ability to retard flow of groundwater in proposed high-level nuclear waste repositories.

Trace-Element Transport in Lithic Material by Fluid Flow

Data collection is continuing for our chemical studies of water-rock interactions in the active geothermal systems at Yellowstone National Park, Wyoming, and the Marysville Geothermal Anomaly, Montana. The Yellowstone

study is directed toward understanding the redistribution of elements during hydrothermal alteration of vitric rhyolite. The Marysville study is directed toward understanding the thermal history of the geothermal system there, and to better characterize the long-term mineralogic effects of hydrothermal alteration of granite.

In this report, oxygen isotope analyses of minerals from both systems and inductively coupled plasma atomic emission spectroscopy analyses of Yellowstone whole rock and mineral samples are reported. The significance of the data is discussed, and some possible interpretations are proposed.

Also reported in this quarter is an examination of the chemical state of iron in basalt near surfaces exposed to water. Iron is the major constituent of basalt that is capable of reducing and thereby immobilizing actinide elements in groundwaters. The ability to measure the chemical state of iron in small volumes of altered rock would permit the relating of natural rock alteration to reactions measured in the laboratory, and allow the prediction of long-term behavior of actinides in altered rock environments.

The influence of colloids on the chemical behavior of americium in three groundwaters has been investigated. Similar to data obtained previously, data were obtained on the major element composition of six groundwaters filtered successively through filters of smaller and smaller pore size. This investigation will permit the determination of the amount of colloids in these groundwaters and how they affect americium behavior.

Reaction of Glass with Water

The development of a Phase II waste form performance test related to the unsaturated zone of the potential repository site at the Nevada Test Site is described. Parametric tests to aid in the interpretation of the Phase II test are also in progress.

The behavior of commercial and defense waste glasses doped with uranium, neptunium, plutonium, and americium in the presence of a gamma-radiation field is being investigated. Preparation of the glass and the irradiation facilities is in progress.

Studies of the hydration of glasses using scanning electron microscopy and energy dispersive X-ray spectroscopy is in progress. The quantitative capability of the latter system was investigated and the system was used to investigate the hydration of some defense-type glasses.

TRU Removal from High-Level Waste

Work on TRU removal from two Hanford PUREX wastes (current acid waste and dissolved sludge waste) by a TRUEX solvent extraction process has been completed. Results of this study will be published in July 1984 as an ANL topical report. Work has begun on TRU removal from another Hanford PUREX waste--complexant concentrate waste, which is a by-product of the Hanford process for ⁹⁰Sr recovery from PUREX waste streams.

Light Water Breeder Reactor Proof-of-Breeding Analytical Support Project

This project involves the processing and destructive analysis of 16 or 17 entire full-length irradiated fuel rods from the Light Water Breeder Reactor (LWBR) during fiscal years 1984-1985. Results of these analyses will be used by the Bettis Atomic Power Laboratory (BAPL) to provide instrument calibration factors and corroboration of results pursuant to its nondestructive assay of the end-of-life (EOL) LWBR core. The EOL core analysis is being carried out to determine the extent of breeding in the LWBR.

Operational concepts developed at ANL for this work were successfully demonstrated in the pilot phase of the project, completed in 1979. Present project activities, reported herein, are concerned with the development, installation, testing, and qualification of full-scale equipment and systems for the EOL fuel rod analyses. Reported upon are: (1) the full-scale shear facility (FSSF), (2) the dual dissolver system (DDS), (3) scrap and waste disposal, (4) computer system and data management, (5) error analysis, (6) analytical operations, (7) hot cell facilities, (8) radiation monitoring systems, and (9) fissile material inventory. The present installation and test efforts are being carried out in the Chemistry Division Hot Cell Facility, located in M-Wing of Building 200 at ANL, also the site of the EOL fuel rod analyses themselves.

I. MODIFICATION OF BACKFILL MATERIALS UNDER REPOSITORY CONDITIONS (R. A. Couture and M. G. Seitz)

A. Introduction

Sodium bentonite is widely used for industrial and scientific purposes because of its great ability to swell in water [LOW, NORRISH]. For example, it is widely used as a sealer because the swollen material is very impermeable to water.

Bentonite has been proposed for use in high-level nuclear waste repositories as an impermeable barrier surrounding the waste package. It may also be used to fill tunnels, shafts, and rooms. In both uses, it may be mixed with sand, crushed rock, and/or other ingredients. The mixture is called "backfill" in this report.

In high-level nuclear waste repositories, the backfill will be subjected to elevated temperatures. In a repository planned for basalt, the backfill is expected to be subjected to a range of severe environmental conditions, with temperatures possibly up to 300°C [ALLEN, RHO], radiation dose rates up to 10^3 Gy/h (10^5 rads/h), and both vapor and liquid water present sequentially [COUTURE, RHO].

The stability of backfill materials has been repeatedly questioned [e.g., ANDERSON, COUTURE, WEAVER], but transformations generally are expected to be sufficiently slow that bentonite is not necessarily disqualified as a backfill material. For example, in a recent study, a mixture of sodium-rich bentonite and crushed basalt with a water/clay ratio of two was heated at 300°C for 379 days [ALLEN]. Extensive uptake of iron, calcium, magnesium, and potassium by the clay was observed, but X-ray diffraction showed that the smectite structure was retained. The swelling properties of the clay after reaction were not determined. However, the authors concluded that, although the clay is metastable, the observed experimental changes should not seriously compromise its effectiveness as a backfill material at 300°C, that the clay presumably retained its desirable swelling and sorption properties, and that the metastable nature of the observed reaction products may not be a critical consideration in repository studies.

In contrast to this conclusion, we have previously observed that the permeability of sand-bentonite mixtures, as measured by flow of liquid water, increases by 10^5 as a result of exposure to water vapor during heating from 25 to 260°C [STEINDLER-1984B]. The increase in permeability was found to be irreversible and was due to a large decrease in the swelling capacity of the clay during the tests. This conclusion prompted a systematic determination of the effects of water vapor on bentonite at high temperatures. We present evidence here for very rapid, extensive degradation of the swelling behavior of bentonite at temperatures as low as 150°C.

B. Methods and Materials

Various amounts of clay and deionized water or basaltic groundwater were reacted in small stainless steel or Inconel autoclaves. The autoclaves were heated in mechanical convection ovens for five to seven days. After reaction, the swelling capacity of the clay was determined by dispersing 0.10 to 0.15 g

(dry weight) of clay ultrasonically in 4 mL of water in graduated conical centrifuge tubes at about 22°C, allowing the clay to settle, and measuring the expanded volume. The expanded volumes did not change after several weeks of standing.

Four types of bentonite from Wyoming were used: two commercial bentonites and two montmorillonite standards. As reported by suppliers, the only pretreatment of the bentonite consisted of drying, crushing, and sieving. All samples consisted mostly of montmorillonite, with sodium as the predominant exchangeable cation. They also contained various proportions of plagioclase and quartz, with small amounts of potassium feldspar (probably sanidine), illite or mica, calcite, gypsum, and apatite. Most of the experiments were done with Envirogel (Wyo-Ben, Inc.), which is described by Peacor et al. [PEACOR].

C. Results

The results are shown in Table I-1. The untreated bentonites swell to very high specific volumes in water. For example, Envirogel expands to a specific volume of 37 cm³/g, and forms a thick gel at specific volumes of 30 cm³/g or less.

Dry heating to 250°C for seven days with no added water appears to reduce the swelling capacity slightly (sample 5), as noted previously [BRADLEY, KRUMHANS�]. This reduction may result from reaction with water of hydration before it escapes, as the following experiments suggest.

Heating the clay to 250°C with a limited amount of water causes a great change in wetting behavior. The unreacted material forms a sticky, gummy paste when mixed with water, but the reacted material is not cohesive in water. Alteration reduced the swelling capacity of all four Wyoming bentonites severalfold (samples 6-11 and 19-21). Envirogel initially contains about 4% water of hydration; even this amount of water, if retained during heating, is enough to severely alter the clay (sample 6). Basaltic groundwater has the same effect as pure water on reducing the swelling capacity (samples 9 and 10). As observed in measurements of vapor pressure versus water content of bentonite (work in progress), the water is partitioned between water of hydration and vapor. Liquid water does not coexist with these samples at 250°C.

The results were different at higher water/clay ratios. Water and bentonite were mixed in a ratio of 20:1 to form a gel. After seven days at 250°C (samples 14 and 15), the samples remained gelled, showing relatively little, if any, loss of swelling capacity. Thus, the most substantial loss of swelling capacity occurs at low water/clay ratios, but not at high ratios.

To verify that liquid water is not responsible for the observed alteration, the clay was altered under controlled conditions in which liquid water was known never to be present. We heated clay (Envirogel) to 250°C in a closed vessel, evacuated the vessel, introduced water vapor at $P_{H_2O} = 3.7$ MPa, maintained the pressure for about 18 hours, released the pressure, cooled the clay to room temperature, and determined the swelling capacity. The maximum pressure was below the vapor pressure of pure water at that temperature, 3.98 MPa,

Table I-1. Thermal Alteration of Bentonite by Water Vapor^a

Sample Number	Clay ^b	Mass of Clay, ^c g	Temperature, °C	Water Clay (wt ratio) ^d	Swelling Capacity, cm ³ /g
1	Envirogel	--	Untreated	--	37
2	SWy-1	--	Untreated	--	37
3	Montmorillonite 27	--	Untreated	--	39
4	National Standard	--	Untreated	--	25
5	Envirogel	4.84	250	0 ^e	28
6	Envirogel	4.84	250	0 ^f	9
7	Envirogel	4.84	250	0.02	9
8	Envirogel	4.84	250	0.04	7
9	Envirogel	4.84	250	0.07 ^g	4
10	Envirogel	4.84	250	0.17 ^g	5
11	Envirogel	4.84	250	0.17	5
12	Purified Envirogel	1.00	250	0.20	7
13	Envirogel	2.00	250	1.06 ^g	10
14	Envirogel	0.25	250	20 ^h	>20 ⁱ
15	Envirogel	0.25	250	20 ^{g,h}	>20 ⁱ
16	Altered Envirogel ^j	0.25	250	20 ^g	4
17	Envirogel	4.84	200	0.07	9
18	Envirogel	4.84	150	0.07	13
19	SWy-1	4.46	250	0.06	5
20	Montmorillonite 27	4.84	250	0.07	13
21	National Standard	4.84	250	0.07	11

^aDuration of heating: 7 days, except samples 5 and 11, 5 days. Autoclave volume 7.6 to 7.9 cm³, except sample 20, 5.4 cm³. Water is partitioned between vapor and hydration layers of clay. Except for sample 16, and possibly 13-15, liquid water was absent at temperature of alteration.

^bWyoming bentonite from the following sources: Envirogel--Wyo-Ben, Inc.; SWy-1--Clay Minerals Society; Montmorillonite 27--Ward's Natural Science Establishment, similar to American Petroleum Institute Montmorillonite 27; National Standard--Baroid Corporation.

^cMass of clay in autoclave.

^dIn addition to initial water of hydration (4% for Envirogel, 4 to 8% for the others).

^eNo water added. Heated in an open vessel.

^fNo water added. Heated in a sealed autoclave to retain 4% water of hydration during experiment.

^gArtificial basaltic groundwater. Composition: 3.0 mM NaCl, 2.0 mM Na₂SiO₃, 2.0 mM NaF, 1.1 mM Na₂SO₄, 0.7 mM NaHCO₃, 0.6 mM Na₂CO₃, 0.03 mM CaSO₄, adjusted to pH 9.9 with HCl.

^hWater and clay mixed ultrasonically before heating.

ⁱSample absorbed all water to form a gel, and remained gelled after hydrothermal treatment.

^jPreviously altered, 7 days, 250°C, water/clay = 0.35.

so pure liquid water was never present. (The temperature was controlled to a precision of less than $\pm 0.1^\circ\text{C}$. The combined accuracy of the pressure and temperature measurements was verified by measuring the vapor pressure of water at 250°C to within 1%.) The swelling capacity of the altered clay was found to be $10\text{ cm}^3/\text{g}$, compared with $37\text{ cm}^3/\text{g}$ for the unaltered clay. This experiment confirmed that liquid water is not responsible for the change in the clay.

To determine whether the effect is reversible on contact with liquid groundwater, we reacted altered clay with a large excess of liquid groundwater. The swelling capacity of the product (sample 16) remained low. Therefore, the effect is not reversible.

The alteration is temperature dependent, as shown by experiments at 200°C and 150°C (samples 9, 17, and 18). A significant effect was observed at a temperature as low as 150°C (sample 18).

The reason for the change in swelling capacity of the unaltered clay is a change in uptake of water in interlayer spaces of the montmorillonite lattice. Previous X-ray diffraction studies have shown that the average basal spacing of sodium montmorillonite expands greatly, in some cases from 10 Å in the dry state to over 100 Å in water [BARRER, NORRISH, STEINDLER-1984A]. However, bentonite altered by water vapor at 250°C expands only to a maximum basal spacing of 19 Å. This spacing corresponds to three water layers in the structure.

The change in swelling capacity is not accompanied by a major change in mineralogy. Both the altered and unaltered clays consist mainly of a dioctahedral smectite with an X-ray diffraction peak at 1.50 Å, and a basal spacing of 17 Å when treated with ethylene glycol.

The reacted samples show evidence of slight uptake of exchangeable calcium from calcite or gypsum, as shown by energy-dispersive analysis in the scanning electron microscope (SEM) and as suggested by a small X-ray reflection at about 14.7 Å (at 33% relative humidity). However, the change in exchangeable cation composition does not appear to explain completely the difference in swelling capacity, because a purified sample showed loss of swelling capacity after reaction, but little change in exchangeable ion composition. A sample was purified by sedimentation in water to remove about 20% sand and silt, and then reacted at 250°C (sample 12). The sample has a low swelling capacity, but an X-ray diffractogram (Fig. I-1) shows little difference due to alteration, except a slight asymmetrical broadening of the (001) peak. The exchangeable ion composition was determined by leaching the sample overnight with water and then with $1\text{M NH}_4\text{Cl}$, and by analyzing the solutions by inductively coupled plasma atomic emission spectroscopy. The results, presented in Table I-2, show only relatively small changes. Analysis of many single flakes of clay with energy-dispersive analysis in the SEM does not show a significant difference between samples 12 (low swelling capacity) and 14 (high swelling capacity). Whatever mineralogical or chemical change is responsible for the change in swelling properties is small.

From Table I-1, the maximum alteration seems to take place at added water/clay ratios between 0.07 and 0.17. Most of this water is held in interlayer positions in the montmorillonite structure. With allowances for initial

Fig. I-1. X-Ray Diffraction of Purified Montmorillonite (Envirogel) Unaltered (top) and Altered (sample 12, bottom). Relative humidity controlled at 33% with saturated solution of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. Basal spacings: 12.4 Å unaltered, 12.5 Å altered, determined from four basal reflections. Complete conversion to the calcium form would shift the spacing to 15.4 Å, at $5.7^\circ 2\theta$ [BROWN]. Cu K α radiation, G.E. diffractometer, slits: 1° entrance, MR divergence, 0.2° receiving, $2^\circ 2\theta/\text{min.}$, time constant 2 s.

Table 1-2. Exchangeable Ions in Bentonite

	Composition, mmol/g			
	Na	Mg	K	Ca
Untreated	0.37	0.05	≤ 0.02	0.16
Treated	0.40	0.01	≤ 0.02	0.13

water content of the clay and water vapor in the autoclave, this corresponds to about one to three water layers per 10-A clay layer in the montmorillonite structure. Evidently the absorbed water promotes rapid reactions with impurities in the clay or among structural ions in the lattice.

D. Discussion

Growth of secondary minerals by alteration of nonhydrous silicates in saturated [BATES, COUTURE] or unsaturated [COUTURE] steam has also been demonstrated. Evidently water vapor has great ability to rapidly alter silicates and, over a long period of time, extensive alteration of the clay may result.

The rapid change in montmorillonite properties in these experiments, as well as possible long-term effects, may have important implications for the reactions of clays and other silicates in vapor-dominated geothermal systems, as well as in nuclear waste repositories. Current plans for a basalt repository call for use of 25% bentonite in loosely compacted backfill, with temperatures possibly up to 300°C [ALLEN, RHO]. Because the repository is to be located about 600 to 900 m below the water table in fractured rock, the repository is expected to fill first with steam and then with liquid water [COUTURE, RHO]. The duration of exposure to steam may be many years [RHO]; whereas, our data show that exposure of few days causes extensive degradation of bentonite. The permeability of the backfill would be greatly increased, and the ability to swell and fill fractures would be greatly decreased.

Bentonite used in repositories with far lower peak temperatures may also be affected. A large effect was observed at 150°C, and the effect may occur at still lower temperatures. Long times and other factors may enhance the effect. Bentonite used to fill tunnels and shafts may also be heated enough to be adversely affected by water vapor.

It is important to note that bentonite is not necessarily disqualified for use in nuclear waste repositories. After reaction, it retains the swelling properties of many of the smectite minerals, but not the extreme swelling ability of the fresh material. The effects we have observed need to be taken into account in further studies of waste package design.

REFERENCES

ALLEN

- C. D. Allen et al., Experimental Studies of Packing Material, in G. L. McVay, (ed.), Scientific Basis for Nuclear Waste Management VII, Mater. Res. Soc. Symp. Proc. 26:105-112, North-Holland, New York (1984).

ANDERSON

- D. M. Anderson, (ed.), Smectite Alteration, Proc. Coll. State Univ. New York at Buffalo, May 26-27, 1982, SKBF-KBS 83-03 (1983).

BARRER

- R. M. Barrer, Zeolites and Clay Minerals as Sorbents and Molecular Sieves, Academic Press, London (1978).

BATES

J. K. Bates et al., Hydration Aging of Nuclear Waste Glass, Science 218:51-54 (1982).

BRADLEY

D. J. Bradley et al., Nuclear Waste Package Materials Testing Report: Basaltic and Tuffaceous Environments, Pacific Northwest Laboratory, PNL-4452 (1983).

BROWN

G. Brown, The X-Ray Identification and Crystal Structures of Clay Minerals, Mineralogical Society, London (1961).

COUTURE

R. A. Couture and M. G. Seitz, Physical Response of Backfill Materials to Mineralogical Changes in a Basalt Environment, in U. S. Nuclear Regulatory Commission, NRC Nuclear Waste Geochemistry '83, NUREG/CP-0052 (1984).

KRUMHANSL

J. L. Krumhansl, Observations Regarding the Stability of Bentonite Backfill in a High-Level Waste (HLW) Repository in Rock Salt, Sandia National Laboratories, SAND-83-1293J (1984).

LOW

P. F. Low and J. E. Margheim, The Swelling of Clay: I. Basic Concepts and Empirical Equations, Soil Sci. Soc. Am. J. 43:473-481 (1979).

NORRISH

K. Norrish, Swelling of Montmorillonite, Discuss. Faraday Soc. 18:120-134 (1954).

PEACOR

D. R. Peacor et al., Analysis of Factors Affecting the Stability of Backfill Materials, in U. S. Nuclear Regulatory Commission, NRC Nuclear Waste Geochemistry '83, NUREG/CP-0052 (1984).

RHO

Rockwell Hanford Operations, Rockwell Hanford Operations Site Characterization Report for the Basalt Waste Isolation Project, DOE/RL 82-3 (1982).

STEINDLER-1984A

M. J. Steindler, Fuel Cycle Programs Quarterly Progress Report, January-March 1983, Section II, Argonne National Laboratory Report ANL-83-68 (1984).

STEINDLER-1984B

M. J. Steindler, Nuclear Technology Programs Quarterly Progress Report, January-March 1984, Section I, Argonne National Laboratory Report ANL-84-37 (1984).

WEAVER

C. E. Weaver, Geothermal Alteration of Clay Minerals and Shales: Diagenesis, Battelle Memorial Institute, ONWI-21 (1979).

II. TRACE-ELEMENT TRANSPORT IN LITNIC MATERIAL BY FLUID FLOW
(N. C. Sturchio, G. Buckau,* N. Luckner,* J. I. Kim,* and M. G. Seitz)

A. Chemical Studies of Active Geothermal Systems
(N. C. Sturchio and M. G. Seitz)

1. Introduction

Data collection is continuing for our chemical studies of water-rock interactions in the active geothermal systems at Yellowstone National Park, Wyoming, and the Marysville Geothermal Anomaly, Montana. The Yellowstone study is directed toward understanding the redistribution of elements during hydrothermal alteration of vitric rhyolite. The Marysville study is directed toward understanding the thermal history of the geothermal system there, and to better characterize the long-term mineralogic effects of hydrothermal alteration of granite.

In this report, oxygen isotope analyses of minerals from both systems and inductively coupled plasma atomic emission spectroscopy (ICPAES) analyses of Yellowstone whole rock and mineral samples are reported. The significance of the data is discussed, and some possible interpretations are proposed.

2. Oxygen Isotope Data

The $^{18}\text{O}/^{16}\text{O}$ ratios in mineral separates from the Yellowstone and Marysville samples have been measured to better assess the nature and extent of water-rock interaction in the respective geothermal systems. Further analyses are in progress. Preliminary results are presented here with a brief discussion of their significance.

a. Analytical Procedure

Oxygen isotope ratios were measured by K. Muehlenbachs of the University of Alberta. Oxygen was liberated from the samples by the BrF_5 method [CLAYTON-1963], and analyzed as CO_2 using a Micromass 602E dual inlet-dual collector mass spectrometer.

Data are reported in δ notation, as per mille deviations from the standard mean ocean water (SMOW) reference value, whereby:

$$\delta^{18}\text{O SMOW} = \frac{^{18}\text{O}/^{16}\text{O sample} - 1}{^{18}\text{O}/^{16}\text{O SMOW}} \quad 1000$$

The analytical uncertainty (σ) of the analyses is 0.14‰ as indicated by replicate analyses of the National Bureau of Standards oxygen isotope standard reference material NBS-28.

*Technical University of Munich, Federal Republic of Germany.

b. Yellowstone Samples

Mineral and glass separates from the flow breccia in drill core Y7 were analyzed. This unit was described earlier [STEINDLER-1984B]. Oxygen isotope data for the Yellowstone samples are presented in Table II-1. The most apparent feature of the data is that the samples are anomalously low in $\delta^{18}\text{O}$ relative to normal (unaltered) granites and rhyolites, in which feldspars, for example, typically have a $\delta^{18}\text{O}$ value of ~ 8 [TAYLOR-1968].

Table II-1. Oxygen Isotope Data for Mineral Separates from Yellowstone Samples

Sample Identification ^a	$\delta^{18}\text{O}$ SMOW
Y7 174 plagioclase	1.1
Y7 196 plagioclase	1.1
Y7 205 plagioclase	1.5
Y7 217 plagioclase	1.6
Y7 239 plagioclase	1.4
Y7 174 glass	-0.4
Y7 196 glass	0.8
Y7 217 glass	-0.1
Y7 239 glass	0.4
Y7 209 calcite	-3.0
Y7 239 celadonite	0.3
Y7 239 β -cristobalite	2.8

^aNumerical value following "Y7" indicates sample depth in feet.

The extensive alteration of the samples and their occurrence in a high-temperature geothermal system indicate that the anomalously low $\delta^{18}\text{O}$ values are probably due to high-temperature oxygen exchange with low $\delta^{18}\text{O}$ meteoric water.

The $\delta^{18}\text{O}$ value for the geothermal water in drill hole Y7 may be estimated from the $\delta^{18}\text{O}$ value for Y7 209* calcite. Calcite-water equilibrium is readily attained at temperatures $>100^\circ\text{C}$ [CLAYTON-1981]. By combining the experimentally determined calcite-water fractionation curve of O'Neil et al. [O'NEIL-1969] with the measured temperature during drilling at 209 ft in drill hole Y7 ($\sim 130^\circ\text{C}$ by linear interpolation between measurements at 170.7 and 240.1 ft [WHITE]) and the measured $\delta^{18}\text{O}$ value for Y7 209 calcite of -3.0, the resulting $\delta^{18}\text{O}$ value for the water is -16.7. This is consistent with other measurements of $\delta^{18}\text{O}$ values in Yellowstone drill-hole waters that range from about -16.5 to -18 [TRUEDELL]. In the following discussion, a value of -17 is assumed for the geothermal water.

*The numerical value following the drill-hole number (Y7 or Y8) indicates sample depth in feet.

At the measured temperatures (110-140°C [WHITE]) plagioclase feldspar with 26 wt% anorthite molecule [KEITH] should have $\delta^{18}\text{O}$ values ranging from -2 to -4.6 in equilibrium with -17 water [O'NEIL-1967]. Thus, the feldspars have apparently not reached equilibrium with the thermal water, probably as a result of kinetic factors.

A rough approximation of the volume of water involved in the alteration of the Y7 drill-core samples may be made using the feldspar $\delta^{18}\text{O}$ values and a few simplifying assumptions. First, we assume that the whole-rock $\delta^{18}\text{O}$ value is that of feldspar. This is not exactly true, but is a satisfactory approximation considering that the rocks are mostly hydrated glass that differs by only -0.3 to -1.7‰ relative to feldspar in the samples analyzed. Second, we assume that the meteoric water involved in the water-rock interactions had an initial $\delta^{18}\text{O}$ value of -19, typical of nonthermal waters at Yellowstone [TRUEDELL]. Third, we assume an initial value of +8‰ for the feldspar. Analysis of a relatively unaltered sample of the Biscuit Basin flow from a surface outcrop will allow a test of the validity of this last assumption, and will provide a more realistic value for later refinements of these calculations.

The minimum water/rock ratio may be constrained by a simple closed system mass balance relation [TAYLOR-1979]:

$$w \delta^i \text{H}_2\text{O} + r \delta^i \text{rock} = w \delta^f \text{H}_2\text{O} + r \delta^f \text{rock}$$

Where δ^i and δ^f refer to initial and final $\delta^{18}\text{O}$ values, respectively, and w and r refer to the exchangeable molar amounts of oxygen contained in water and rock, respectively. The water/rock ratio in terms of mass can be written:

$$\frac{\delta^f \text{rock} - \delta^i \text{rock}}{\delta^i \text{H}_2\text{O} - \delta^f \text{H}_2\text{O}} \times \frac{\text{wt \% O rock}}{\text{wt \% O H}_2\text{O}}$$

For the Y7 samples, using the above assumptions and a value of 1.5‰ for δ^f rock, the water/rock mass ratio is:

$$\frac{1.5 - 8.0}{-19 - (-17)} \times \frac{0.48}{0.89} = 1.75$$

Assuming a specific gravity of 2.5 for the rock and 1.0 for the water, the volumetric water/rock ratio is ~4.4.

Using a chloride inventory method, Fournier et al. [FOURNIER] have estimated that at least 10^8 metric tons of thermal water are discharged yearly by Yellowstone hot springs. This is equivalent to a volume of water of at least 0.1 km^3 . If the entire Yellowstone caldera ($\sim 2500 \text{ km}^2$) is underlain to a depth of 2 km by hydrothermally altered rock that has been altered by a volumetric water/rock ratio of ~4, as calculated above, then at the current rate of discharge it would take 2×10^5 years for the alteration to have occurred. The volume of water discharged per year ($> 0.1 \text{ km}^3$) is very small relative to the integrated volume of water indicated by the oxygen data ($\sim 10^4 \text{ km}^3$).

The instantaneous water/rock ratio in Y7 and Y8 may be estimated from the porosity of the rock. Keith et al. [KEITH] report porosities for altered flow breccia in drill cores Y7 and Y8 of 17% and 13%, respectively; pumiceous tuff in drill core Y8 has a porosity of 39%. Assuming a conservative average porosity of 15%, the instantaneous volumetric water/rock ratio is 0.15. If this is representative for the whole Yellowstone system, then the thermal water must have been replaced at least 25-30 times over the lifetime of the system, with a mean residence time on the order of 7000-8000 years. Of course, these estimates are critically dependent on the volume of altered rock and the other assumptions discussed above. Further refinements are possible and will be pursued.

c. Marysville Samples

A blind geothermal anomaly was discovered in 1965 near Marysville, Montana, during routine heat flow studies by D. Blackwell of Southern Methodist University. The anomaly was subsequently drilled to a depth of 2 km to evaluate its potential for the extraction of geothermal energy. Geological, geophysical, and geochemical results of surface exploration and drill hole studies conducted in the early 1970s are summarized by Tammemagi et al. [TAMMEMAGI]. The temperatures at depth were determined not to exceed 100°C, and the Marysville Geothermal Anomaly was abandoned.

Present interest in the Marysville drill core samples is directed toward the nature and extent of hydrothermal alteration of the granite of the Empire Creek Stock, which now contains convecting water at ~95°C, as observed in the Marysville deep drill hole. Previous petrographic and X-ray diffraction studies have revealed evidence for a late to postmagmatic high-temperature hydrothermal event associated with numerous molybdenite-bearing veins in the upper part of the granite, as well as extensive low-temperature alteration in the middle and lower parts of the cored interval of granite. Further study by workers at ANL and RE/SPEC, Ltd. (Calgary) is aimed at collecting more detailed petrographic, fluid inclusion, microprobe, oxygen isotope, and apatite fission-track data. These data will be used to better understand the thermal history of the anomaly and the consequences of long-term reaction between granite and heated groundwater. The results of the study will aid in evaluating the potential of granite as a repository site for high-level nuclear waste.

Oxygen isotope ratios were measured in quartz and feldspar separates from samples of the upper (~300 m), middle (~1300 m), and lower (~2000 m) parts of the granite core, in kaolinite from the middle part of the granite core (albite alteration product), and in narrow (1-2 cm) sericite-biotite alteration zones around a molybdenite-bearing vein in the upper part of the granite core. Data are given in Table II-2. More analyses are in progress, but the present data reveal several interesting features. The significance of the data and some possible interpretations are discussed below.

As noted in Section II.A.2.b, primary $\delta^{18}\text{O}$ values in unaltered granites are typically ~9.5 for quartz and ~8 for feldspar [TAYLOR-1968]. It should be noted that quartz is generally very resistant to oxygen exchange at temperatures below ~250°C [TRUEDELL], as concluded from studies of quartz in active geothermal systems. This is probably due to the slow rate of oxygen diffusion in quartz at low temperature.

Table II-2. Oxygen Isotope Data for Mineral Separates from Marysville Samples

Sample Identification	$\delta^{18}\text{O}$ SMOW
M5 dark green alteration zone	5.2
M5 pale green alteration zone	3.1
M5 quartz	7.0
M5 alkali feldspar	-0.6
M9 chalcedony vein	7.8
M12 quartz	9.5
M12 alkali feldspar	6.4
M12 kaolinite	2.4
M15 quartz	9.1
M15 alkali feldspar	6.8

Assuming an initial $\delta^{18}\text{O}$ of 9.5, the measured $\delta^{18}\text{O}$ value for quartz (7.0) in M5 (upper part of granite core) indicates some exchange of oxygen with a relatively low $\delta^{18}\text{O}$ fluid at a temperature probably in excess of 250°C. The $\delta^{18}\text{O}$ values for quartz in the middle (M12) and lower (M15) parts of the granite core are 9.5 and 9.1, respectively, indicating negligible deviation from primary values and, thus, negligible evidence for high-temperature (>250°C) water-rock interaction in this portion of the granite. However, assuming an initial $\delta^{18}\text{O}$ value of 8 for the feldspars, the measured $\delta^{18}\text{O}$ values for feldspar indicate that significant volumes of water have reacted with the rock, even in the middle and lower parts of the granite core. Using the present data for feldspars, available data on $\delta^{18}\text{O}$ values for thermal water from the Marysville drill hole and well water in the vicinity of the drill hole, and some reasonable assumptions, it is possible to ascertain that a limited volume of water may have reacted with granite. However, considerable caution must be exercised in the interpretation of the data, because the thermal and hydrogeologic history of the Marysville system is poorly understood.

Oxygen isotope data for Marysville deep drill-hole water, and for near-surface water in the vicinity of the drill hole, are given in McSpadden et al. [McSPADDEN]. The deep drill-hole water samples have $\delta^{18}\text{O}$ values that range from -19.0 to -18.6, and the near-surface water has a $\delta^{18}\text{O}$ value of -19.2. The maximum oxygen isotope shift ($\delta^i - \delta^f$), resulting from water-rock interaction, that may be inferred for the water from these data is -0.6

Assuming for simplicity that the granite behaves as alkali feldspar with respect to oxygen exchange, then the inferred oxygen isotope shift for the rock is given by the difference between the assumed primary $\delta^{18}\text{O}$ value for feldspar (8) and the measured $\delta^{18}\text{O}$ values for feldspar ($\delta^f - \delta^i$). Thus, in sample M5, the oxygen isotope shift is -8.6‰ and in sample M12 it is -1.6‰.

As done in Section II.A.2.b, volumetric water/rock ratios were calculated using these oxygen isotope shifts, and the resulting values are ~ 21 for sample M5 and ~ 3.1 for sample M12. These seem unrealistically high. For comparison, in a closed system at equilibrium at 95°C , the values would be ~ 37 and ~ 0.3 for M5 and M12, respectively. The latter value seems more realistic for M12, but the former is even less realistic for M5. If, as mentioned above, the oxygen exchange in M5 occurred at a high temperature (e.g., 300°C), then the equilibrium volumetric water/rock ratio would be reduced to a more reasonable value of ~ 1 . However, in a closed system at equilibrium, the oxygen isotope shifts in the respective waters would be much larger, according to the fractionation curve for feldspars [O'NEIL-1969]. At 300°C , the $\delta^{18}\text{O}$ shift in M5 water would be -12.9 and, at 95°C , the shift in M12 water would be -7.34 . At equilibrium at 300°C , the shift in M12 water would be -18.1 , but the volumetric water/rock ratio would be only ~ 0.13 .

Average water/rock ratios are usually not much greater than 1 in hydrothermal systems associated with discrete intrusions, because of the heat balance involved [TAYLOR-1979]. Therefore, the lower water/rock ratios implied by the equilibrium approximations, especially for M5 at 300°C , seem more appropriate. The M12 closed system equilibrium water/rock ratio is not much different at 300°C (0.13) than at 95°C (0.3) due to the relatively small oxygen shift (-1.6‰) in the rock. However, the very small observed oxygen shift ($\leq -0.6\text{‰}$) in the water is not consistent with such low (equilibrium) water/rock ratios. In M5, a possible explanation is that the postulated high-temperature exchange occurred during a late to postmagmatic hydrothermal event, and that the rock permeability was effectively decreased by self-sealing during this event, thereby severely decreasing later water flux through this portion of the granite. This is consistent with temperature logs from the drill hole that indicate the actively convecting water is restricted to depths below ~ 500 m (the M5 core sample is from ~ 300 m). Thus, the current system may bear little relation to the low $\delta^{18}\text{O}$ values in M5.

In lower portions of the granite core, where 95°C water is now convectively circulating, the observed oxygen shift in the rock is reasonably attributable to present conditions. This case implies continuous recharge of surface water into the system to account for the minimal $\delta^{18}\text{O}$ shift observed in the drill-hole water. Alternatively, the oxygen shift in the rock could have been effected by early high-temperature exchange to a smaller extent than observed in M5, and subsequent low-temperature exchange under present conditions may be limited by very low diffusion rates at 95°C . These hypotheses will be evaluated quantitatively in future work, and temporal constraints on thermal history derived from ongoing fission-track studies will prove useful in this regard.

The magnitudes of kaolinite-water and chalcedony-water fractionations are consistent with these minerals forming under the present temperature conditions, near equilibrium with -19‰ water. However, the kaolinite value is slightly higher than expected, probably due to albite contamination. Therefore, another sample will be purified and analyzed.

3. Inductively Coupled Plasma Emission Spectroscopy (ICPAES) Data

Most of the Yellowstone samples, for which descriptive information and instrumental neutron activation analysis (INAA) data were reported [STEINDLER-1984B], have been analyzed by ICPAES (E. Huff, ANL/Analytical Chemistry Laboratory analyst).

Standards from NBS were analyzed with the Yellowstone samples; standard analyses indicate that the method has good accuracy. Analytical uncertainties range from 3-10% of the amount present. Some first-order trends are evident in the data, and are briefly discussed here.

a. Bulk Vitrophyre

The bulk vitrophyre analyses are given in Table II-3. It should be noted that the Y7 vitrophyre samples range from nearly unaltered to extensively altered. The only extensively altered sample is Y7 233.6BV. The remaining samples generally show increasing alteration with increasing depth, from nearly unaltered (Y7 174BV) to moderately altered (Y7 239BV). Even in Y7 174BV, however, the glass is extensively hydrated (6.8 wt % H₂O), as reported earlier [STEINDLER-1984B].

In Y7 239BV, glass is replaced by celadonite along all perlitic hydration cracks, and is locally replaced by clinoptilolite, especially near throughgoing veinlets and open fractures; pyroxenes are partly replaced by celadonite.

In Y7 233.6BV, glass is totally replaced by celadonite and clinoptilolite, and pyroxenes are almost completely replaced by celadonite. Phenocrysts of feldspars, quartz, oxides, and accessory minerals are not visibly affected by alteration in Y7 samples.

Samples Y8 190BV and Y8 202BV are both extensively altered, whereas Y8 194.5BV is only moderately altered.

The major oxides, TiO₂ and Al₂O₃, remain virtually constant in Y7 and Y8 vitrophyre samples, with the exceptions of extensively altered samples, Y7 233.6BV and Y8 202BV, that have significantly elevated Al₂O₃ concentrations. It is possible that this may be due to dissolution of glass followed by precipitation of a relatively more aluminous zeolite in its place. The similarity in concentration of these relatively immobile elements supports the other geochemical evidence for homogeneity of the Biscuit Basin flow breccia [STEINDLER-1984B] and also indicates that the sample size is adequate for observing changes in bulk composition due to hydrothermal processes.

The major alkalis (Na and K), the alkaline earths (Mg and Ca), and Fe all show significant variability [STEINDLER-1984B]. General trends, best observed relative to Al as a frame of reference, are that Na increases with increasing degree of alteration and temperature, whereas K shows the opposite trend. This is probably a reflection of the glass ion-exchange effect previously reported [STEINDLER-1984B].

Table II-3. ICPAES Analyses of Bulk Vitrophyre and Pumiceous Tuff Separates from Flow Breccia of Biscuit Basin Flow, Yellowstone Drill Holes Y7 and Y8

Constituent	Composition of Samples, ^a wt % for compounds, ppm for elements							
	Y7 174BV	Y7 175BV	Y7 205BV	Y7 211BV	Y7 217BV	Y7 220.3BV	Y7 233.6BV	Y7 239BV
Al ₂ O ₃	11.8	11.8	11.9	11.9	11.8	11.5	12.8	11.7
CaO	1.29	1.48	1.61	1.57	1.53	1.50	1.78	1.48
FeO ^b	2.53	2.93	3.14	3.00	3.04	3.13	5.00	3.15
K ₂ O	4.19	4.44	4.00	4.25	4.31	4.24	2.14	4.23
MgO	0.16	0.38	0.45	0.42	0.42	0.45	0.57	0.42
TiO ₂	0.42	0.42	0.43	0.43	0.43	0.42	0.43	0.45
Ba	970	940	970	930	940	850	1550	820
Be	4.3	4.3	4.4	4.4	4.6	4.4	3.0	4.4
Co	6	6	7	6	7	7	7	7
Cr	15	7	17	12	17	17	13	9
Cu	13	11	7	5	10	8	6	6
Li	20	14	13	14	14	16	46	23
Sc	6.2	6.3	6.9	6.7	6.7	6.3	6.9	6.8
Y	52	50	51	51	51	51	35	51
Mn	390	610	690	670	600	690	630	630
Ni	3	3	4	3	5	3	3	3
Sr	97	104	111	106	103	100	137	95
V	56	60	66	63	76	62	66	63
Zn	82	83	82	81	80	86	87	81

Constituent	Composition of Samples, ^a wt % for compounds, ppm for elements			
	Y8 190BV	Y8 194.5BV	Y8 202BV	Y7 190PM
Al ₂ O ₃	11.6	11.6	12.5	12.3
CaO	1.76	1.60	2.17	1.55
FeO ^b	2.83	2.84	2.78	3.14
K ₂ O	2.02	1.84	2.12	3.81
MgO	0.26	0.31	0.31	0.35
TiO ₂	0.43	0.42	0.43	0.43
Ba	920	550	630	970
Be	4.4	3.7	4.3	4.2
Co	7	6	7	7
Cr	7	7	7	13
Cu	5	12	13	14
Li	63	62	60	57
Sc	6.5	6.5	6.7	6.8
Y	49	50	48	50
Mn	530	580	490	630
Ni	3	3	2	3
Sr	109	94	99	122
V	62	62	71	61
Zn	74	79	76	72

^aTwo-letter suffix in sample number: BV = bulk vitrophyre, PM = pumiceous tuff. Numerical value between drill-hole number (Y7 or Y8) and suffix indicates depth in feet.

^bTotal Fe as FeO.

Minor increases in Fe and Mg are shown with increasing alteration and temperature in Y7, but both elements are generally lower in Y8. This is probably related to the sequence and extent of alteration: in Y7, most alteration is manifest in the initial replacement of glass near hydration cracks by high Fe-Mg clay, whereas in Y8, the remaining glass is largely replaced by low Fe-Mg zeolite [STEINDLER-1984B]. Thus, Fe and Mg released during zeolitization of glass may be incorporated "downstream" in hydrothermal clays.

A slight increase in Ca is shown with increasing alteration and temperature in Y7, and a jump in Ca is shown in Y8. This is probably a function of the preferential incorporation of dissolved Ca in zeolites that replace glass. Preliminary microprobe data [STEINDLER-1984B] indicate that Y8 zeolites are more Ca-rich (~ 2.1 wt % CaO) than Y7 zeolites (~ 0.45 wt % CaO).

Most of the analyzed trace elements do not exhibit significant variability. The most mobile appears to be Li. It is fairly constant in Y7 above 233.6 ft (13-16 ppm, excluding an anomalous point at 174 ft). In Y7 233.6BV, Li jumps to 46 ppm; Y8 samples have 60-63 ppm Li. These elevated Li values may be related to the high celadonite content of these altered samples. Celadonite having 700 ppm Li is reported from Volhyrian basalt [WEAVER, p. 49], and hydrothermal lepidolite has been discovered in Yellowstone drill core samples [BARGAR].

b. Matrix Samples

Compositions of the matrix samples (Table II-4) show greater variability than those of the vitrophyre samples. This is due to the generally more extensive alteration of the matrix material to clays and zeolites, as well as to the precipitation of silica, clays, and zeolites in the pore space of the matrix. For example, the matrix from 220 to 239 ft in Y7 is well sealed with silica; the added silica has effectively diluted the concentrations of the relatively immobile elements (e.g., Ti and Al) by as much as 20% relative to their concentrations in less altered matrix higher in the core.

A trend in the matrix samples similar to that observed in the vitrophyre samples is shown by Na, suggesting that similar mechanisms are responsible for its behavior. However, K exhibits more erratic behavior. This is probably due in part to the precipitation of the K-bearing phases (clay and zeolite) in pore spaces, which counteracts the mechanisms responsible for the trend of decreasing K noted in vitrophyre samples.

No clear trend is shown by Fe and Mg, as in the vitrophyre samples, suggesting that additions due to formation of replacement clays or precipitated clays is balanced by subtractions due to zeolitization or dilution by silica precipitation.

A similar trend by Ca to that noted in the vitrophyre samples is shown. Concentrations of Li and Ba are generally higher in matrix samples than in vitrophyre samples.

Table II-4. ICPAES Analyses of Matrix Separates from Flow Breccia of Biscuit Basin Flow, Yellowstone Drill Holes Y7 and Y8

Constituent	Composition of Samples, ^a wt % for compounds, ppm for elements					
	Y7 174MX	Y7 199MX	Y7 205MX	Y7 209MX	Y7 211MX	Y7 217MX
Al ₂ O ₃	13.2	12.1	11.7	11.6	11.5	11.3
CaO	1.86	1.48	1.39	1.41	1.47	1.39
FeO ^b	4.25	3.28	3.14	3.06	2.96	3.11
K ₂ O	3.45	2.52	4.06	2.52	3.23	4.04
MgO	0.40	0.38	0.33	0.33	0.33	0.35
TiO ₂	0.57	0.43	0.42	0.43	0.40	0.42
Ba	940	900	890	1010	1010	1100
Be	4.8	4.5	4.4	4.2	4.1	4.2
Co	10	7	7	7	7	7
Cr	12	9	10	11	8	10
Cu	29	11	23	14	14	18
Li	67	39	37	39	37	34
Sc	9.2	6.8	6.5	6.9	6.7	6.8
Y	51	53	51	51	50	47
Mn	510	840	650	590	490	540
Ni	7	3	3	3	3	4
Sr	145	109	100	107	110	107
V	73	57	61	65	57	63
Zn	130	79	79	81	75	81

Constituent	Composition of Samples, ^a wt % for compounds, ppm for elements					
	Y7 220.3MX	Y7 223MX	Y7 226.6MX	Y7 233.6MX	Y7 239MX	Y8 202MX
Al ₂ O ₃	10.7	9.77	10.6	10.0	10.3	11.5
CaO	1.39	1.48	1.39	1.34	1.54	1.93
FeO ^b	2.64	2.43	2.53	2.65	2.77	3.10
K ₂ O	3.69	3.66	3.82	3.79	3.94	2.63
MgO	0.30	0.24	0.30	0.28	0.28	0.30
TiO ₂	0.37	0.35	0.38	0.37	0.38	0.42
Ba	1060	950	940	1050	1230	1040
Be	4.2	4.3	4.1	4.1	4.0	4.2
Co	6	6	7	6	7	6
Cr	9	7	18	7	5	9
Cu	9	11	5	7	14	13
Li	23	22	23	26	36	59
Sc	6.1	5.4	6.0	6.2	5.8	6.8
Y	46	49	47	48	46	47
Mn	430	530	480	470	430	440
Ni	3	3	3	3	4	4
Sr	106	86	101	103	106	106
V	63	60	56	51	64	65
Zn	73	70	70	73	70	74

^aTwo-letter suffix in sample number: MX = matrix. Numerical value between drill-hole number (Y7 or Y8) and suffix indicates depth in feet.

^bTotal Fe as FeO.

c. Mineral and Xenolith Separates

Separates of β -cristobalite from Y7 239 and mordenite from Y8 191.1 were analyzed. Both separates came from open fracture deposits. Data are given in Table II-5, and indicate that the cristobalite contains ~7 wt % of coprecipitated contaminants, most likely clay and zeolite minerals. The mordenite separate contains a significant proportion of β -cristobalite, as indicated by an X-ray diffraction pattern (B. Tani, ANL/Analytical Chemistry Laboratory, analyst) and the low concentrations of zeolite-forming oxides. The atomic proportions of Al, Na, K, and Ca indicate that the analysis is acceptable, and can be corrected for silica dilution.

Table II-5. ICPAES Analyses of Mineral and Xenolith Separates from Flow Breccia of Biscuit Basin Flow, Yellowstone Drill Holes Y7 and Y8

Constituent	Composition of Samples, ^a wt % for compounds, ppm for elements		
	Y7 239CT	Y8 191.1MO ^b	Y7 189XE
Al ₂ O ₃	2.53	1.80	12.2
CaO	2.03	0.21	8.12
FeO ^c	0.36	0.048	14.5
K ₂ O	1.48	0.157	0.95
MgO	0.07	0.01	4.21
TiO ₂	0.02	0.01	3.09
Ba	220	16	480
Bc	2.8	<2	3.4
Co	<2	<10	59
Cr	5	35	40
Cu	6	20	110
Li	18	15	59
Sc	<1	<2	31
Y	6	<2	49
Mn	32	9	5880
Ni	3	<10	19
Sr	16	<2	250
V	19	14	300
Zn	<10	<20	280

^aTwo-letter suffix in sample number:

CT = β -cristobalite, MO = mordenite, XE = xenolith.
Numerical value between drill-hole number (Y7 or Y8) and suffix indicates depth in feet.

^bMordenite separate diluted by significant amount of SiO₂ phase.

^cTotal Fe as FeO.

A dark green xenolith fragment separated from pumiceous tuff sample Y7 189 was also analyzed. Its composition is that of a high Fe-Ti basalt.

4. Uranium Analysis of Water Samples

Drill core Y7 water samples were analyzed for U concentrations using the Scintrex UA-3 uranium analyzer (A. Essling, ANL/Analytical Chemistry Laboratory, analyst). Data are reported in Table II-6.

Table II-6. Uranium Concentrations
in Thermal Water from
Yellowstone Drill
Hole Y7

Sample Depth, ft	U, ng/L
200	1.5
240	0.92

5. Further Work

Fifteen additional samples of the pumiceous tuff underlying the flow breccia in Y8 are now being analyzed by instrumental neutron activation analysis (INAA) and ICPAES, including mineral separates and whole rocks. Further microprobe analyses of zeolites and clays will also be acquired. Oxygen isotope analyses for several feldspar separates from the Y8 samples, and kaolinite separates from the Marysville core, will be conducted.

Fission-track and isotope studies of the matrix U anomaly in Y7 [STEINDLER-1984B] are now in progress.

B. Chemical State of Iron in Surfaces of Altered Basalt (M. G. Seitz, N. Luckner,* and J. I. Kim*)

This effort was performed to examine the chemical state of iron in basalt near surfaces exposed to water. X-ray photoemission spectroscopy (XPS) methods were used to analyze the chemical state of iron in very small volumes of material near rock surfaces. Iron is the major constituent of basalt that is capable of reducing and, hence, immobilizing actinide elements in groundwaters. The ability to measure the chemical state of iron in small volumes of altered rock would be used in this program to relate natural rock alteration to reactions measured in the laboratory. This relationship would help make possible the prediction of long-term behavior of actinide elements in altered rock environments.

*Technical University of Munich, Federal Republic of Germany.

Meyer's study [MEYER] of the reaction of basalt with neptunium ion in solution indicates that the neptunium is adsorbed by the basalt, then reduced, possibly by Fe^{2+} , to be permanently fixed on the basalt surface. Migration studies [SEITZ] indicate that neptunium is strongly bound to fresh surfaces of basalt and immobilized but is nearly unimpeded past altered surfaces of basalt. This behavior may be due to the absence of Fe^{2+} on altered basalt surfaces, a point to be explored experimentally in this work.

In related work [PERRY], Perry investigated the chemical states of uranium and thorium adsorbed onto basalt surfaces using XPS methods, but did not explore the relationship of $\text{Fe}^{2+}/\text{Fe}^{3+}$ to the mixed complexes of actinide elements he observed on the basalt surfaces.

1. Laboratory Work

The steps taken to investigate XPS methods in this work are the following:

- (1) View basalt surfaces with XPS to determine if Fe can be detected.
- (2) View altered and fresh basalt material to determine if a change in the chemical state of the iron can be detected.
- (3) Develop standards for quantifying the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in basalts. This ratio may be easily measured in basalt, compared to iron-poor rocks such as granites, and is of most importance regarding redox reactions of the basalt with actinide elements in solutions.
- (4) Study laboratory-modified surfaces of the basalt to be able to correlate $\text{Fe}^{2+}/\text{Fe}^{3+}$ with depth away from altered surfaces.

Steps (1) and (2) have been completed and the concepts for developing $\text{Fe}^{2+}/\text{Fe}^{3+}$ standards have been outlined. Continuation of this project will require the additional step of analyzing the XPS data using theoretical models of binding energies that include matrix effects.

2. X-Ray Photoemission Spectroscopy (XPS) Technique

X-ray photoemission spectroscopy, commonly referred to as electron spectroscopy for chemical analyses (ESCA), is performed by irradiating a sample in vacuum with monoenergetic soft X-rays and analyzing the energies of the electrons emitted. Magnesium $\text{K}\alpha$ X-rays of 1253.6 eV energy were used in this work. These photons penetrate materials to a depth of 1 to 10 μm and interact with electrons in the penetrated surface, causing electrons to be emitted. In addition to the photoelectrons emitted, Auger electrons are also emitted due to relaxation of the energetic ions left after photoemission.

The probability of interaction of the electrons with matter far exceeds that of the photons, so the path lengths of the electrons are much less than for photons, and are of the order of tens of angstroms. The short range of the electrons establishes the thickness of the surface analyzed by XPS.

Analyses in this work were done using a Perkin Elmer PHI Model 550 ESCA/SAM instrument. The area required for analyses is a circular area of ~ 2 mm diameter, giving the amount analyzed to be 1×10^{-9} g for basalt of ~ 3 g/cm³ density.

Specific Perkin Elmer physical electronics components of the instrument are the following: Specimen Stage, PHI Model 15-610; ESCA/Auger System Control, PHI Model 11-055; Ion Gun Control, PHI Model 32-096; and Analyzer Control, PHI Model 20-805.

3. Sample and Preparation

The rock used in this work was taken from the Pomona flow of the Columbia River basalt in the vicinity of the Near Surface Test Facility at Hanford, Washington. The Pomona flow is part of the Saddle Mountains basalt formation and consists of high-magnesium (~ 7.0 wt % MgO) tholeiite that occurs at a depth of 250 m at the reference location of the proposed repository [Fig. 6-1 of RHO]. The rock used in this study is fine- to medium-grained basalt that is altered on its surfaces, has a density of 2.92 g/cm³, and has the average bulk chemical composition shown in Table II-7.

Interior and exterior (weathered) surfaces of the basalt were prepared for ESCA analyses by cutting the rock with a diamond-impregnated brass saw blade with distilled water as coolant. Also, other interior surfaces were prepared by splitting the rock with a chisel and hammer in an argon atmosphere.

These surfaces were looked at directly in the ESCA instrument or were prepared further as follows. One of the interior surfaces cut from the rock was reacted in a hydrogen gas stream at 600°C for one hour to produce a reduced surface. Another of the interior surfaces was reacted in an oxygen gas stream at 600°C for one hour to produce an oxidized surface. Differences seen in these two surfaces could be used as a guide when searching for differences in the spectra for iron between the interior unaltered material and the material near the surface that was altered by natural weathering. Also, some surfaces were ion milled between XPS analyses to identify constituents associated with the prepared surfaces.

4. Experimental Results

Elements detected by XPS are the major elements of the basalt, with peaks of Si, O, Al, Na, Mg, Ca, and Fe identified. Also identified was carbon. Carbon is normally found in XPS spectra, being a contaminant on all exposed surfaces. Peaks identified for iron were from the $2p_{1/2}$ (723-eV) and the $2p_{3/2}$ (709-eV) electrons, with a typical spectrum given in Fig. II-1. The energy scale in the figure includes a shift due to a 4-V charging potential.

The spectra of iron from the interior of the rock and from material near the altered surface of the rock are similar, but differences in intensities of the electron peaks and slight shifts in energy are apparent. These changes likely reflect changes in the chemical state of the iron and offer the promise of quantifying the chemical alteration of iron in basalt surfaces due to weathering.

Table II-7. Pomona Flow Basalt Average Whole Rock Analyses

Constituent	Average of 13 Analyses, ^a wt %	Rock Used in This Study, ^b ppm
SiO ₂	53.5	
Al ₂ O ₃	13.0	
Na ₂ O	2.34	c
K ₂ O	0.46	
MgO	7.45	
CaO	9.6	
FeO ^d	11.0	c
TiO ₂	1.65	
Sc		36.2
Cr		111
Co		44.8
Rb		20
Sr		240
Cs		0.6
Zr		180
Ba		230
U		0.6
La		17.6
Ce		37
Nd		21
Sm		4.9
Eu		1.59
Tb		0.9
Yb		2.8
Lu		0.41
Hf		0.41
Ta		0.7
Th		2.8

^aThese analyses are by microprobe as reported by Ames [AMES].

^bThese analyses are by neutron activation as conducted by N. Sturchio of Argonne National Laboratory.

^cValues for Na₂O and FeO are 2.21 and 10.8 wt %, respectively.

^dTotal Fe as FeO.

The laboratory-modified surfaces (oxidized and reduced) also reveal differences in the XPS spectra of iron; but the differences are subtle even though substantial modification of the iron is expected from the laboratory treatment. This would suggest that detailed analyses of the resulting spectra will be required for identification of the chemical state of iron and quantification of changes caused by weathering. Proposed for these analyses are theoretical models of binding energies that account for matrix effects and can identify chemical states based on a reproduction of the curve shapes obtained experimentally.

Fig. II-1. Portions of the Binding Energy Spectra for Electrons from the Interior Surface of Pomona Flow Basalt. Lines at 727 and 713 eV are identified to be from iron $2p_{1/2}$ and $2p_{3/2}$ electrons at 723 and 709 eV, respectively, as the result of a shift due to a 4-V charging potential.

C. Americium Complexation with Groundwater Colloids
(M. G. Seitz, G. Buckau,* and J. I. Kim*)

The objective of this task was to determine the influence that colloids in three groundwaters from basalt flows within the Columbia River Plateau have on the chemical behavior of an actinide element.

The task was conducted by first filtering and centrifuging the groundwaters to separate suspended materials and by analyzing the suspended materials and groundwaters. Then, the association of americium added to these groundwaters was studied by filtering the waters and analyzing the filtrates and dialysates for radioactivity. The analyses were repeated after ethylene diamine tetraacetic acid (EDTA) was added to the groundwaters to determine if it destroys the association of americium with the colloid particles.

*Technical University of Munich, Federal Republic of Germany.

Important to characterizing the influence of colloidal particles are analyses of the total organic carbon (TOC) of the suspended materials and groundwaters.

Existing data on six other waters from the Columbia Plateau show strong fractionation of TOC together with major and trace elements [STEINDLER-1984A]. These analyses suggest that similar correlations may be detected with these groundwaters. Analyses of water to which EDTA has been added can be used to determine the amount by which the colloids are destroyed by the complexant.

The results of this investigation will be determinations of the amount of filterable colloid particles in these three groundwaters. In addition, the work will show to what extent these colloids can influence the behavior of americium. The results can be combined with existing results for the other six groundwaters to provide a survey of the colloids in these groundwaters from basalt terrains. Also, the results, being obtained in parallel with results on groundwaters from Gorleben, Federal Republic of Germany, can be used to compare behavior of americium in different groundwaters.

The new features of this work will be (1) the application to basalt terrain, (2) the combination of organic and inorganic analyses to the study of colloids, and (3) the influence of these colloids on americium behavior.

1. Groundwaters and Previous Results

The three groundwaters used in this study were from a group of nine total groundwaters collected by basalt aquifers on the Columbia Plateau by Professor S. Boggs, Jr., University of Oregon. The three groundwaters are listed in Table II-8. The waters were filtered through a 0.4- μ m pore size filter, then portions of the water were characterized by filtering and analyzing the filtered waters for major cationic constituents. Also, americium was added to portions of the three groundwaters at concentrations of $\sim 1 \times 10^{-6}$ M, $\sim 1 \times 10^{-8}$ M and $\sim 1 \times 10^{-10}$ M prior to the waters being filtered or centrifuged.

Table II-8. Wells from Which Groundwaters from
Columbia River Basalt Were Obtained

Well Name	Oregon Location
Brown No. 13	3N-29E, Sec 20 dcc
Gary Grieb	Location T, In., R. 26E, Sec 4
L & L Farms No. 2	3N-28E, Sec 26 ba

The six waters studied previously [STEINDLER-1984A] had been filtered through 0.4- μ m pore size filters, then passed through a 1000 MWCO filter (Nuclepore Ultra-Fil filter, Part No. 17853) to obtain two waters, one concentrated in particles stopped by the filter and the other depleted in the particles stopped by the filter.

The six groundwaters previously investigated showed evidence of the existence of colloids as deduced from analyses of the filtered and unfiltered portions of the waters. The waters that did not pass through the filter (and hence were concentrated in particles) contained amounts of Mg, K, Ca, Zn, Sr, Ba, F, S, and organic material at higher concentrations than in the original waters. The waters that passed through the filter (and hence were depleted in particles) contained lesser amounts of these materials.

Removal of major fractions of some inorganic constituents in groundwaters by filtering have also been reported for groundwaters from Gorleben, Federal Republic of Germany [KIM].

2. Characterization of Colloids in Groundwaters

a. Filtration

The three groundwaters used in this study were investigated for the existence of filterable particles that had passed through a 0.4- μ m pore size filter. Such particles were separated from each of the groundwaters by filtering with 15-, 5-, 3-, 1-, and 0.5- μ m particle size filters. Amicon filter assembly Model 8010 with a cell capacity of 10 mL, membrane diameter of 25 mm (effective membrane area of 4.1 cm²), and a holdup volume of 0.2 mL was used without the stirring bar. The procedure for filtering was as follows.

The filters were washed twice in a Petri dish with 30 mL of distilled water and were refrigerated in water until used. The filter apparatus was washed in distilled water, then soaked in distilled water overnight before use. The apparatus was assembled with the filter and the entire assembly was washed by passing 10 mL of distilled water through it. Then, 5 mL of groundwater was passed through the filter and discarded.

A total of 50 mL of groundwater was filtered and collected in polyethylene plastic bottles for further analysis. Thus, sufficient dialysate was obtained to allow analysis of major elements by ICPAES and by analysis of TOC.

b. Centrifuging

A Beckman Ultracentrifuge, Model L8-80M, was used with a fixed angle, Type 80 Ti, rotor. The centrifuge and rotor are capable of speeds to 80,000 rpm, with maximum g forces of 602,000. The rotor geometry is depicted in Fig. II-2. The clearing factor of the rotor is 28 at maximum speed, and the rotor capacity is 108 mL, eight tubes of 13.5-mL capacity each.

Quick-Seal thinwall polyallomer tubes were used. The tubes were filled and then heat sealed to provide a completely sealed liquid throughout the centrifugation.

Fig. II-2.

Geometry and Radii of Rotation of Sealed Tubes in the Type 80 Ti Rotor

The 13.5-mL capacity polyallomer tubes were filled with groundwater that had been filtered through a 0.4- μ m pore size filter. All tubes were sealed, then refrigerated until used. Four tubes of each of two different groundwaters were used to fill the rotor. The centrifuge was loaded and run at one of the conditions shown in Table II-9.

Table II-9. Speed, Time, and Calculated Size Above Which All Particles Are Cleared during the Centrifugation Run

Condition	Centrifuge Velocity, rpm	Time, h	Cleared Particle Size, ^a μ m
1	80,000	24	2.2
2	40,000	24	4.4
3	20,000	24	9.0
4	20,000	4.9	18.0

^aCalculated using a particle density of 1.4 g/cm³ (that of soluble protein), a settling distance of 40 mm, an average radius of rotation of 62.5 mm, and the viscosity of water at 20°C of 0.000102 Pa·s [0.00102 P or 0.000102 kg/(m·s)].

The centrifuge was run at a temperature of 20°C and programmed to complete the centrifugation cycle immediately prior to groundwater recovery and pellet sampling. The tubes were removed from the rotor and cut open at the top; then 12 mL of water was withdrawn with a syringe and needle from each tube. The remaining contents of the tubes (v1 mL water and the pellet formed upon centrifugation) were dried in an oven at 50°C, with each tube being weighed before and after drying to determine the amount of water that was evaporated.

Concentrations of elements remaining in solution will be determined by ICPAES analyses. The compositions of the pellets and evaporated residues will be determined by neutron activation analyses.

c. Calculation of Sedimented Particle Diameter

The diameters of particles that could be expected to be settled by the centrifuge conditions given in Table II-9 were calculated so that they could be compared with the size of particles collected with filters of various pore sizes.

The diameter of a symmetrical particle, d , is related to its settling velocity, $\bar{v}$, at the rotational velocity of the centrifuge, ω , by the equation

$$d^2 = \frac{\mu \bar{v} \times 18}{(\rho_d - \rho_m) \omega^2 r}$$

where μ is the viscosity of the medium (0.000102 Pa's, or 0.00102 P, at 20°C for pure water); ρ_d and ρ_m are the densities of the particles and medium, respectively; and r is the radius of rotation.

Taking the radius of rotation to be the average radius for the rotor, 62.5 mm, and the density of particles to be that typical of dissolved protein, 1.4 g/cm³, then for particles settling through a distance of 40 mm during the run times, their dimensions at various centrifuge velocities are those given in Table II-9. The calculation indicates that all particles of these sizes or larger would be collected in the pellet from these centrifuge runs.

The calculation can be refined using various travel paths followed by particles in the sealed test tube. The results of such calculations would show that all particles larger than a certain size are cleared from the solution. That particle size is dependent on run conditions and can be calculated for each condition specified in Table II-9. Particles smaller than this size are partially cleared from the solution, with the fraction cleared decreasing with decreasing particle size. The calculated range of particle sizes recovered would be further broadened if diffusional effects were included in the calculation. Given the present lack of knowledge of the particle densities and the complications that originate from complex particle shapes, a more detailed calculation does not appear to be warranted at this time.

3. Analyses of the Separated Particles and Groundwaters

Chemical compositions of the particles separated by filtering and centrifuging and the amount of americium associated with them will be measured to determine the extent to which the particles can influence the migration of americium under natural conditions. Analyses completed or in progress include the determination of particle composition by neutron activation analysis and determination of solution composition by ICPAES, neutron activation analyses, and analyses of TOC. Americium concentration in filtered or centrifuged solutions will be determined by radiochemical counting.

REFERENCES

AMES

L. L. Ames, Hanford Basalt Flow Mineralogy, Battelle Pacific Northwest Laboratory, PNL-2847 (1980).

BARGAR

K. M. Bargar, R. Beeson, R. Fournier, and L. Muffler, Present-Day Deposition of Lepidolite from Thermal Waters in Yellowstone National Park, Am. Mineral. 58:901-904 (1973).

CLAYTON-1963

R. Clayton and T. Mayeda, The Use of Bromine Pentafluoride in the Extraction of Oxygen from Oxides and Silicates for Isotope Analysis, Geochim. Cosmochim. Acta 27:43-52 (1963).

CLAYTON-1981

R. Clayton, Isotopic Thermometry, in R. Newton and A. Navrotsky (eds.), Thermodynamics of Minerals and Melts, Springer-Verlag, New York, pp. 85-109 (1981).

FOURNIER

R. Fournier, D. White, and A. Truesdell, Convective Heat Flow in Yellowstone National Park, in Proc. 2nd U.N. Symposium on Development and Use of Geothermal Resources 1:731-739 (1975).

KEITH

T. Keith, M. Beeson, and D. White, Hydrothermal Alteration and Self-Sealing in Y-7 and Y-8 Drill Holes in Northern Part of Upper Geyser Basin Yellowstone National Park, Wyoming, U.S. Geol. Sur. Prof. Pap. 1054-A, 26 pp. (1978).

KIM

J. I. Kim, G. Buckau, F. Baumgaertner, H. G. Moon, and L. Lux, Colloid Generation and the Actinide Migration in Gorleben Groundwaters, Mater. Res. Soc. Symp. Proc. 26:31-40 (1984).

McSPADDEN

W. McSpadden et al., Final Report, The Marysville, Montana Geothermal Project, submitted to U.S. Energy Research and Development Administration (1975).

MEYER

R. E. Meyer, W. D. Arnold, and F. I. Case, Laboratory Control of Valence State, U.S. Nuclear Regulatory Commission, NRC Nuclear Waste Geochemistry '83, NUREG/CP-0052, pp. 106-123 (1984).

O'NEIL-1967

J. O'Neil and H. Taylor, The Oxygen Isotope and Cation Exchange Chemistry of Feldspars, Am. Mineral. 52:1414-1437 (1967).

O'NEIL-1969

J. O'Neil, R. Clayton, and T. Mayeda, Oxygen Isotope Fractionation in Divalent Metal Carbonates, J. Chem. Phys. 51:5547-5558 (1969).

PERRY

D. L. Perry, The Reaction of Uranium and Thorium with Hanford Basalt at Elevated pH, U.S. Nuclear Regulatory Commission, NRC Nuclear Waste Geochemistry '83, NUREG/CP-0052, pp. 53-69 (1984).

RHO

Rockwell Hanford Operations, Rockwell Hanford Operations Site Characterization Report for the Basalt Waste Isolation Project, DOE/RL 82-3 (1982).

SEITZ

M. G. Seitz, G. F. Vandegrift, D. L. Bowers, and T. J. Gerding, Effect of Aged Waste Package and Aged Basalt on Radioelement Release, U.S. Nuclear Regulatory Commission, NRC Nuclear Waste Geochemistry '83, NUREG/CP-0052, pp. 492-512 (1984).

STEINDLER-1984A

M. J. Steindler, Fuel Cycle Programs Quarterly Progress Report, July-September 1983, Argonne National Laboratory Report ANL-83-88 (1984).

STEINDLER-1984B

M. J. Steindler, Nuclear Technology Programs Quarterly Progress Report, January-March 1984, Argonne National Laboratory Report ANL-84-37 (1984).

TAMMEMAGI

H. Tammemagi, G. Grisak, and D. Parrish, A Case History of the Marysville Geothermal Anomaly from a Nuclear Waste Disposal Perspective, INFO-0092, Atomic Energy Control Board, Canada, 55 pp. (1983).

TAYLOR-1968

H. P. Taylor, The Oxygen Isotope Geochemistry of Igneous Rocks, Contrib. Mineral. Petrol. 19:1-71 (1968).

TAYLOR-1979

H. P. Taylor, Oxygen and Hydrogen Isotope Relationships in Hydrothermal Mineral Deposits, in H. Barnes (ed.), Geochemistry of Hydrothermal Ore Deposits, Wiley and Sons, New York, pp. 236-277 (1979).

TRUESDELL

A. Truesdell and J. Hulston, Isotopic Evidence on Environments of Geothermal Systems, in P. Fritz and J. Fontes (eds.), Handbook of Environmental Isotope Geochemistry 1:179-226 (1980).

WEAVER

C. Weaver and L. Pollard, The Chemistry of Clay Minerals, Elsevier, Amsterdam, 213 pp. (1975).

WHITE

D. White, R. Fournier, L. Muffler, and A. Truesdell, Physical Results of Research Drilling in Thermal Areas of Yellowstone National Park, Wyoming, U.S. Geol. Surv. Prof. Pap. 892, 70 pp. (1975).

III. REACTION OF GLASS WITH WATER

(J. K. Bates, T. J. Gerding, D. F. Fischer, and M. J. Smith*)

A. Nevada Nuclear Waste Storage Investigations (NNWSI)

Test Development

(J. K. Bates, T. J. Gerding, and D. F. Fischer)

In work for Lawrence Livermore National Laboratory (LLNL), ANL is developing a Phase II test procedure that will be used to provide licensing information for the Nevada Test Site repository location. Part of the program is to develop the test procedure (T1), part is to demonstrate that the test results will provide the necessary information, and part is to perform actual testing.

Current effort in T1 development has been to produce the reaction vessels that will be used in actual long-term Phase II testing and to initiate a series of these tests using uranium doped defense glass. Additionally, parametric tests are being conducted to establish source term release rates from the waste form/package. Also, analog-type tests (T2) using tuff rock cores and radioactive defense glass are in progress, and results from two five-week Phase II tests using prototype reaction vessels were obtained and compared with previous test results. An abstract describing the Phase II test procedure and the results of initial testing was prepared and submitted for presentation at the Materials Research Society meeting in November 1984.

1. Test 1 (T1) Development

Based on observations made during T1 tests that were conducted using a preliminary vessel design and test procedure, two prototype vessels were constructed and two five-week tests were run (Table III-1). Initial results from these tests have been presented [STEINDLER]. Additional results have been obtained and are presented in Table III-2.

Test 14 was conducted for five weeks using only a waste package. The liquid from the addition of the J-13 water was collected in the bottom of the reaction vessel and analyzed for selected cations by inductively coupled plasma spectroscopy (ICP) and for uranium by fluorescence. The solution analyses and weight-loss results are in good agreement with the data from the preliminary testing reported previously [STEINDLER].

As was noted therein, there was considerable reaction in the interface region between the glass and the stainless steel (SS), and also between the two bottom pieces of SS that are spot welded together. This reaction accounts, in part, for the large amounts of SS components found in solution, and also is the likely cause for the depressed amount of silicon in solution. The cause for this reaction was investigated by determining whether the SS used in the waste-form holder was really Type 304 L, and whether it had been sensitized during manufacture or during welding when the two upright studs were welded to the base.

*Student research participant, Providence College, Providence, RI.

Table III-1. Description of Prototype T1 Testing

Description	Test No.	Analysis No.	Test Period, weeks	Vessel Type	Collection Mode	Glass Weight, g		Surface Area, cm ²	Solution Volume, mL
						Initial	Final		
Prototype Test	14	TF-55	5	304 L	Vessel	11.0722	11.0711	12.23	20.54
	14	TF-56	5	stainless					20.21
	14	TF-61	5	steel					19.98
Prototype Test	15	TF-57	5	304 L	Planchet on tuff	10.9871	10.9860	12.20	20.10
	15	TF-58		stainless					21.2
	15	TF-59		steel					20.0
	15	TF-60							20.0
	15	TF-62							19.99

All the Type 304 L SS components used were analyzed for elemental content, including carbon. All SS analyses were within the error limits of the certification data received from the suppliers.

Sections of SS, as received from the supplier, were checked for sensitization by both the manufacturer and by ANL. No sensitization was detected. The etched appearance of the as-received SS was likely caused by somewhat excess pickling during manufacture, but is not unusual and should not affect the performance of the SS. The SS used in the waste-form holders meets specifications for Type 304 L SS and appears typical of that received from any supplier.

A waste-form holder with two welded areas was sent to LLNL to see if there was any sensitization in the welded areas. The results have not yet been reported.

Recent evidence [DAYAL] indicates that crevice corrosion of SS may be an important mode of corrosion, even in low-carbon steels; crevice corrosion occurred more readily when the grain diameter became less, thereby increasing the grain boundary area. The grain boundary diameter of the SS used in our waste-package holders was ten times less than observed by Dayal [DAYAL], and may be one reason for the pronounced crevice attack. It is also possible that the Fe and Cr silicates that were found on the glass and SS surfaces act as a sink for Fe, Cr, and Si and, thus, promote corrosion of both the glass and the SS.

Test 15 was conducted for five weeks using a SS planchet placed on a tuff cup to divert and collect the water. The results (Table III-2) are in agreement with those of Test 14 and earlier preliminary tests, and reinforce the conclusions that Li and B can be used to measure the release from the glass, that improperly treated tuff releases caliche material, and that good reproducibility of results can be achieved.

Based on appraisals of the preliminary and prototype testing and discussions with personnel of the Savannah River Laboratory (SRL), 30 T1 vessels and waste-package holders are being produced by ANL Central Shops. The production of the vessels has been completed and the waste-package holders are scheduled to be completed by July 1984.

Table III-2. Results of Prototype T1 Testing

Test No.	Analysis	Elemental Analysis, ng (total in solution), except as noted															
		Al	B	Ba	Ca	Co	Cr	Fe	Li	Mg	Mn	Na	Ni	Si	Sr	U	Zn
	J-13 water, ng/mL	<100	130	<10	13600	<20	<20	<10	49	2180	<5	46700	28	30900	41	<1	<10
	SRL 165 glass, element %	2.17	2.11		1.07			8.60	2.18	0.48	2.25	7.64	0.71	25.29	0.13	0.99	
14	Vessel acid soak	2260	5340	225	8200	500	25250	162000	10000	1640	195000	43100	17250	26700		527	
14	Waste package rinse	3030	3030		9900			10100	6470	900	1230	42400	1430	10300	220	1717	
14	2nd vessel soak	4000			7400		16200	64000	460	880	50000	3000	11600	4000		24	3000
14	Total	9300	8400	225	25500	500	41450	236000	16900	3400	246000	88500	30300	41000	220	2268	
15	Vessel acid soak	2400	3800	240	338000		23000	149000	960	8800	153000	301500	13900	54300	3000	119	
15	Waste package rinse		2250		4000			850	14626	640	190	67800	450	16500		466	
15	Tuff support ring	1200			3800		2600	30000		440	580	2000	2100			188	
15	Planchet overnight	1500			3400		13600	68000		860	15400	2400	5800	3800		644	
15	2nd vessel soak	1300			11800		7200	46000	400	1100	50000	9600	7600	4000		58	
15	Total	6400	6050	240	361000		46400	294000	16000	11800	219000	383000	29800	78600	3000	1475	7600

Using these new vessels, previously constructed waste-package holders, tuff vessels made from caliche-free tuff, uranium-doped SRL 165 glass, and pretreated J-13 water, a set of Phase II tests was initiated on June 14, 1984. Complete details of the procedures and materials used will be documented in a topical report. Test results will be reported as they become available.

2. Parametric Testing

The Phase II test procedure incorporates a specific set of physical parameters (test conditions) in a test matrix. These parameters were chosen to be representative of anticipated repository conditions and are not variables in the test matrix. However, many of these parameters may not be fixed in the repository, and they may have significant effects on the eventual release of radionuclides from the waste package.

Some of these parameters include

- (1) the test temperature and the temperature differential between the waste package and the test vessel;
- (2) the contact time between the water and glass (drop rate);
- (3) surface area of the glass contacted by a volume of water (SA/V). This can be a function of the ability of the canister to retain water or the ability of the water to remain on the surface, i.e., vertical vs. horizontal surfaces, and;
- (4) aging of test components.

The effects of these parameters on the degradation of the waste package are being studied in parametric testing. The results will be used to complement the data obtained from the rigorous Phase II tests.

The initial series of parametric tests (P-I) was conducted to investigate the effect of SS on the reaction and its role in controlling the SA/V effect of standing water on the horizontal end pieces of the waste form. We observed that, upon termination of Phase II testing, ~0.3 gm of water remained in contact with the glass, collected mainly in the holes in the top and bottom canister sections. We recognize that SA/V plays an important role in glass/water reactions: the smaller the SA/V the longer it takes for the solution to reach saturation and the greater the amount of material that is released into solution.

The amount of water that remains in contact with the waste form could be a function of the parameters itemized above; however, the experiments were concerned with the effect of altering the SA/V, not the cause of the alteration. The initial tests were conducted without any canister present, and the water was introduced at various drop rates. Some details of the tests were reported previously [STEINDLER]. For most tests, no water remained in the test vessel at the end of the test period because the Teflon test vessels could not be completely sealed. For this reason, the P-I series of tests was terminated and the design of the series was reevaluated.

We had hoped that the P-I set of experiments could be done in Teflon containers so that any effect due to SS could be eliminated; subsequent parametric experiments would be conducted in SS vessels to duplicate Phase II test conditions as closely as possible. However, it was necessary to develop a Teflon vessel for which the release of water during the test period was less than the input. This was accomplished by using longer threaded Teflon vessels (Saville #562), using an epoxy sealer (Torr Seal) to seal the metal-to-Teflon interface where the fitting was threaded into the vessel lid, and tightening the lid twice before beginning an experiment and then once after one day had elapsed.

Teflon was used because of relative inertness, convenience, and low cost. It has the drawback that it represents the introduction of a material other than Type 304 L SS that is porous to certain gases and is physically difficult to seal, the effect of which needs to be interpreted.

Liquid-loss testing conducted without any glass present indicated that the average liquid-loss rate was ~ 0.007 g/d and that, for the test period (up to 30 days), the rate was constant. Additionally, the loss rate for vessels with a threaded feedthrough fitting was no greater than for vessels with a blank lid. This loss represents $\sim 33\%$ of the water added, but some compensation for lost water may be realized by adding additional water to the bottom of the test vessel when the test is initiated.

Using the newly developed test vessels, a new series of P-I experiments, renamed P-II, was begun. In these experiments, the glass was placed on a Teflon grid (Saville #26SC), the top of which was made of sharp inverted vees to reduce the contact area between the grid and the glass. The grid was set in the center of the reaction vessel by placing its four feet in holes drilled into the vessel bottom. The drop feedthrough mechanism was the same as that used in Phase II testing, and 0.075 mL of non-pretreated J-13 water was introduced every 3.5 days. The glass used in testing was SRL black frit (165) with added Cs, Sr, and U. The test matrix and data are given in Tables III-3 and III-4.

Tests have been conducted through 13 weeks. Tests P-II-1 and P-II-2 were sampled and continued after the 6- and 13-week periods. Test P-II-3 was stopped after 6 weeks and Test P-II-4 was stopped after 13 weeks.

Both tests P-II-3 and P-II-4 showed a weight gain, in contrast to a weight loss as observed for Phase II tests done with a SS canister present. The weight gains are small. For test P-II-3, the gain of 0.0001 g is within the uncertainty of the measurements, which is ± 0.0002 g. However, the gain of 0.0007 g for test P-II-4 is definitely indicative of a weight gain.

In all experiments, less Ca, Mg, Sr, and Si were found in solution than were added to the system in the J-13 water. These elements were incorporated into calcium and calcium silicate minerals found covering the top surface of the glass. Photomicrographs and corresponding spectra of two of the minerals are shown in Figs. III-1 to III-4. Identification of these minerals is not complete, but they do contain predominantly Ca and Si and likely account for the decreased amount of these elements in solution. Several other minerals were also noted on the surface and they are being identified also.

Table III-3. Test Matrix for Parametric Testing

Test No.	Time Period, weeks	Date		Sample Mass, g		Surface Area, cm ²			J-13 Water Added, ^a g	Water Lost, ^b g
		Start	End	Initial	Final	Ends	Sides	Total		
P-II-1a ^c	6	2/20/84	4/02/84	9.9678		3.82	9.70	13.52	0.9	
1b	7	4/02/84	5/21/84						1.05	0.66
1c	6.5	5/21/84	7/05/84							
1d	6.5	7/05/84	8/20/84							
1e	6.5	8/20/84	10/04/84							
1f	6.5	10/04/84	11/19/84							
1g	6.5	11/19/84	1/10/85							
1h	6.5	1/10/85	2/25/85							
P-II-2a ^c	6	2/20/84	4/02/84	10.0990		3.82	9.56	13.38	0.9	0.58
2b	7	4/02/84	5/21/84						1.05	0.61
2c	6.5	5/21/84	7/05/84							
2d	6.5	7/05/84	8/20/84							
2e	6.5	8/20/84	10/04/84							
2f	6.5	10/04/84	11/19/84							
2g	6.5	11/19/84	1/10/85							
2h	6.5	1/10/85	2/25/85							
P-II-3 ^d	6	2/20/84	4/02/84	9.9378	9.9379	3.82	9.56	13.38	0.9	0.61
P-II-4	13	2/20/84	5/21/84	10.0620	10.0627	3.82	9.65	13.47	1.95	1.33
P-II-5	26	2/20/84	8/20/84	9.6495		3.73	9.39	13.12		
P-II-6	39	2/20/84	11/19/84	9.5870		3.66	9.34	13.00		
P-II-7	52	2/20/84	2/25/85	9.6366		3.71	9.36	13.07		

^aThe J-13 water was not pretreated.

^b0.5 mL of deionized water (DIW) was added to the test vessel at the beginning of each test period. 0.075 mL of J-13 water was added to each test vessel every 3.5 days. Water lost represents the difference between all water added during a test period and the total water remaining in the vessel at the end of a test period. It is a measure of how well the vessel was sealed.

^cTests P-II-1 and -2 are sampled about every 6.5 weeks. At the end of a test period the glass and water that remains on the glass surface are carefully transferred to a new test vessel and a new teflon stand. The vessel lid is rinsed with DIW and reused as the test continues. Data are presented for each sampling period. An additional 0.5 mL of water is added to the bottom of the test vessel before the test is restarted.

^dAt the termination of the test the waste package is rinsed with DIW. The solution analyses include contributions from the rinsed waste package and the residual solution.

Table III-4. Results of Parametric Testing

Test No.	Analysis No.	Solution Volume, mL	Elemental Analysis, ng (total in solution), except as noted															
			Al	B	Ca	Cr	Cu	Fe	Li	Mg	Mn	Na	Ni	Si	Sr	Zn	U	Ba
	J-13 water, ng/mL		<100	130	13000	<20		<10	49	2130	<5	46700	28	30900	41	<10	<1	
	SRL 165 glass, element %		2.17	2.11	1.07		8.60	2.18	0.48	2.25	7.65	0.71	25.29	0.13			0.99	
P-II-1a	TF 63	20.57	1650	18100	4300		1000	2470	4320	1970	450	28400		9460		820	420	
1b	TF 69	20.75	10375	16200	3940		1700	2280	3110	930	290	28600	435	5800		1900	504	228
1c																		
1d																		
1e																		
1f																		
1g																		
1h																		
P-II-2a	TF 64	20.60	3900	8650	1850		640	1440	1100	560	160	8240		2680		680	250	
2b	TF 71	20.76	12250	5400	2000		540	1300	3100	460	150	23700		4150		500	378	
2c																		
2d																		
2e																		
2f																		
2g																		
2h																		
P-II-3	TF 65	20.45	1060	7630	3480	410	1060	1000	9800	760	1900	76300	2300	16550		530	730	
P-II-4	TF 70	20.77	1120	24300	2000		540	1300	24000	350	2300	173600	2300	33600		660	1800	
P-II-5																		
P-II-6																		
P-II-7

Fig. III-1. A Reaction Product Formed on the Surface of SRL Defense Waste Glass During Parametric Test No. P-II-3

Fig. III-2. Energy Dispersive X-Ray Spectrum of the Reaction Product Shown in Fig. III-1

Fig. III-3. A Second Reaction Product Formed on the Surface of SRL Defense Waste Glass During Parametric Test No. P-II-3

Fig. III-4. Energy Dispersive X-Ray Spectrum of a Calcium-Rich Precipitate from the Surface of Test No. P-II-4

More Al, B, Fe, Mn, Na, Ni, and U were found in solution than can be accounted for by the addition of J-13 water. These elements have been released from the glass. Before any trends can be established or any firm conclusions drawn about the release behavior of these elements, more testing must be conducted. However, it appears that the release of most elements is only slightly decreased from that observed in the Phase II tests.

A correlation between the tests that are being continued (P-II-1a,b and P-II-2a,b) with those that have been terminated (P-II-3 and P-II-4) is not straightforward. Test P-II-2 has a lower release for most elements than does test P-II-1. Additionally, the summed Li and Na results (P-II-2a plus P-II-2b) are less than the amounts observed for terminated test P-II-4. Some solution remains on the waste package when it is transferred to the new reaction vessel, but it seems unlikely that this can account for the difference. Further testing may resolve this point.

Additional parametric tests are planned and will be conducted in the Parr reaction vessels used for the gamma radiation tests after new lids have been built to accommodate drop (liquid) transfer.

3. Test 2 (T2) Development

A T2 analog-type test is in progress using the rationale described previously [STEINDLER]. The goal of T2 is to provide support for the Phase II test method. If the reactions observed in the T2 tests, which attempt to duplicate repository conditions as closely as possible, are similar to those obtained in the Phase II (T1) test, then additional credence is added to the T1 method.

The initial T2 test was begun using a rock core taken from caliche-containing rock. The core was placed in deionized water (DIW) at 90°C for 3-1/2 days, then dried and weighed. It was then soaked in J-13 water and placed in the reaction apparatus for further pretreatment and preliminary testing to adjust the flow rate.

During this final pretreatment stage, the volume of liquid collected was adjusted to ~1.5 mL/d by controlling the temperature and pressure of the water in the input vessel. This value is the largest anticipated flow that would be experienced by this cross section of rock, based on Phase II test conditions for defense waste. To produce a flow of this magnitude, the water in the input vessel was set at 170°C and the pressure was ~165 kPa (gage) (~24 psig).

The output from the system was collected and cation/anion analyses were conducted on the first two samples and last two samples collected. These analyses (Table III-5) indicate that there is caliche material in the core and, while the amount of material decreases as the system is flushed, not all has been removed. No more conditioning was done.

Upon terminating the pretreatment test, the core was cooled overnight, opened, and examined. No water was released during the cooling process. When disassembled, there was 5.59 g of water in the cavity and the core had gained 2 g over the weight obtained during the 3-1/2 day soak. It would be desirable to avoid collecting water in the cavity, although 5.59 g would not be enough to cause direct contact between the liquid and the waste package.

Table III-5. Conditions and Results of Analog Pretreatment Tests^a

Sample Dates	Vol- ume, mL	Concentration, µg/mL								
		Al	B	Ba	Ca	Cr	Cu	Fe	Li	Mg
3/7+3/15	8.95	0.179	9.200	0.140	150	0.029	0.179	<0.027	0.37	11.6
3/22+3/29	9.29	<0.134	3.600	<0.027	335	0.045	0.094	<0.027	0.27	2.4

Sample Dates	Vol- ume, mL	Concentration, µg/mL									
		Mn	Na	Ni	Si	Sr	V	Cl ⁻	F ⁻	NO ₃ ⁻	SO ₄ ²⁻
3/7+3/15	8.95	0.240	171	0.320	81.3	1.05	0.120	134	33	155	305
3/22+3/29	9.29	0.070	91	<0.050	144.5	0.270	0.090	50	30	52	87

^aWeight of tuff core dry - 1173.0 g.
tuff core soaked - 1205.1 g.
tuff core reacted - 1207.2 g.
water in cavity on opening - 5.6 g.

The system was reassembled with a heated input line, and a waste package [STEINDLER] was placed in the cavity. The test was begun with the intention of adjusting the flow to a lower level that would be more realistic of repository conditions. This was accomplished by reducing the input temperature and pressure. With reduced flow, it takes the system longer to equilibrate; a flow of ~ 0.2 mL/d has been achieved.

4. Quality Assurance Plan

The quality assurance (QA) plan was reviewed by LLNL during an onsite visit on May 11, 1984. Suggestions made by the QA representative will be incorporated into the plan. He suggested that only those items essential for the ongoing work be included in the plan. The plan is being reviewed accordingly.

B. Gamma Radiation Testing

(J. K. Bates, T. J. Gerding, and D. F. Fischer)

A set of experiments has been designed to measure the behavior of waste-package components in a gamma radiation field under selected near-term conditions applicable to a repository located in the unsaturated zone in tuff. The experiments are being conducted as part of the Waste Package Task of the NNWSI project.

These conditions were chosen to augment the results from the rock-cup, Phase I tests, which simulate transient standing water that might exist in the unsaturated zone, and include several different test configurations to permit interpretation of the physical processes that occur.

Tests will be done using

- (1) glass disks, Type 304 L SS holders, and aged J-13 well water with SA/V of 0.3 cm^{-1} ;
- (2) glass disks, Type 304 L SS holders, tuff rock, and aged J-13 well water with SA/V of 0.3 cm^{-1} ; and
- (3) crushed glass and aged J-13 well water with SA/V of 1 cm^{-1} .

Each series of tests will be conducted using a Type 304 L SS reaction vessel, at 90°C , for time periods of 7, 14, 28, and 56 days, in a gamma radiation field of 2×10^5 R/h, and with enough air so as not to exhaust the nitrogen available for reaction. Each series of tests will be performed using four glasses: SRL 165 glass containing uranium; SRL 165 glass containing uranium, ^{237}Np , ^{239}Pu , and ^{241}Am ; PNL 76-68 glass containing uranium; and PNL 76-68 glass containing uranium, ^{237}Np , ^{239}Pu , and ^{99}Tc .

At the conclusion of each test, solutions will be analyzed for pH, cations, anions, and radionuclides. The test components will be analyzed for type and degree of reaction using scanning electron microscopy (SEM), energy dispersive X-ray (EDX) analysis, and secondary ion mass spectroscopy (SIMS). The results of these tests will be compared with similar tests conducted without the radiation field.

Current effort has been to make and prepare the SRL glasses, to prepare the PNL glasses, and to set up the ^{60}Co facility for testing. In addition, an abstract describing the proposed experiments and expected results was submitted for presentation at the Materials Research Society meeting in November 1984.

1. SRL Glass Preparation

The SRL glass was made by taking black frit supplied by SRL and doping it with uranium, ^{237}Np , ^{239}Pu , and ^{241}Am . Additionally, to make the composition equivalent to that being used in the Phase I and Phase II tests, small amounts of Cs and Sr were also added. The actinide levels were chosen to be close to those expected in actual Defense Waste Processing Facility (DWPF) glass, but modified slightly to ensure detectability in solution. The levels used are similar to those suggested by SRL.

The glass-making and sample-preparation processes will be detailed in a topical report describing this work. Because there is the possibility of incomplete mixing of the actinides (due to safety restrictions in the CMT facility), several homogeneity checks were made. The homogeneity between different samples was determined by gamma-ray spectroscopy for ^{237}Np , ^{233}Pa , and ^{241}Am , whereas the homogeneity of individual samples was checked by total alpha counting of opposite surfaces of each disk. Two batches of glass were prepared. Generally, for batch No. 2, the homogeneity between samples is $\pm 20\%$, and the variance between each sample surface is $\pm 3\%$. For batch No. 1, the homogeneity between samples is $\pm 20\%$, but the opposite-surfaces variances are larger than expected.

Samples from batch No. 2 are being matched according to total activity and used in test 1 (listed above), whereas samples from batch No. 1 are being used in test 2 where there is tuff in the system.

Crushed samples were prepared from batch No. 2 glass, and gamma-ray variances between samples were less than 3%. Samples of crushed glass and glass disks have also been dissolved for actinide analysis.

2. PNL Glass Preparation

The PNL glass samples were received from LLNL by way of the Materials Characterization Center (MCC). These samples were prepared for testing in the same fashion as SRL glass, and identical test matrices will be run for each glass type. The PNL glass disks were counted with gamma-ray spectroscopy to determine homogeneity (although MCC procedures certainly should produce homogeneous samples). The PNL glass contains large amounts of ^{233}Pa ; thus, only ^{237}Np and ^{233}Pa could be detected. The homogeneity between samples is less than 5%. A sample of crushed PNL glass was also dissolved and analyzed for ^{237}Np and ^{239}Pu .

3. Oven and Vessel Preparation

The tests will be run in a hot-pack oven placed as close as possible to the ^{60}Co source. Because of the geometry of the source, a complete dosimetry of the oven was performed to ensure that each test position receives a dose rate of $2 \times 10^5 \pm 0.1$ R/h.

The tests will be conducted in 22-mL Parr vessels made from Type 304 L SS. Fifty-six tests will be run simultaneously, and six shelves were constructed to accurately position each vessel.

The gasket material used to seal the vessels will be silicone rubber. This material was tested as the gasket in a 22-mL Parr vessel to see whether it would maintain its integrity when exposed to the total dose expected for 56 days. The vessel received 4×10^8 rad over a period of 50 hours at 40°C. Although the gasket hardened somewhat, it was still pliable. There was no weight change in the water added to the vessel. Analysis of the solution in the vessel (Table III-6) indicated an increase in Si and Zn in solution and generation of NO_3^- .

Table III-6. Water Composition in Blank Silicone Gasket
Test No. TF-66^a

Composition, ppm							
Al	B	Ba	Ca	Cu	Fe	Li	Mg
0.18	<0.03	<0.01	0.1	0.52	<0.01	<0.02	0.13

Composition, ppm							
Mn	Na	Ni	Si	Zn	F^-	Cl^-	NO_3^- SO_4^{2-}
0.007	<0.1	0.13	2.5	1.16	0.25	0.1	13.5 0.3

^aThe test used a 22-mL Parr reaction vessel made of Ti to which 10.55 mL DIW was added. The test duration was 50 h, with a total irradiation of 4×10^8 rad at 40°C.

The tests will use J-13 water that has been equilibrated with caliche-free tuff. The water was pretreated according to LLNL instructions and analyzed prior to use (Table III-7).

The tests had been scheduled to begin in June, but Parr has delayed delivery of the reaction vessels and the tests are now scheduled to begin on July 5. Results will be reported as they become available and will be compiled in an ANL topical report describing the program.

C. Glass Hydration Studies

(M. J. Smith* and J. K. Bates)

1. Background

The hydration of simulated nuclear waste glass has been studied extensively. The contact of the glass with water vapor results in both the formation of surface minerals and the formation of a double or single hydration

*Student research participant, Providence College, Providence, RI.

Table III-7. Analysis of Pretreated J-13 Water To Be Used in Irradiation and Phase II Testing

Volume of Water Batch, ^a L	Composition, ppm								
	Al	B	Ca	Fe	Li	Mg	Na	Si	Sr
2	0.78	0.18	4.5	0.018	0.064	0.39	46.6	35.3	0.03
1	0.63	0.16	9.1	0.010	0.044	0.96	46.5	34.4	0.045

^aA 2-L batch was made for gamma radiation testing and a 1-L batch was made for Phase II testing. Different samples of crushed tuff were used in the equilibrations.

layer. The hydration process appears to occur in two stages. During the initial, slower stage, trapezohedral crystals of analcime are formed and the surface attains a sponge-like appearance due to the formation of a montmorillonite. Analcime is a mineral of composition, $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$. Montmorillonite is a group of clay minerals that may contain sodium, aluminum, silicon, manganese, iron, calcium, and nickel, as well as other elements. During the second stage, the reaction rate speeds up and the surface becomes covered with calcium silicates, primarily tobermorite, $\text{Ca}_5(\text{OH})_2\text{Si}_6\text{O}_{16} \cdot 4\text{H}_2\text{O}$.

This research was to determine how the concentration of the various elements varies as the reaction proceeds. Because the layer thicknesses vary between about 3 and 30 μm , one of the easiest means of determining the elemental composition of the layers is through EDX analysis.

2. Instrumentation

To examine specimens and to locate an appropriate location for X-ray analysis, the ISI-SS40 scanning electron microscope (SEM) was used. The ISI-SS40 has a resolving power of 40 Å. It magnifies a sample from 10 to 200,000 times in its normal operating mode. Acceleration voltage can be set at 2, 5, 10, or 20 keV. Its electron gun contains a tungsten hairpin-type filament. The signal can be detected through either secondary electrons or backscattered electrons with the Robinson backscattered electron (RBSE) detector. The electrons emitted by a solid as a consequence of primary excitation by the electron beam are called secondary electrons. Backscattered electrons are those that emerge from a solid as a result of inelastic collisions.

The Princeton Gamma-Tech (PGT) System III X-ray analyzer consists of a display screen, a keyboard, a computer with two disk drives, and software programs. Also attached to the System III are a line printer and an x-y plotter. The software, PGT Microanalysis System Version 4.22 (January 1983), can be used to collect, store, display, and manipulate X-ray data. The instrument uses a 12.5-mm^2 Si(Li) detector with 155-eV resolution, and is interfaced with the ISI-SS40.

3. Experiment

Initial studies were performed to determine if EDX analysis gives acceptable quantitative analyses of the composition of glasses. The results are given in Table III-8.

All standards proved to be acceptable. The SRL 211 glass with 8% calcium was arbitrarily chosen as the standard to be used in further analyses, and the standard intensities were stored on disk.

Samples identified as W-3A, W-4A, W-7, W-9, W-10, and W-5A were previously reacted at 202°C using the procedure described by BATES et al. [BATES]. They were initially coated with gold to conduct electrons off the sample surface. Inasmuch as the presence of gold interferes with quantitative analysis, the gold coating was removed, and the samples were coated with carbon. Carbon also conducts electrons; but, because its X-rays are too low in energy to be detected, it does not interfere with quantitative analyses. The procedure for removing the gold was as follows.

- (1) As much gold as possible was removed by rubbing the sample with a cloth soaked in alcohol. Likewise, a ring of silver paint was removed with alcohol.
- (2) The sample was polished on a 1- μ m diamond wheel for about two minutes.
- (3) The sample was then placed in a polisher of 0.05- μ m Al_2O_3 in kerosene. It was left there until no gold remained visible to the naked eye, about one hour.
- (4) The sample was then washed off, carbon coated, and the outside edge was painted with silver paint.
- (5) Finally, the sample was examined with a SEM using the RBSE detector to determine if all the gold had been removed.

Samples M1 through M7 were reacted and treated by the following procedures.

The samples were cut from an ingot of SRL 131 defense waste glass, the composition of which is given in Table III-9, using an Isomet saw with a low-concentration diamond wafering blade using water as the cutting fluid. The rough-cut samples were polished on both sides and one edge using 600-grit Al_2O_3 paper with water, and were then cleaned ultrasonically with ethanol.

The reaction vessel was a tantalum-lined SS bomb made by Parr, Inc. The vessel consisted of a body, lid, and Teflon washer; the washer was compressed to form a seal between the body and the lid. The volume of the vessel was 21.3 cm³, within which, at 202°C, 0.17 g of water was required to maintain water vapor saturation. A slight excess of water was added to offset water losses during heating.

Table III-8. Tests of Glass Standards^a

Element ^c	Composition, wt % ^b		
	Original	Normalized	BSAM ^d
STEP 1			
<u>Standard:</u> USNM 111240 basaltic glass			
<u>Analysis:</u> SRL-211 glass with 2% Ca			
Na	11.90		11.02
Al	2.09		2.10
Si	21.61		21.68
S	0.13		0.16
Ca	1.69		1.53
Mn	2.34		2.01
Fe	10.01		10.15
Ni	1.19		1.39
O	43.91		36.57
			<u>86.59</u>
B	2.37		7.62 B ₂ O ₃
Li	1.37		2.95 Li ₂ O
	<u>98.61</u>		<u>97.16</u>
<u>Analysis:</u> SRL-211 glass with 5% Ca and without rare earths			
Na	11.31		10.88
Al	2.13		2.35
Si	21.71		21.47
S	0.34		0.52
Ca	3.85		3.64
Mn	2.84		1.92
Fe	8.68		8.60
Ni	0.86		0.94
O	43.50		37.08
			<u>87.40</u>
B	2.21		7.12 B ₂ O ₃
Li	1.35		2.91 Li ₂ O
	<u>98.78</u>		<u>97.43</u>
<u>Analysis:</u> SRL-211 glass with 8% Ca			
Na	11.10		10.74
Al	2.09		2.14
Si	20.89		20.97
S	0.30		0.45
Ca	5.56		5.25
Mn	2.32		1.91
Fe	8.55		8.33
Ni	0.86		0.95
O	43.55		36.69
			<u>87.43</u>
B	2.20		7.10 B ₂ O ₃
Li	1.33		2.87 Li ₂ O
	<u>98.75</u>		<u>97.40</u>

(contd)

Table III-8. (contd)

Element ^c	Composition, wt % ^b		
	Original	Normalized	BSAM ^d
STEP 2			
<u>Standard:</u> SRL-211 glass with 2% Ca (normalized values)			
<u>Analysis:</u> SRL-211 glass with 2% Ca			
Na		12.05	12.08
Al		2.12	2.11
Si		21.88	22.05
S		0.13	0.16
Ca		1.71	1.70
Mn		2.37	2.36
Fe		10.14	10.12
Ni		1.20	1.19
O		44.46	37.48
			89.25
B		2.50	7.72 B ₂ O ₃
Li		1.39	2.99 Li ₂ O
		99.85+0.15 ^e	99.96
<u>Analysis:</u> SRL-211 glass with 5% Ca and without rare earths			
Na		11.39	12.02
Al		2.15	2.37
Si		21.87	21.92
S		0.34	0.53
Ca		3.88	4.04
Mn		2.86	2.25
Fe		8.74	8.58
Ni		0.87	0.82
O		43.81	38.24
			90.77
B		2.23	7.17 B ₂ O ₃
Li		1.36	2.93 Li ₂ O
		99.50+0.50 ^e	100.87
<u>Analysis:</u> SRL-211 glass with 8% Ca			
Na		11.20	11.82
Al		2.11	2.16
Si		21.07	21.35
S		0.30	0.46
Ca		5.61	5.83
Mn		2.34	2.24
Fe		8.62	8.31
Ni		0.87	0.83
O		43.93	37.81
			90.81
B		2.22	7.16 B ₂ O ₃
Li		1.34	2.89 Li ₂ O
		99.61+0.39 ^e	100.86

(contd)

Table III-8. (contd)

Element ^c	Composition, wt % ^b		
	Original	Normalized	BSAM ^d
STEP 3			
<u>Standard:</u> SRL-211 glass with 8% Ca (normalized values)			
<u>Analysis:</u> SRL-211 glass with 2% Ca			
Na		12.05	11.57
Al		2.12	2.06
Si		21.88	22.01
S		0.13	0.11
Ca		1.71	1.63
Mn		2.37	2.46
Fe		10.14	10.49
Ni		1.20	1.24
O		44.46	37.31
			88.88
B		2.40	7.72 B ₂ O ₃
Li		1.39	2.99 Li ₂ O
		99.85±0.15 ^e	99.59
<u>Analysis:</u> SRL-211 glass with 5% Ca and without rare earths			
Na		11.39	11.45
Al		2.15	2.31
Si		21.87	21.81
S		0.34	0.37
Ca		3.88	3.88
Mn		2.86	2.35
Fe		8.74	8.89
Ni		0.87	0.85
O		43.81	37.71
			89.62
B		2.23	7.17 B ₂ O ₃
Li		1.36	2.93 Li ₂ O
		99.50±0.50 ^e	99.72
<u>Analysis:</u> SRL-211 glass with 8% Ca			
Na		11.20	11.30
Al		2.11	2.11
Si		21.07	21.30
S		0.30	0.32
Ca		5.61	5.60
Mn		2.34	2.33
Fe		8.62	8.61
Ni		0.87	0.86
O		43.93	37.39
			89.82
B		2.22	7.16 B ₂ O ₃
Li		1.34	2.89 Li ₂ O
		99.61±0.39 ^e	99.87

(contd)

Table III-8. (contd)

Element ^c	Composition, wt % ^b		
	Original	Normalized	BSAM ^d
STEP 4			
<u>Standard:</u> USNM 111240 basaltic glass, except SRL-211 glass with 2% Ca for Mn			
<u>Analysis:</u> SRL-211 glass with 2% Ca			
Na	11.90		11.08
Al	2.09		2.11
Si	21.61		21.72
S	0.13		0.16
Ca	1.69		1.53
Mn	2.34		2.35
Fe	10.01		10.14
Ni	1.19		1.37
O	43.91		36.73
			<u>87.19</u>
B	2.37		7.62 B ₂ O ₃
Li	1.37		2.95 Li ₂ O
	<u>98.61</u>		<u>97.76</u>
<u>Analysis:</u> SRL-211 glass with 5% Ca and without rare earths			
Na	11.31		10.99
Al	2.13		2.36
Si	21.71		21.56
S	0.34		0.53
Ca	3.85		3.64
Mn	2.84		2.25
Fe	8.68		8.60
Ni	0.86		0.94
O	43.50		37.33
			<u>88.20</u>
B	2.21		7.12 B ₂ O ₃
Li	1.35		2.91 Li ₂ O
	<u>98.78</u>		<u>98.23</u>
<u>Analysis:</u> SRL-211 glass with 8% Ca			
Na	11.10		10.80
Al	2.09		2.15
Si	20.89		21.00
S	0.30		0.45
Ca	5.56		5.25
Mn	2.32		2.23
Fe	8.55		8.33
Ni	0.86		0.95
O	43.55		36.85
			<u>88.01</u>
B	2.20		7.10 B ₂ O ₃
Li	1.33		2.87 Li ₂ O
	<u>98.75</u>		<u>97.98</u>

(contd)

Table III-8. (contd)

Element ^c	Composition, wt % ^b		
	Original	Normalized	BSAM ^d
STEP 5			
<u>Standard:</u> USNM 111240 basaltic glass, except Si for Ba and Pb			
<u>Analysis:</u> NBS glass			
Na	2.03		-
Al	1.94		1.99
Si	31.78		31.63
K	6.07		5.25
Ca	0.13		0.08
Fe	0.07		0.00
Ba	0.25		0.23
Pb	0.08		1.35
O	52.10		39.04
			<u>79.57</u>
B	5.35		17.22 B ₂ O ₃
Li	0.22		0.47 Li ₂ O
	<u>100.02</u>		<u>97.26</u>

^aStandard conditions: takeoff angle = 30.5°
working distance = 33.5 mm
tilt = 0°
probe current = 4 x 10⁻⁹ A
potential = 19 keV
time = 200 s

Ar and Ge used for background windows for analyses.

Efficiency: USNM basaltic glass used for efficiency spectrum.

Mg and P used for efficiency fitting windows.

Ar and Ga used for background windows in efficiency.

^bData are instrumental indications; proper accuracy will be implied by rounding all values to one decimal position.

^cFe in +3 oxidation state; O by stoichiometry.

^dBSAM: a bulk sample quantitative data-reduction program.

^eOther elements.

The reaction vessel was boiled in a solution of 1 vol % nitric acid for one hour and then in a solution of distilled water for one hour.

The samples were suspended from a 125- μ m (5-mil) Teflon thread tied around the sample and attached to a Teflon support. Duplicate samples were placed in each vessel. Care was taken to ensure that no piece of glass was touching another piece or the side of the vessel.

Table III-9. Composition of
SRL 131 Defense
Waste Glass^a

Oxide	Composition, wt %
SiO ₂	44.0
Na ₂ O	13.7
Fe ₂ O ₃	14.3
B ₂ O ₃	10.9
CaO	1.4
MnO	3.1
Al ₂ O ₃	3.5
Li ₂ O	4.2
NiO	1.8
TiO ₂	0.7
MgO	1.6
ZrO ₃	0.4
La ₂ O ₃	0.4

^aThe detector cannot detect B or Li because the energies of the X-rays they emit are too low. La and Zr are present in quantities too low to detect accurately.

A measured amount of DIW (pH 6) was added to each vessel and the vessel was sealed. The vessels were placed in a constant-temperature ($\pm 1.5^{\circ}\text{C}$) oven, and held for a predetermined period of time.

At the end of the reaction the lower portion of the vessel was quenched immediately in water. The container was opened and the Teflon support removed. The lid was placed back on and the vessel weighed. When the vessel had cooled, the pH of the water was tested. The results of the reaction of the samples are tabulated in Table III-10.

The samples were examined to see if they were evenly reacted, if they were touching the sides, or if any water had condensed on them. Each sample was then taken off the holder and held on a mount by double-sided

Table III-10. Results of Reaction of Samples at 202°C

Sample No.	Reaction Time, h	Mass of Water, g		pH	Layer Thickness, μm	Comments
		Initial	Final			
M-1	52	0.2570	0.2277	5-6	3.9 ± 0.5	Analcime + some calcite formation (impurity)
M-2	122	0.2603	0.1095	5-6	-	Contaminated w/chlorine
M-3	167	0.2546	0.0678	8-9	13.3 ± 0.9	Analcime, very limited calcium silicate formation
M-4	217	0.3152	0.1830	8	15.3 ± 1.0	Only one sample reacted, layer broken away from large part of other sample
M-5	275.5	0.2648	0.1030	5-6	3.7 ± 0.4	Limited analcime formation
M-6	331	0.2429	0.1852	6-7	22.1 ± 1.3	Sponge + large analcimes + calcium silicate formation
M-7	378	0.2765	0.0938	8	25.0 ± 2.3	Sponge + large analcimes + calcium silicates
W-3A	48	0.2707	0.2535	8	9.2 ± 0.6	Analcime, sponge, puffy
W-4A	96	0.2844	0.2549	9	12.3 ± 0.5	Analcime, sponge, somewhat puffy
W-7	144	0.2697	0.1400	6	13.8 ± 1.6	Analcime, some tobermorite
W-9	169	0.2694	0.2481	8	15.9 ± 2.0	Analcime, sponge, somewhat puffy covering analcime
W-10	235	0.2678	0.2422	8	18.0 ± 1.0	No surface picture
W-5A	192	0.2681	0.2133	7	27.0 ± 1.5	Analcime, some tobermorite

adhesive tape, where it was broken in half with a hammer and chisel. One half was removed to be placed in an epoxy. The other half was carbon coated and labeled, in preparation for surface examination.

To mount a sample in the epoxy for examination of the cross section, the mold was first wiped with ethanol. A release reagent was then swished around the mold. The epoxy was created by mixing 4.8 g of Epon V-40 curing agent and 8.0 g of Epon 815 resin. The desired edge of the sample was placed at the bottom of the mold and the epoxy was dried overnight. It was then placed in a 40°C oven for two hours, after which the mount was removed from the mold.

The back of the mount was labeled with permanent ink. The sample was first polished with 600-grit Al_2O_3 polishing paper with water until the surface had been removed from both the glass and the layer. The sample was then cleaned ultrasonically in water for about 30 seconds to remove particles, and then rinsed off in distilled water and air dried. Next, it was polished on 6- μm diamond paper for about 30 seconds, until the scratches from the 600-grit paper had been removed. The sample was again cleaned ultrasonically in water and rinsed off. It was then polished with 1- μm diamond paper for about 30 seconds and cleaned off.

The sample was carbon coated and the outside edge painted with silver paint. The cross section was then examined with the SEM, and a quantitative analysis of the hydration layer was performed using the X-ray analyzer. The standard conditions were the same as those used in testing the glass standards, as listed in the footnotes to Table III-8. The samples were analyzed for oxides of sodium, magnesium, aluminum, silicon, calcium, titanium, manganese, iron, and nickel. Oxygen was computed using stoichiometry with iron in the +3 oxidation state. Silicon was used as the scaling standard for titanium and magnesium. Results of the analyses are given in Table III-11.

Table III-11. Results of Analyses of Glass Samples^a

Oxide	Composition, wt % ^b		
	M-5	M-1	W-3A
Na_2O	5.18 $\pm$ 1.39	2.29 $\pm$ 1.37	5.66 $\pm$ 1.67
MgO	2.29 $\pm$ 0.47	2.92 $\pm$ 0.39	3.12 $\pm$ 0.89
Al_2O_3	3.40 $\pm$ 0.42	2.86 $\pm$ 0.50	2.24 $\pm$ 0.22
SiO_2	43.27 $\pm$ 3.27	45.35 $\pm$ 1.57	41.42 $\pm$ 3.07
CaO	1.35 $\pm$ 0.57	1.26 $\pm$ 0.22	1.98 $\pm$ 0.19
TiO_2	1.35 $\pm$ 0.23	1.41 $\pm$ 0.16	1.55 $\pm$ 0.11
MnO	2.93 $\pm$ 0.25	3.41 $\pm$ 0.21	3.34 $\pm$ 0.29
Fe_2O_3	12.84 $\pm$ 1.33	14.24 $\pm$ 0.72	14.02 $\pm$ 0.77
NiO	1.66 $\pm$ 0.66	1.92 $\pm$ 0.20	1.97 $\pm$ 0.11
	74.27	75.66	75.30

Oxide	Composition, wt % ^b		
	W-4A	M-3	W-7
Na_2O	3.73 $\pm$ 1.01	4.26 $\pm$ 1.73	4.35 $\pm$ 2.16
MgO	3.44 $\pm$ 0.59	3.05 $\pm$ 0.23	3.94 $\pm$ 0.35
Al_2O_3	2.45 $\pm$ 0.31	2.06 $\pm$ 0.20	2.20 $\pm$ 0.26
SiO_2	40.69 $\pm$ 2.18	45.46 $\pm$ 2.19	42.04 $\pm$ 1.72
CaO	1.51 $\pm$ 0.23	0.89 $\pm$ 0.32	2.04 $\pm$ 0.15
TiO_2	1.44 $\pm$ 0.16	1.46 $\pm$ 0.16	1.36 $\pm$ 0.07
MnO	3.82 $\pm$ 0.26	3.60 $\pm$ 0.15	3.14 $\pm$ 0.25
Fe_2O_3	15.15 $\pm$ 0.95	16.39 $\pm$ 0.56	13.17 $\pm$ 0.98
NiO	2.11 $\pm$ 0.20	1.81 $\pm$ 0.12	1.81 $\pm$ 0.13
	74.34	78.98	74.05

(contd)

Table III-11. (contd)

Oxide	Composition, wt % ^b		
	M-4 ^c	W-9	W-10
Na ₂ O	1.84 ± 1.33	3.77 ± 1.70	3.48 ± 1.14
MgO	3.14 ± 0.63	3.16 ± 0.53	2.87 ± 0.31
Al ₂ O ₃	4.70 ± 0.28	2.10 ± 0.24	2.32 ± 0.15
SiO ₂	43.31 ± 3.05	39.68 ± 1.17	39.91 ± 1.07
CaO	1.71 ± 0.64	1.53 ± 0.43	1.91 ± 0.58
TiO ₂	1.63 ± 0.16	1.57 ± 0.08	1.64 ± 0.10
MnO	2.99 ± 0.13	3.37 ± 0.12	3.45 ± 0.15
Fe ₂ O ₃	20.56 ± 1.40	13.99 ± 0.75	14.77 ± 0.66
NiO	1.85 ± 0.16	1.87 ± 0.10	1.88 ± 0.11
	81.73	71.04	72.23

Oxide	Composition, wt % ^b		
	M-6	M-7	W-5A
Na ₂ O	2.62 ± 0.94	4.19 ± 1.52	3.68 ± 0.87
MgO	2.17 ± 0.32	2.73 ± 0.23	3.32 ± 0.27
Al ₂ O ₃	1.98 ± 0.15	2.40 ± 0.18	2.06 ± 0.17
SiO ₂	46.84 ± 1.38	47.79 ± 0.75	45.21 ± 1.68
CaO	0.48 ± 0.15	0.75 ± 0.24	1.37 ± 0.30
TiO ₂	1.42 ± 0.20	1.40 ± 0.09	1.81 ± 0.13
MnO	3.75 ± 0.24	3.46 ± 0.16	3.47 ± 0.10
Fe ₂ O ₃	17.12 ± 0.90	16.34 ± 0.62	15.60 ± 0.55
NiO	1.78 ± 0.12	1.83 ± 0.06	1.99 ± 0.11
	78.16	80.89	78.51

^aListed in order of increasing hydration-layer thickness.

^bData are instrumental indications; proper accuracy will be implied by rounding all values to one decimal position.

^cNot necessarily a representative sample, because the layer was broken away from most of the sample and only a few spectra were taken.

After analysis of several samples, it became apparent that the micro-processor was assigning too high a background to the layer analyses in the energy range below 2 keV. To correct for this, a new efficiency spectrum was run; SRL 211 glass with 2% Ca was used as the new efficiency spectrum with Ar and Ge as the background-fitting windows and Mg and P as the efficiency-fitting windows. The reconstruction of the background in the energy region below 2 keV was thereby improved.

During analysis of the bulk glass, the count rate usually averaged about 1000 c/s; it varied between about 950 and 1050 c/s. When the layer was not level with the bulk glass, the count rate was significantly higher or lower, thus affecting the analyses. For this reason, several of the spectra were not used in tabulating the average oxide composition in some samples.

4. Conclusions

Samples M-6, M-7, and W-5a are all in the second stage of hydration, based upon both hydration layer thickness and surface topography. All other samples are in the first stage of hydration.

In all samples, there is noticeably less Na_2O in the hydration layer than there was in the bulk glass. This is expected because the first surface features to appear are analcimes, which contain sodium.

On the other hand, MgO is present in higher concentrations in the layer than in the bulk glass. It is not incorporated into any of the surface minerals in a significant amount. As other oxides are removed from the layer and are replaced by water, the MgO concentration should increase.

The CaO concentration is generally above 1.4 wt % during the first stage of the reaction, and below 1.4 wt % during the second stage when calcium silicates begin to form. One exception to this is sample M-3, which has a low concentration of CaO . There is some calcium silicate formation on this sample, even though the hydration layer thickness indicates that it is in the first stage of the reaction.

The concentration of Al_2O_3 is roughly 1 wt % lower in the layers than it was in the original glass. The concentration should be lower, because aluminum is present in analcime.

In all "W" samples (i.e., those previously reacted by Bates et al. [BATES]) with the exception of W-5A, the SiO_2 concentration is appreciably below its bulk glass concentration of 44 wt %. Silicon is present in both analcime and tobermorite, so this is expected. In samples M1-M7, the count rates were generally above 1000 c/s. This increases the observed percentage of SiO_2 significantly. The SiO_2 seems to be more affected by the count rate than any of the other oxides on an absolute scale.

The concentration of Fe_2O_3 varies from sample to sample with no apparent pattern. Oxides of manganese, titanium, and nickel all have relatively stable concentrations throughout the reaction.

In general, the concentrations of the oxides vary in accordance with the surface features. Further testing on samples reacted at other temperatures and with different glasses should be performed and the results compared with those obtained here.

REFERENCES

BATES

J. K. Bates et al., The Hydration Process of Nuclear Waste Glass: An Interim Report, Argonne National Laboratory Report ANL-82-11 (1982).

DAYAL

R. K. Dayal et al., Intergranular Attack During Crevice Corrosion of Stainless Steels, Mater. Lett. 2(3):248 (1984).

STEINDLER

M. J. Steindler, Nuclear Technology Programs Quarterly Progress Report, January-March 1984, Argonne National Laboratory Report ANL-84-37 (1984).

IV. TRU REMOVAL FROM HIGH-LEVEL WASTE (G. F. Vandegrift and R. A. Leonard)

A. Introduction

The objective of this program is to develop a series of conceptual flowsheets for removing and concentrating transuranic elements (TRU) in Hanford current acid waste (CAW) and dissolved sludge waste (DSW) by two solvent extraction systems. One of the extractants is dihexyl-N, N-diethylcarbamoylmethylphosphonate (DHDECMP); the other extractant is octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (O Φ D[IB]CMPO). Both extractants are diluted by ~30 vol % tributyl phosphate (TBP) in a normal paraffinic hydrocarbon (NPH) mixture of C₁₁-C₁₄ chain length. These two solvents are referred to as CMP- and CMPO-TRUEX, respectively.

A study was done at Rockwell Hanford Operations (RHO) that showed a substantial cost advantage to separating the TRU from the vast bulk of the waste, thereby converting the latter to nonTRU waste and making it eligible for near-surface disposal. The concentrated and greatly reduced mass of TRU waste could then be buried in a deep geologic repository. To qualify commercial waste as nonTRU waste, the concentration of alpha activity must be less than 100 nCi/g; there is no prescribed limit, at this time, for defense waste. Therefore, we are studying the reduction of the TRU content in the bulk of the waste to levels of 100 and 1000 nCi/g.

Along with conceptual flowsheets with complete material balances, this project has defined other elements of this process, such as (1) process flexibility, (2) equipment, (3) safety, and (4) availability and cost of the solvent inventory and makeup.

After the flowsheets were computed using literature data and information supplied by E. Philip Horwitz et al., Separations Group, Chemistry Division, ANL, two countercurrent laboratory tests of the CMPO extraction of TRU from DSW were performed. The extraction scheme was tested twice: a cold experiment performed to collect samples for inductively coupled plasma (ICP) analysis of important fission products, and an experiment performed to collect radionuclide data. The feed solution for the second test contained radioisotopes of americium, plutonium, neptunium, and technetium.

B. Progress

1. Experimental Verifications of Flowsheets for TRU Removal from DSW

Two countercurrent experiments were performed using the CMPO-TRUEX solvent to extract TRU from synthetic DSW. The first countercurrent experiment was run to establish the behavior of fission product, corrosion product, and chemical reagent species (e.g., Fe and Al) that are present in the DSW. After this experiment had been continued long enough to assure most species had reached a near steady-state condition in the apparatus, samples of both phases were removed from each stage, and the remaining volumes were left in the system to initiate the second experiment. The inactive feed solution was replaced by one of a composition that was the same except for containing americium, plutonium, neptunium, and technetium. The volumes of the feed

additions were decreased to those commensurate with the lower phase volumes in each stage. The experiment was continued until the precalculated requisite number of raffinate samples were collected so that the TRU concentrations in them increased to greater than 90% of their steady-state concentrations.

The phases in these experiments demonstrated good disengagement, and there were no signs of third phase or interfacial crud formation. The extraction behavior of all DSW components, except neptunium, was as expected. The distribution ratios for neptunium were lower than expected and diminished from stage to stage, indicating that all the neptunium was not present as the highly extractable Np(IV) species; the concentration of the much less extractable NpO_2^+ species was $\sim 1/7$ that of Np(IV) . Even with the disappointing behavior of neptunium, the ability to reduce the TRU level in the solidified raffinate to less than 100 nCi/g with seven extraction stages was demonstrated.

The stripping behavior of the loaded organic phase was shown to need more work. The stripping behavior of americium and plutonium was adequate with a strip solution of dilute nitric acid containing hydroxylammonium nitrate, but that of neptunium was not.

On the whole, the TRUEX process has shown great signs of success. However, there is still much work to do before pilot plant testing can begin. The results of this study will be published in July 1984 [VANDEGRIFT].

2. TRU Removal from Complexant Concentrate Waste Solution

Work has begun on designing a flowsheet to decrease the TRU content below 100 nCi/g of solid raffinate of another Hanford PUREX waste--complexant concentrate waste (CCW). This waste is a result of the Hanford process for ^{90}Sr recovery from PUREX waste by a solvent extraction process using a mixed bis(2-ethylhexyl)phosphoric acid/tributyl phosphate solvent. During ^{90}Sr extraction, tripositive metal ions were held in the aqueous phase with a variety of complexing agents. These complexants and their radiolytic/hydrolytic decomposition products are present in CCW at a concentration of ~ 70 g/L of organic carbon. The TRU content of this waste is ~ 200 -400 nCi/g of solid and, therefore, must be reduced to qualify the bulk of this waste as nonTRU waste.

Experimental work is beginning by preparing a synthetic CCW solution. Distribution ratios of TRU and important inert elements will be measured under a variety of process conditions to determine the best conditions for a reference flowsheet for TRU removal. The synthetic CCW solution will be treated by ^{60}Co radiation to simulate radiolytic decomposition of the complexants before distribution ratio measurements begin.

REFERENCE

VANDEGRIFT

G. F. Vandegrift, R. A. Leonard, M. J. Steindler, E. P. Horwitz, L. J. Basile, H. Diamond, D. G. Kalina, and L. Kaplan, Transuranic Decontamination of Nitric Acid Solutions by the TRUEX Solvent Extraction Process--Preliminary Development Studies, Argonne National Laboratory Report ANL-84-45 (1984).

V. LIGHT WATER BREEDER REACTOR PROOF-OF-BREEDING (LWBR-POB) ANALYTICAL SUPPORT PROJECT

(N. M. Levitz, R. A. Benson, E. L. Callis,* T. F. Cannon, G. L. Chapman,[†]
P. G. Deeken, J. E. Fagan, D. G. Graczyk,* R. R. Heinrich,* J. C. Hoh,
R. W. Kessie,[‡] J. E. Kincinas, R. A. Leonard, F. J. Martino,
R. E. Nelson, D. J. Raue, L. N. Ruppert, and C. G. Wach)

Current project efforts are directed toward demonstrating operational readiness for the end-of-life (EOL) campaign, scheduled to begin with the arrival at ANL of the first LWBR fuel rod in August 1984. Thus far, a demonstration of operational readiness has occurred in two stages. First, all equipment systems and operating procedures developed at ANL for shearing fuel rods into segments, dissolving those segments, and conducting uranium and fission product analyses on the resulting solutions were individually subjected to a series of qualification tests, according to plans developed by ANL and agreed to by the Bettis Atomic Power Laboratory (BAPL). Following successful completion of the qualification tests, ANL processed one full-length, irradiated, experimental GRIP-II[‡] rod [Rod No. 79-440, also referred to as a validation rod (VR)], using the qualified shear and dissolver equipment and procedures. A delay in the shipment of the initial LWBR fuel rod afforded the opportunity to expand the previously planned training of project personnel and, thus, provided each operator with a more detailed, hands-on review of shear, dissolver, and general facility operations. Technical progress on the major subactivities is reported below.

A. Full-Scale Shear Facility (FSSF)

(J. C. Hoh, R. A. Benson, T. F. Cannon, J. E. Fagan, and C. G. Wach)

Classroom and hands-on training sessions were held this quarter to familiarize shear operators with the most recent version of the computerized full-scale shear operating procedure, OPRFSS. Several minor software problems noted in OPRFSS as a result of these training sessions were brought to the attention of the project programmers for software update; some minor changes were also recommended. Overall, the facility is in a state of readiness for the start of the EOL campaign.

Installation of a newly designed, two-piece swivel booting over the Cell M-3 master/slave (M/S) manipulators and of a portable radiation monitor probe are scheduled for early next quarter. The jointed booting is designed to permit the lower section to rotate independently of the fixed, upper section. These installations will require suited entries into the alpha barrier containment.

B. Dual Dissolver System (DDS)

(F. J. Martino, P. G. Deeken, R. A. Benson, T. F. Cannon, J. C. Hoh,
J. E. Kincinas, D. J. Raue, L. N. Ruppert, and C. G. Wach)

The dual dissolver system (DDS) was made ready this quarter for the EOL campaign with the completion of the following remaining DDS-associated work.

*Analytical Chemistry Laboratory (ACL), ANL.

[†]Chemical Technology Division Computer Section.

[‡]Grid-Rod-In-Pile.

Two newly designed blend tank (BT) support/heater assemblies were bench tested out-of-cell and later installed in-cell at dissolver systems 1 and 2. New features of the stainless steel assembly include (1) a drip pan that completely covers a recessed BT balance, protecting it from dissolver solution spillage or dropped equipment, e.g., tools; (2) a stanchion-supported, insulated bucket-like secondary vessel to improve the rate of heating of the BT solution; (3) a bottom-mounted ring heater (700-W capacity) in direct contact with the BT to reduce solution heating time; and (4) an air-line connection to the secondary vessel to speed BT cooling. The secondary vessel, with the BT in place, can be tipped to provide more complete draining of waste solution and facilitate subsequent rinsing of the BT at the end of a dissolution run. As is the case with virtually all in-cell hardware, the BT assemblies can be remotely assembled and disassembled. Tests of the BT assembly heating capability showed that 5-6 L of water, used to simulate a maximum volume of acid collected during an EOL fuel segment dissolution, can be heated to 100°C (as for a MBS-950a spike dissolution) in less than one hour; cooling of the solution took about two and three-quarter hours. The time required for the heating/cooling cycle (~4 h) represents savings in the overall dissolution time for a fuel segment of about two hours over the earlier setup.

The BT heater assemblies used during the VR dissolution at dissolver system DS1 will be maintained in-cell as a spare for EOL use. A second assembly, which malfunctioned during processing of the VR at DS2, was disposed of after being stripped of usable parts.

Integration of the DDS computerized operating procedure (OPRDDS) with selected computerized piping and instrumentation (P&I) diagrams was completed; debugging the coordinated use and display of the diagrams with specific OPRDDS procedure steps was also successfully completed. The completed program of procedures and graphics is now ready for EOL use.

Documentation of OPRDDS, which started in May, was continued through this quarter. This task mainly involves preparation of descriptive narrative for the ~150-step overlays (individual slave programs that execute a given part of the procedure) that make up the heart of the OPRDDS automated procedures. The completed document will be reviewed and available before the EOL campaign commences.

The delays in shipment to ANL of the first irradiated LWBK fuel rod provided DDS operators with an opportunity during the quarter for expanded, hands-on training at the DDS and related facilities. Operators, in groups of two to three, were able to review OPRDDS and the P&I diagrams in greater detail than was afforded them during VR processing. An upgrading of OPRDDS, stemming from comments and questions that evolved from these training sessions, was completed before the end of the quarter. All operator-designated personnel have satisfactorily reviewed the numerous OPRDDS steps and performed the operations required for the successful processing of a fuel segment. New personnel scheduled to arrive before the EOL campaign commences will receive written DDS procedures and other training materials, as well as hands-on dissolver experience as needed.

C. Scrap and Waste Disposal
(R. E. Nelson and J. C. Hoh)

Dissolution and analysis of the 16 or 17 full-length fuel rods will generate some 600 L of liquid analytical residues that can be stored briefly, but ultimately must be packaged and shipped from the ANL site. We propose to mix the solution with cement to form a monolithic product, and to package and ship it to Rockwell-Hanford (R-H) for interim (20-y) storage; this work will be dovetailed with the actual processing of the fuel rods. All approvals for shipment and storage of the waste have been received from DOE-CH, the Nuclear Regulatory Commission (NRC), and the storage site operator (R-H).

Pursuant to the ANL plan for disposing of these wastes, technical work has been moving along three paths: (1) experimental efforts to develop procedures for preparing the cement waste form and to characterize the product; (2) development of an acceptable package for waste shipment, including design and approval of the package and fabrication/procurement of package components; and (3) installation of hot-cell facilities for in-cell preparation and packaging of the waste material. Work on items (1) and (2) is essentially complete. Progress during the current report period is indicated below by subcategory of effort.

1. Waste Packaging

The waste package comprises cans of cemented waste in a shielded cask which, in turn, resides in an approved 55-gal drum. Manufacturing and quality verification plans for fabrication of the casks were received from the vendor. The plans were reviewed, and approval granted, for the fabrication of the remaining 48 radwaste casks under order. The casks are under fabrication, although two prototype casks were returned to the vendor for upgrading after examination. As noted in the plan, all of the steel sections of the casks will be fully assembled before any pouring of lead begins. However, as outlined in the QA plan, when the vendor has scheduled the pouring of the lead liner (presently scheduled for mid-August), ANL must be notified so that an ANL representative may be present to witness the pouring procedure. The vendor estimates the job will be completed before the end of FY 1984.

Foaming of the void areas of the reusable wooden boxes that will be used as restraints in the packaging of the 55-gal waste drums in M-3 metal bins has been completed.

2. In-Cell Installations

The two cement-mixing stations, assembled and bench tested out-of-cell last quarter, were installed in Cell K-1 and again tested to verify in-cell performance; both units operated as designed. In a follow-up test, a batch of cement was prepared at each mixing station, with water used as a substitute for the acidic dissolver solution.

The two solution metering stations, which supply waste dissolver solution from the Cell K-1 solution feed vessels to the cement mixing stations, have been calibrated and set to pump ~15 mL/min, as required. A metering station comprises a Cole-Parmer Master-Flex, variable speed,

peristaltic pump mounted in a locally built stainless steel and plastic enclosure, which is penetrated by bulkhead fittings, to accommodate leakage or pump failure.

The waste can-out system, which provides a contamination-free secondary container for the solidified waste product from Cell K-1, was assembled and installed in the cell this quarter. Minor design modifications were made to improve the performance of the hatch assembly, which holds the secondary lid during can loading. The can-out system was checked for proper operation after installation.

A second monorail hoist was installed in Cell K-1. This hoist, which is located in the drying oven portion of the alpha barrier in the cell, will facilitate the handling of primary waste cans when loading and unloading ovens.

Several small tasks that remain to be completed in Cell K-1 for EOL readiness include (1) calibration of the liquid level probe of the waste solution feed vessel at mixing station 1, (2) rerouting of the overflow return lines for both feed vessels so that excess waste solution is returned to the DDS waste tanks (in Cell M-1), (3) installation of tantalum liquid-detection probes in both feed lines, and (4) installation of solution leak detector devices in the drip pans at both solution metering stations.

3. Procedures

Except for associated hard-copy computer printouts of figures, which will be completed in July, drafting of the detailed operating procedure for the scrap/waste system has been completed.

D. Computer System and Data Management

(J. Osudar,* G. L. Chapman,† R. W. Kessie,† and J. Leddin‡)

An integrated computer system is being developed for use by the LWBR-POB Analytical Support Project. This system will provide (1) automatic data acquisition; (2) various monitoring functions; and (3) several degrees of automated control for the equipment, instrumentation, and procedures by which ANL will analyze fuel rods. In addition, the computer system will be used for compilation of data, calculation of results, and generation of reports. Development of the computer system was initiated in 1980, with the specification of the main elements of the hardware systems and scoping of the major software requirements. Ancillary hardware items have been added as needs were identified during system development. Although the overall design of the software systems has remained constant, refinement of these systems has continued during their development, particularly after experience in their use had been gained. A detailed description of computer hardware and software systems was presented in a previous report [STEINDLER]. Progress during this quarter on the hardware and software systems is described in this section; related work is described in other parts of Section V.

*Science Applications, Inc., Schaumburg, IL.

†Chemical Technology Division Computer Section.

‡Co-op student from Lewis College, Romeoville, IL.

1. Hardware System

A plan is still in effect to upgrade the PDP-11/23-PLUS* computer to a PDP-11/73,* which operates at three to five times the speed of the present system and doubles the program memory size. This plan will be implemented next quarter. There were no significant hardware developments during the quarter. The system is stable and operational.

2. Software Systems

Effort on project software was expended in two major areas: (1) development of report-generation programs and (2) modifications and enhancements to the DDS procedures and programs to implement post-dissolution and plenum dissolution procedures.

a. Report-Generation Programs

Several programs were written to process data files from shearing, dissolution, and analytical operations, to produce both summary data files and reports. A program for the manual entry of fission gas data obtained from the puncture of a fuel rod was written, and a program that combines the gas measurements from five separate files into one file was also produced. This file is used by the program that generates the Fission Gas Report, which was implemented during this quarter. Also, programs were written to (1) produce the fission product reports, (2) process data from the thermal ionization mass spectrometer, and (3) collect uranium data and produce an Error Analysis Report for analysis of uranium. In addition, work was initiated on the Historical Log of Dissolver Equipment Usage (HISLOG) reporting system for the tracking and status reporting of DDS equipment items (i.e., BTs, gas sampling cylinders, and solution filter assemblies).

b. Dissolver Procedures

Post-dissolution procedures for BT decontamination and gas-sampling cylinder purge operations were implemented. A modified dissolution procedure (a form of OPRDDS in which the secondary dissolution is omitted) was implemented for plenum segments, which will automatically perform the appropriate steps when segment 00 (the plenum segment) of any fuel rod is dissolved. A sequence of BT weighing operations in which the BT is lifted off the balance pan and weight readings are taken (and repeated three times) was automated and is now computer controlled by OPRDDS, thus freeing the operator from manual weighing routines.

3. Summary

Hardware and software systems for the LWBR-POB EOL campaign are virtually complete. Numerous report-generation programs have been written, and the remainder are being completed in preparation for the EOL campaign.

*Digital Equipment Corp., Inc., Maynard, MA.

E. Error Analysis
(D. G. Graczyk*)

The analytical nature of the LWBR-POB project at ANL and the stringent tolerances required for measurements on the EOL fuel rods demand that extensive characterization and testing of project equipment and operations be performed in a manner that serves to reliably evaluate and demonstrate ANL measurement capabilities. The Analytical Chemistry Laboratory (ACL) has played a key role in these efforts by taking responsibility for carrying out a comprehensive error analysis for the project. Insight into the sources of errors associated with each measurement by the project, as provided by this error analysis, guides the statistical analysis of data and aids the generation of reports. Consequently, effort expended in such activities usually involves and is reported on by the ACL as part of its error analysis support function.

During this report period, work in this area was focused on the development of computer programs to compile, reduce, statistically analyze, and report data from the processing of LWBR fuel rods. Specific software programs were worked on, which provide computerized reports on the results of fission gas (krypton plus xenon) measurements, fission-product (^{137}Cs , ^{144}Ce , and ^{95}Zr) determinations, and uranium analyses (assays and isotopic measurements).

Each report-generation program performs several tasks in sequence; in some cases, all the tasks are performed by one program, whereas, in other cases, separate programs are used to carry out each task. The first task to be performed is a compilation and reduction of data from project files to produce a summary data file specific to the results expected from the program. All data needed to compute the desired results for an individual fuel rod as well as intermediate calculated values, such as averages and standard deviations of replicate measurements, are stored in this summary file. During this compilation, information from many project operations areas are brought together. For example, calculation of a single uranium or fission product assay will require data on solution weights from the DDS, aliquot weights from the analytical cell (Cell K-3) operations, uranium data from the mass spectrometry laboratory, and counting data from the alpha/gamma spectrometry system. The second task carried out by the report-generation programs is to perform a comprehensive statistical analysis of any replicate data obtained during processing of the rod under consideration and to combine the results of this statistical analysis with data from characterization testing and information from other sources to produce realistic estimates of the uncertainties associated with each result to be reported. The results of this analysis of errors, including all intermediate calculation results, are stored in a separate computer file. In performing its final task in the sequence, each computerized report-generation program reads information from the data summary and errors files and creates tables of results, uncertainties, statistical parameters, etc., in a form suitable for review by project management or for transmission to BAPL as an ANL report on the destructive assay for the fuel rod.

*Analytical Chemistry Laboratory (ACL), ANL.

Work completed on the report-generation programs during this quarter included the full complement of programs required to produce computerized reports on fission gas measurement and fission product determinations as well as the programs to perform the data compilation and error analysis of uranium measurements. The program that will tabulate the uranium results was started and is roughly 20% complete. As each section of each program was finished, it was tested by processing the data accumulated during the processing of the VR and comparing the results of the computer calculations with those generated by manual computation at the time the VR was processed. In a few instances, discrepancies between the computerized and manual calculations were found. Upon investigating each of these disagreements, it was discovered that an error was made in the manual data compilation or reduction and that, in spite of several rechecks, the errors had escaped detection. This experience emphasizes the value of the computerized data-handling procedures that will be in place for the EOL campaign. Moreover, the manual processing of data from the VR required more than three weeks to perform; with the computerized system, error-free generation of reports, in virtually camera-ready form, can be accomplished in a matter of hours.

F. Analytical Operations

(D. G. Graczyk, E. L. Callis, and R. R. Heinrich)*

Chemical and radiometric analyses of samples obtained from operations with the FSSF and DDS are provided by the ACL. Only a few samples, generated during testing and cleaning operations at the DDS, were processed this quarter. However, a substantial effort was expended during the report period on the ACL portion of the computerized data-handling system, toward updating and finalizing operations documentation, and toward ensuring a smooth startup of operations when the first EOL rod is received. This effort is described according to the various areas of ACL operations in the following paragraphs.

1. Mass Spectrometer

The final portion of the data-transfer system between the project-dedicated mass spectrometer (used for uranium isotope ratio measurements) and the VAX-11/780† central computer was finished this quarter with the installation of a program, at the VAX end of the data link, that sorts data received from the HP-9845‡ computer on the mass spectrometer and puts it in a form that is easily searched and read by the POB report-generation programs on the VAX. Special features provided in this program include a variety of checks for validity of sample numbers and consistency of data as well as an ability to handle a random ordering of samples in the HP-9845 data files. The program output consists of files that summarize the mass spectrometric data for each particular fuel rod and a directory for each rod that tells which of the HP-9845 data files contains information relevant to any particular sample. Both the data summaries and the directory files are sorted into alphabetical order for easy reference.

*Analytical Chemistry Laboratory (ACL), ANL.

†Digital Equipment Corp., Inc., Maynard MA.

‡Hewlett-Packard, Inc., Loveland, CO.

2. Analytical Hot Cell (Cell K-3)

The analytical hot cell (Cell K-3) is the site at which solution samples from DDS operations are divided into aliquots and where processing of the aliquots to remove unwanted radioactivity is carried out. A thorough review and updating of the written procedures that direct operations in processing samples at Cell K-3 were made this quarter. This effort was aimed at making the written procedures as accurate and complete as possible from the standpoint of directing operations; it included the clarification of instructions provided for some steps and the addition of sections describing new tools, jigs, or other conveniences that have been incorporated into the operations since the procedure documents were drafted. No fundamental changes to the procedures themselves were made nor are they planned.

Modifications were also made to the computer program that serves the Cell K-3 aliquoting operation. These changes arose partly from operator comments assembled during the VR campaign and partly from tests carried out during this quarter. The changes were made to improve the readability of text displayed by the program and to eliminate the need for operator response to certain information-bearing messages that are not critical to the operations. The need to acknowledge these messages slowed the operations and had become annoying to the program operators.

A general cleaning of the Cell K-3 work areas was carried out, including radiation surveys of various sample-transfer areas. A physical inventory of supplies on hand for starting up EOL operations was also performed; stocks were replenished as necessary to provide for processing several complete fuel rods.

3. Laboratory M-150

Operations carried out by the ACL in Laboratory M-150 include purification, by ion-exchange chromatography, of uranium samples for mass spectrometric or alpha-counting analysis and the electrodeposition of uranium on alpha-counting planchets. Written procedures directing these operations were reviewed and updated. Revisions were made to incorporate changes recommended by ACL staff during the processing of the VR. They serve to reduce the amount of waste generated by the operations (e.g., by allowing reuse of beakers and transfer pipettes in ways that do not increase the risk of cross-contamination between samples) and to clarify the instructions provided for a few steps. Details of the electrodeposition procedure used in preparing the alpha-counting planchets were also added.

The stock of reagents and supplies maintained in the laboratory was inventoried and replenished to a level that should accommodate the processing of several EOL fuel rods.

4. Alpha/Gamma Counting

The project-dedicated, fully automated, alpha/gamma spectrometer system was checked out and serviced late in the quarter. The vacuum pump on the alpha ports in the counting system was found to be in need of minor repairs, which were made.

A check was also made on the gamma standards used in routine monitoring of the gamma system performance. The ^{95}Zr standards prepared for use in the VR campaign were found to have decayed (^{95}Zr half-life is 64 days) to a point where their usefulness was limited. A new standard solution of ^{95}Zr , from which standards for the EOL campaign will be prepared, was procured.

G. M-Wing Hot Cell Facility
(J. C. Hoh)

1. Manipulators

Three M/S manipulators were installed in the waste treatment cell (Cell K-1) during this quarter, completing the complement of manipulators for this cell. These M/S units were rebuilt by POB personnel last year, but installation was delayed until other in-cell work was completed.

Three other manipulators currently in use required repair during this reporting period. A manipulator in the DDS cell (Cell M-1) failed due to a broken counterweight tape. The manipulator was removed and repaired by project personnel; during the repair it became evident that the other counterweight tape was also in poor condition, so it too was replaced. The second machine, which is being prepared for the Isotope Correlation in Surveillance and Accountancy Methods (ICSAM) project* in Cell A-1, required replacement of the control wiring. The third machine, the PaR† polar manipulator outside of Cell K-3, required repair of a faulty switch on the control panel.

Work was also completed on the entire rewiring of four American Machine and Foundry (AMF) extended-reach manipulators, which consisted of replacing the electrical control system with one similar to that used in Central Research Laboratory (CRL) manipulators. The new control units were fabricated and installed on the machines by project personnel.

Fabrication of modified booting for the slave portion of the M/S manipulators, i.e., incorporating the new swivel-joint feature, was completed this quarter; 26 boots were fabricated. The new swivel-type booting was previously installed in Cell M-1, and recently installed in Cells A-1 and K-1. This type boot is scheduled to be installed in Cells M-3 and K-3 early next quarter. The installation will require suited entries into the cells, i.e., entries using respirator protection and double paper suits. All booting will be completed prior to the EOL campaign.

2. ICSAM Project

Preparation of Cell A-1 for the ICSAM project (unrelated to the POB project) was carried out during this reporting period. The cell was decontaminated by ANL Reclamation - Waste Management Operations, so that work could begin on the installation of an alpha barrier. The barrier is presently

*P. J. Persiani, Applied Physics Division (ANL), Principal Investigator.

†Programmed and Remote System Corp., St. Paul, MN.

95% complete and all required utilities have been installed in the cell. The manipulators have been inspected and tested, and necessary repairs completed. The new swivel-type booting also has been installed on the slave portion of the manipulators. With most of the required cell work completed, the cell will be operational early next quarter.

The samples to be processed arrived the first week of June. The unloading of the fuel samples presented some difficulties because the shipping container was a type requiring vertical loading. Due to the height of the container, it was not possible to use the crane located on the megacurie (lower) level of the cave. Instead, to remove the lid of the container, a floor plug on the kilocurie (upper) level of the facility was removed so that the hook of the 5-ton monorail crane on the upper level could be lowered through the hole in the upper level floor. This arrangement provided sufficient head room for lid and sample container removal. Snatching of the sample container bail was accomplished with the aid of a mirror to peer through the open hole in the upper level floor. A survey over the open hole indicated a field of 200 mR/h at floor level. After unloading, the sample container was moved to one of the storage pits in the facility corridor.

3. Cell M-4

The clean out and decontamination of Cell M-4 was completed in preparation for installing a storage rack for multiple POB fuel rod shipments. A pair of M/S manipulators was installed at window M-4-E for handling of the fuel rod shipping containers. The final designs for the rack and rod carrier have been determined, and work on them will be completed before the first shipment arrives.

H. Radiation Monitoring Systems

(R. A. Leonard, J. C. Hoh, and N. M. Levitz)

A multipurpose, automated, stack monitor system will measure the discharge of radioactive effluents as irradiated fuel is processed in the LWBR-POB project. The system was designed and assembled by ANL Electronics Division personnel (R. Fergus, Group Leader). The overall task was coordinated by Frank Marchetti, ANL Occupational Health and Safety Division.

The system was installed prior to the processing of the VR in December 1983, and was operated during the VR run to determine its radiation monitoring capabilities. Tests focused on the ability of the system to detect and quantitatively measure the release of gaseous ^{85}Kr . Overall operation of the automated stack monitoring system was good. However, some discrepancies in data were found, such that further system calibration will be required. Although some calibration tests were made during this quarter, further testing is required. As a first step in this new round of calibration tests, the gas flow measured by the computer was correlated with Pitot tube measurements made at the stack exits. Before the EOL campaign begins, the monitors for the exhaust stacks of both Cells M-1 and M-3 will be calibrated with gas samples containing known amounts of ^{85}Kr obtained and analyzed by ACL during the VR run.

I. Fissile Material Inventory (R. A. Leonard)

A procedure is being developed to track and inventory the fissile material (FM), mainly ^{233}U , in M-Wing POB operations during the EOL campaign. This procedure can be implemented using an electronic spreadsheet (DIGICALC).^{*} A preliminary spreadsheet was set up and demonstrated for one of the two waste tanks in Cell M-1. The waste tanks are the most complex items in the FM inventory because there are (1) liquid additions, following which concentrations are updated as analytical results become available; (2) evaporative losses; and (3) liquid withdrawals, all being made in more or less random fashion to the total liquid that has accumulated in the waste tank. The results of the spreadsheet demonstration were very favorable because the spreadsheets are easily set up and afford easy data entry and viewing of calculated values. Based on these results, the FM inventory will be implemented through use of the electronic spreadsheets.

Inasmuch as spreadsheets can be interconnected, a separate spreadsheet will be set up to represent each area in M-Wing where POB FM will be located, i.e., the hot-cell corridor; Cells M-1, -3, and -4; corridor storage tubes; Cells K-1 and -3; Analytical Laboratory M-150; and the mass spectrometry laboratory (B-146). Additional spreadsheets will be set up for initial and updated fuel rod FM information, the measured FM concentrations of the various dissolver solutions, the measured volumes in each dissolver, the FM inventory in each of the two waste tanks, and elsewhere as needed. An overall spreadsheet will summarize this information and complete a material balance for the FM in the system. This material balance will compare the FM entering M-Wing (less the FM leaving M-Wing) with the FM accounted for at the various locations throughout M-Wing. The summary spreadsheet will show the amount of FM (in grams or, if appropriate, in grams per liter) at each location in M-Wing where FM will be located. (No location is to have more than 450 g of FM or have a liquid concentration of more than 5 g/L.) Details of the FM at a particular location will be obtainable by calling up the spreadsheet for that location.

Two spreadsheets have been prepared during this quarter, one for the initial fuel rod file (INITIAL) and one for the updated fuel rod file (UPDATE). The UPDATE spreadsheet shows how the ACL measurements of the FM in a fuel rod differ from the initial estimated value. These spreadsheets will be tied into the other spreadsheets as they are developed.

REFERENCE

STEINDLER

M. J. Steindler, Fuel Cycle Programs Quarterly Progress Report, July-September 1983, Argonne National Laboratory Report ANL-83-88 (1984).

^{*}Why Systems, Inc., Redmond, WA.

Distribution for ANL-84-57Internal:

J. K. Bates	J. E. Harmon	J. Osudar
R. A. Benson	R. R. Heinrich	D. J. Raue
R. L. Breyne	J. C. Hoh	L. N. Ruppert
L. Burris (11)	R. B. Keener	M. G. Seitz
E. L. Callis	R. W. Kessie	M. J. Steindler
T. F. Cannon	J. E. Kincinas	N. C. Sturchio
G. L. Chapman	J. M. Leddin	G. F. Vandegrift
R. A. Couture	R. A. Leonard	C. G. Wach
D. F. Fischer	N. M. Levitz	ANL Patent Dept.
T. J. Gerding	F. J. Martino	ANL Contract File
D. G. Graczyk	R. E. Nelson	ANL Libraries (3)
D. R. Hamrin		TIS Files (6)

External:

DOE-TIC, for distribution per UC-70, -11, -80 (407)
 Manager, Chicago Operations Office, DOE
 S. A. Mann, DOE-CH
 C. D. Bingham, DOE-NBL
 Chemical Technology Division Review Committee Members:
 S. Baron, Brookhaven National Lab.
 R. Winston, U. Chicago
 R. Wymer, Oak Ridge National Lab.
 C. K. Anderson, Combustion Engineering
 R. E. Barletta, Brookhaven National Lab.
 Battelle-Columbus Labs.
 G. Birchard, Office of Nuclear Regulatory Research, USNRC
 S. Boggs, U. Oregon
 D. Bowersox, Los Alamos National Lab.
 W. Carbiener, Battelle-Columbus Labs.
 J. M. Cleveland, U. S. Geological Survey, Lakewood, Colo.
 F. E. Coffman, Office of Terminal Waste Disposal and Remedial Action, USDOE
 D. L. Condotta, Exxon Nuclear Idaho Co., Inc., Idaho Falls
 E. Conti, Office of Nuclear Regulatory Research, USNRC
 C. R. Cooley, Jr., Div. of Waste Repository Deployment, USDOE
 R. Cunningham, Nuclear Materials Safety and Safeguards, USNRC
 G. H. Daly, Office of Dep. Asst. Secy. for Nuclear Materials, USDOE
 P. G. Deeken, Commonwealth Edison Co., Chicago
 R. G. Dosch, Sandia National Labs., Albuquerque
 J. E. Fagan, Fermi National Accelerator Lab.
 W. A. Freeby, Bechtel Corp., San Francisco
 M. Frei, Office of Commercial Radioactive Waste Management, USDOE
 R. G. Geier, Rockwell Hanford Operations
 S. Goldsmith, Battelle-Columbus Labs.
 J. P. Hamric, Idaho Operations Office, USDOE
 T. B. Hindman, Jr., Savannah River Operations Office, USDOE
 L. J. Jardine, Bechtel National, Inc., San Francisco
 J. J. Jicha, Office of Defense Waste and By-products Management, USDOE
 K. S. Kim, Office of Nuclear Regulatory Research, USNRC
 J. F. Kircher, Battelle-Columbus Labs.
 R. Lambert, Electric Power Research Inst., Palo Alto

R. C. Liikala, Battelle Pacific Northwest Lab.
Los Alamos National Lab., Librarian
R. Maher, Savannah River Plant
W. H. McVey, Fuel Cycle R&D, USDOE
C. Northrup, Sandia National Labs., Albuquerque
D. A. Orth, Savannah River Lab.
V. Oversby, Lawrence Livermore National Lab.
W. W. Schulz, Rockwell Hanford Operations
M. J. Smith, Providence, R. I.
R. J. Starmer, Office of Nuclear Material Safety and Safeguards, USNRC
D. M. Strachen, Battelle Pacific Northwest Lab.
R. Strickert, Battelle Pacific Northwest Lab.
F. Swanberg, Jr., Office of Nuclear Regulatory Research, USNRC
J. L. Swanson, Battelle Pacific Northwest Lab.
R. L. Tallman, EG&G Idaho, Inc.
R. D. Walton, Jr., Office of Defense Waste and By-products Management, USDOE
G. Buckau, Technical U. Munich, Germany
J. I. Kim, Technical U. Munich, Germany
N. Luckner, Technical U. Munich, Germany