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NUCLEAR TECHNOLOGY PROGRAMS QUARTERLY PROGRESS REPORT

January - March 1984

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NUCLEAR TECHNOLOGY PROGRAMS
QUARTERLY PROGRESS REPORT

January-March 1984

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for
Nuclear Technology
Programs

Chemical Technology Division

October 1984

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Previous reports in this series

ANL-84-15	October-December 1983
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MASTER

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ABSTRACT

Compacted mixtures of bentonite and sand or basalt have been tested for permeability at temperatures from 25 to 260°C. Permeabilities increased with increasing temperature and remained at the high levels after subsequent temperature decreases. An irreversible decrease in swelling ability occurred at high temperature. Using neutron activation analysis, data regarding chemical mobility during hydrothermal alteration in lithic samples from an active geothermal system have been acquired. The significance of the data are discussed. A test procedure to assess the reaction of nuclear waste glass with water has been evaluated by preliminary testing, showing it to be capable of meeting its objectives. Prototype tests that confirm the preliminary tests have been completed, and the actual study of waste form degradation is expected to begin soon. Two extraction systems for the separation of transuranic elements from high-level waste will be investigated. Conceptual flowsheets have been computed and other issues regarding implementation of the process have been addressed. Destructive analyses of full-length irradiated fuel rods from the Light Water Breeder Reactor will be conducted using equipment and systems being developed, installed, tested, and qualified. Included are a full-scale shear facility, dual dissolver system, and other facilities and systems.

SUMMARY

Modification of Backfill Materials under Repository Conditions

Mixtures of 25% bentonite and 75% sand or powdered basalt, compacted to dry bulk densities of about 1.6 g/cm³, were tested for permeability in distilled water at temperatures from 25 to 260°C and in groundwater at 250°C. The measurements were made at minimal flow rates to obtain representative values without damaging the columns. At zero or low flow rates, the permeability does not vary detectably with time for as long as three months at 25°C.

The permeability to distilled water increased monotonically by 4 1/2 orders of magnitude with increasing temperature from 25 to 260°C. At 250°C the permeability was about the same in groundwater as in distilled water. The permeability remained nearly constant after subsequent decreases in temperature. The reason for the high permeabilities is an irreversible decrease in the swelling ability of the clay at high temperature. In unheated clay, the basal spacing of the montmorillonite lattice expands in water at room temperature to several times its dry value, probably to over 100 Å; heating in the permeability tests restricted the expansion to about 19 Å and caused a corresponding decrease in the bulk swelling ability.

The results may place serious restrictions on the use of bentonite-based backfill material in high-level nuclear waste repositories. The cause of the degradation, the temperature-time relationship, and the stability of other sodium bentonites must be determined to improve the predictions of long-term behavior.

Trace-Element Transport in Lithic Material by Fluid Flow

Important additions have been made to the data set for the continuing study of chemical mobility during hydrothermal alteration of the rhyolite flow breccia of the Biscuit Basin Flow in drill holes in Yellowstone National Park. Most of the new data have been acquired by instrumental neutron activation analysis. There is evidence of significant mobility of many elements in the shallow portion of this high-temperature geothermal system, and the mineralogical sources and sinks for some of the elements have been tentatively identified. This report contains the new data and a brief discussion of their significance.

Reaction of Glass with Water

Detailed results of nine preliminary Phase II tests are given. They indicate that the test procedure will meet the uses and limitations for which it was planned. Radionuclide release can be measured by solution analysis and tuff dissolution. The elements boron and lithium show little interaction with the tuff, so they may be used to indicate the degree to which the waste form degrades. However, boron release is somewhat depressed, possibly because of interaction with other test components. Weight loss measurements of the waste form also provide an indication of the rate at which the waste form reacts.

Prototype tests have been concluded and confirm the results of the preliminary tests. A final vessel cost/availability estimate is provided, and we anticipate that vessels can be fabricated and actual testing can begin soon.

TRU Removal from High-Level Waste

The objective of this program is to develop a series of conceptual flowsheets for removing and concentrating transuranic elements in Hanford current acid waste and dissolved sludge waste by two extraction systems. One of the extractants to be tested is dihexyl-N,N-diethylcarbamoylmethylphosphonate; the other extractant is octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide. Both extractants will be diluted by ~30 vol % tributyl phosphate in a normal paraffinic hydrocarbon mixture of C₁₁-C₁₄ chain length.

The work this quarter centered on computing conceptual flowsheets (with relative flows and mass balances of process streams) and addressing issues important to implementing the process, such as process flexibility, equipment, safety, and availability and cost of the solvent inventory and makeup. An informal letter report containing this information was sent to Rockwell Hanford Operations in March 1984. A final report, to be issued as an ANL topical report in July 1984, will discuss this and additional information to be collected next quarter.

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

This project involves the processing and destructive analyses of 16 or 17 intact, 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 instrumental 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 R. W. Bane*)

A. Introduction

This report describes laboratory measurements of permeability of backfill materials to be placed around the waste canister in a high-level nuclear waste repository. The methods are being used to measure the properties of materials over a wide range of possible repository conditions. The measurements are designed to be directly applicable to repository environments.

A primary function of the backfill is to limit flow of groundwater past the waste canisters. The essential property of the backfill is low permeability; secondarily, the backfill must have the ability to swell to fill cracks and to fill the available volume under all conditions. It is expected to be exposed to temperatures up to 250 or 300°C. It is very important to limit water flow through a repository at these temperatures. The main issue addressed in this report is whether bentonite-based backfill materials will retain their low permeabilities and swelling abilities at these temperatures.

Significant questions have been raised about the ability of mixtures of bentonite and basalt to perform the essential functions at high temperatures and as a result of mineralogical changes after a prolonged period of aging at high temperatures in a radiation field [COUTURE, PEACOR]. These include, among others, the possibilities of formation of channels, embrittlement and cracking as a result of alteration of basalt, and alteration of the clay to less expandable products or dehydrated products (with ensuing reduction in volume), although recent studies have failed to find evidence of rapid degradation [PEACOR, WOOD].

Little testing has been done on the physical properties of altered backfill materials. Krumhansl [KRUMHANSL] has very recently reported a reduction in the ability of bentonite to swell in brine after heating to 150 to 300°C. However, in dilute solutions the material reportedly recovered part of its ability to swell. Bradley [BRADLEY] has reported a slight loss of swelling ability of bentonite after gamma irradiation or prolonged heating.

This report describes laboratory measurements of permeability of bentonite-based backfill at temperatures up to 260°C and the properties of the materials following the tests. For test purposes, the backfill was compacted to a dry bulk density of about 1.6 g/cm³, a value that is reasonably attainable in the field but not at the limit of attainable densities, as it is possible to fabricate highly compressed bricks. However, these measurements amply demonstrate the relevant phenomena.

B. Methods

Figure I-1 shows a simplified schematic of the equipment used for permeability measurements. Groundwater is pumped under pressure through a column of backfill; the volume of water flowing through the column is determined at the pump and at the outlet of the system. A back-pressure regulator valve maintains pressure in the column so that the equipment can be used at high

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Fig. I-1.

Diagram of the Apparatus Used to Measure Permeability of Backfill Materials. Flow rate and pressure are recorded continuously.

temperatures. Leak-free performance of the fittings is essential for reliable measurement, especially above 100°C, and static metal-to-metal seals used were found to be effective. They can also be inspected readily for evidence of leaks, even after use above 100°C. Measuring the flow rate into and out of the column offers an independent means of testing for leaks. Measurement of the flow rate into the column with the back pressure regulator closed is a second method of testing for leaks. Hydration of long columns can also be studied without waiting for breakthrough of the water. The equipment also has a valve (not shown) for reversing flow in high-temperature tests. By reversing flow through the column, it is possible to test for clogging of the outlet frit or clogging of the column itself due to flow. The equipment is very sensitive at low flow rates. Multiples of $3\frac{1}{3}$ μL are recorded; by thermostating the system, flow rates as low as 0.1 $\mu\text{L}/\text{min}$ have been measured at 25°C. This type of equipment was used for measurements presented in this report, except that the back-pressure regulator valve and the differential pressure transducer were omitted from apparatus used for measurements at 25°C.

Columns were heated at the temperature of the test, with the ends open to the atmosphere. They were then saturated with liquid water or groundwater* at the same temperature by pumping at a very low rate. The pressure difference was monitored continuously and was kept at a minimum practical value during filling. The columns were easy to fill at temperatures of 200°C and above.

*Artificial 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, and 0.03 mM CaSO₄, adjusted to pH 9.9 with HCl.

Once the columns were filled with water, flow was intermittent, and was restricted to the minimum necessary for measurements, to minimize the effect of flow on permeability. Any changes in permeability are believed to be due mainly to the effects of groundwater and high temperature during testing.

The pressure difference across the column was determined as a function of flow rate. Permeability was calculated from the formula

$$k = \frac{\mu F}{A \nabla P}$$

where k = permeability, m^2 ,
 μ = viscosity, Pa's,
 F = flow rate of liquid at the temperature of the test, m^3/s ,
 A = cross-sectional area of the column, m^2 , and
 ∇P = pressure gradient, Pa/m.

By definition, permeability is compensated for changes in viscosity of the fluid with temperature and, therefore, should depend only on the properties of the backfill and should not change as a result of change of viscosity with temperature.

C. Results

1. Measurements at 25°C

Two columns, labeled A and B, were prepared with 25% bentonite (Envirogel, 200 mesh, from Wyo-Ben, Inc.) and 75% crushed, sieved quartz sand packed in stainless steel tubes. A size analysis of the sand is given in Table I-1. The bentonite is a typical Wyoming bentonite, consisting mostly of montmorillonite, with a trace of illite or mica, and about 10% sand and silt. An analysis of the montmorillonite, presented in Table I-2, shows that it is a typical sodium montmorillonite. It is capable of swelling to many times its dry volume in water.

Column A was prepared using sand crushed to 80-140 mesh size (105-180 μm). The dimensions of the column were 1.89 cm inside diameter x 7.00 cm long, and the dry bulk density was 1.59 g/cm³. Column B was prepared using sand with 20-80 mesh size (180-840 μm). The dimensions were 1.89 cm in diameter x 6.85 cm long, and the dry bulk density was 1.72 g/cm³. Fritted stainless steel discs with 2- μm nominal pore size were used, and the column was connected to a capillary tubing with commercial high-pressure, low-dead-volume fittings. The flow rate into the column was recorded continuously; the flow rate out of the column was measured with glass capillaries.

Figure I-2 shows the impedances of the two columns at 25°C during the saturation period, plotted as a function of total water in the columns. (The impedance is defined as the hydraulic pressure divided by the flow rate, and is an inverse function of permeability.) The impedances of the columns increased as the columns filled, and it appears that the initial increase of each was generally linear.

Thus, the permeability of a hypothetical wetted portion of the column is constant. On this basis, an equivalent permeability can be calculated by dividing the column into a hypothetical dry portion and a water-saturated

Table I-1. Sieve Analysis of Sand
Used in Permeability
Measurements

Size, μm	Proportion, wt %
500-841	10.8
250-500	51.7
180-250	21.5
<180	15.7
Total	99.7

Table I-2. Energy-Dispersive Analysis of Montmorillonite
from Envirolgel 200 Bentonite^a

Oxide	Weight %
Na ₂ O	3.3
K ₂ O	0.13
CaO	0.70
MgO	4.0
Fe ₂ O ₃ ^b	3.2
Al ₂ O ₃	20.5
SiO ₂	68.1
Total ^c	100

Calculated formula:^d

^aThe unpurified bentonite also contains 0.21% CO₂ present as calcite. This corresponds to a Ca/Na equivalent ratio of 0.09.

^bOxidation state assumed.

^cAdjusted to 100% for anhydrous compound.

^dCalculated for 11 oxygens in anhydrous compound.

Fig. I-2.

Hydraulic Impedance at 25°C
(pressure divided by flow rate) vs.
Total Flow into Two Columns Contain-
ing 75% Sand, 25% Bentonite. Dry
bulk densities: (A) 1.59 g/cm³;
(B) 1.72 g/cm³.

portion, and calculating the equivalent pressure gradient from the length of the water-saturated portion. At any point on the curves in Fig. I-2, the permeability is proportional to the abscissa divided by the ordinate. On the assumption that the permeability does not decrease with time, the equivalent permeability establishes an upper limit for the permeability of the backfill material. The initial linear portions of the curves give equivalent permeabilities of $8 \times 10^{-18} \text{ m}^2$ and $3 \times 10^{-18} \text{ m}^2$ for columns A and B, respectively, which are, in fact, the highest permeabilities measured on those columns.

When water emerged from the outlet of Column A, the flow rate was measured. The flow was then reversed and cycled through monotonically increasing rates followed by a reduced rate. The flow rates and permeabilities are shown in Fig. I-3.

Reversing the flow caused a twofold increase in permeability. The lower permeability observed before reversing the flow may have been due to movement of clay particles within the column, resulting in partial clogging of the column or the frit. Inspection of the column after the measurements were made rules out compaction as a cause of the lower permeability. The permeability increased with pressure difference. At the lowest pressure difference (0.29 MPa) the permeability was only $0.89 \times 10^{-18} \text{ m}^2$. Extrapolation to zero pressure difference suggests a permeability not much lower or higher than this value.

An increase in flow rate from 0.07 to 1.27 μL/min caused an irreversible decrease in permeability by about 1/4, as determined by subsequent measurements at a low flow rate (point 3 in Fig. I-3). The reduction of permeability by rapid flow was apparently somewhat greater during filling of the column than it was later.

Fig. I-3.

Flow Rate and Permeability at 25°C of Sand-Bentonite Column A with a Dry Bulk Density of 1.59 g/cm³. Experimental sequence: (1) initial flow direction; (2) reversed flow, low pressure followed by high pressure; (3) reversed flow, low pressure. Permeability is shown only for (2).

A repeated measurement 86 days after saturation gave a permeability of $0.75 \times 10^{-18} \text{ m}^2$. Thus, the permeability did not change significantly with time.

2. Measurements at 200 and 240°C

For permeability measurements at 200°C, column 272-11 was prepared from 75% sand plus 25% bentonite. The column had a dry bulk density of 1.59 g/cm³. It was preheated to 200°C, and the resulting formation of steam (the mixture consists of about 2.5% water that is loosely bound to the bentonite) purged the column of air. The fittings and valves were completely filled with water before the start of the experiment.

The column was saturated with liquid water by pumping water into the system very slowly and carefully. The pressure difference across the column was monitored continuously. It was less than 1.4 kPa until liquid began to form. After liquid formed, the pressure difference never exceeded 0.2 MPa. The highest pressures were maintained only briefly.

The results are shown in Figs. I-4 and I-5. Pumping causes an increase in the pressure difference. Cessation of pumping leads to an exponential decay, as shown in Fig. I-4. The exponential pressure decay shows that Darcy's law is obeyed; that is, the pressure difference is proportional to the flow rate. Figure I-5 shows the flow rate vs. pressure difference, as measured by both flow into the column and flow out of the column. There is good agreement between the two methods. The total leakage from the system, including leakage through the back-pressure regulator and the pump check valves, was repeatedly and independently found to be negligible--less than 0.06 μL/min.

Fig. I-4.

Pressure Decay Due to Flow through Sand-Bentonite Column 272-11 at 200°C. Exponential decay in both tests demonstrates validity of Darcy's law. Slight deviation from straight lines at bottom right is not significant.

Fig. I-5.

Flow Rate vs. Pressure Difference across Sand-Bentonite Column 272-11 at 200°C. Symbols show method of measurement: Xs - flow rate into column by pump displacement; dots - flow rate out of column by glass capillary.

The average of the measurements gives a permeability of $0.8 \times 10^{-16} \text{ m}^2$ at 200°C , which is about 100 times the value of $0.9 \times 10^{-18} \text{ m}^2$ obtained at 25°C . The apparently lower permeability at the highest flow rate at 200°C (Fig. I-5) may be due to a gradual, irreversible decrease in permeability caused by movement of particles, as noted above at 25°C .

The temperature was then increased to 240°C . Part of the water in the column boiled away because the pressure was not sufficiently high. The column was then rehydrated at higher pressure and the permeability measured; it increased to $2.3 \times 10^{-15} \text{ m}^2$. The increase could be due to physical damage caused by boiling, or to the increase in temperature. However, we will show that the increase in temperature is the more likely cause.

3. Measurements at 260 to 51°C

Measurements on other columns are shown in Figs. I-6 to I-8. The measurements were made with groundwater or deionized water flowing through 25% bentonite mixed with sand or powdered basalt. A size analysis of the basalt is shown in Table I-3. Highly reproducible results were generally obtained. The columns were easily hydrated because the permeabilities were very high above 240°C . At the low flow rates shown, Darcy's law was obeyed.

Fig. I-6. Permeability of Column 272-16 in Water at Descending Temperatures. Bentonite + basalt. Height 6.74 cm, diameter 1.00 cm, dry bulk density $1.66 \text{ g}/\text{cm}^3$.

Fig. I-7.

Permeability of Column 272-17 in Water at Descending Temperatures. Sand + bentonite. Height 6.82 cm, diameter 1.00 cm, dry bulk density 1.64 g/cm^3 .

Fig. I-8.

Permeability of Column 272-36 in Groundwater at 250°C. Bentonite + basalt. Height 6.80 cm, diameter 1.89 cm, dry bulk density 1.66 cm^3 .

Table I-3. Sieve Analysis of
Crushed Pomona Basalt
Used in Permeability
Measurements

Size, μm	Proportion, wt %
>850	0.04
425-850	12.00
250-425	17.95
180-250	9.11
150-180	4.22
100-150	9.76
75-100	7.61
46-75	38.51
<46	0.80
Total	100.00

In two columns, the temperature was decreased after hydration, but there was little resulting decrease in permeability at the lower temperatures.

4. Summary of Measurements

All the columns contained 25% bentonite plus 75% powdered basalt or quartz sand. The dry bulk densities were about the same in all columns. Distilled, deionized water was used for most of the tests; groundwater was used at 250°C.

There is an extremely large temperature effect on permeability, as shown in Fig. I-9. The column material or water used apparently had little effect. The permeability depends mainly on the highest temperature reached, and increases by nearly five orders of magnitude from 25 to 260°C.

The increase in permeability with increase in temperature is irreversible. Subsequent lowering of the temperature resulted in little decrease in permeability.

Fig. I-9. Permeability of Backfill as a Function of Temperature, Plotted on a Logarithmic Scale. Arrows show temperature changes after saturation with liquid water. Numbers show dry bulk densities in g/cm³. Permeability is mainly a function of the highest temperature reached.

5. Examination of the Columns and Clay

a. Injection of Dye

To determine whether water bypassed through cracks or between the backfill and the wall, the column used at 260°C was examined after the conclusion of the test. The column was cooled while pressure was maintained on the system. The system was then depressurized, the column was disconnected from the system, and 0.05% fluorescein solution was injected into the column until fluorescein was detected at the outlet. This occurred after 1.47 mL of flow, corresponding to 27% of the total column volume. This is virtually

equal to the estimated porosity of 28%.^{*} The column was then opened and inspected under ultraviolet light. At the outlet of the core, fluorescein was present at all points of the outlet area. There was somewhat more fluorescein around the edges; but at less than 1 mm from the outlet, and at all points further into the core, the distribution of fluorescein was uniform. Both observations show that flow through the column was nearly ideal, i.e., the axial flow velocity was nearly constant across the area, and suggest that the permeability measurements are representative of the material.

b. Swelling and Plastic Behavior of the Clay

The swelling and plastic behavior of backfill from the columns was very different from that of fresh backfill. When wet, the fresh material is very sticky and hard to disperse. The material taken from columns 272-11 and 272-17 (used at temperatures of 240 and 260°C, respectively) was not sticky. When mixed with water and dispersed in a test tube, the clay component of a fresh mixture expands to several times the volume of the dry mixture. The altered mixture that had been used in the columns expanded much less. Figure I-10 shows the difference in expansion between the fresh and altered materials.

The fresh and altered clays also show very different expandabilities as determined by X-ray diffraction. The fresh material shows basal spacings of over 100 Å in a moist condition; the altered material shows a spacing of 19 Å but little evidence of a larger spacing. We will collect additional mineralogical and chemical data.

D. Discussion

The permeabilities of the two columns containing 75% sand and 25% bentonite were very low at 25°C. The column with a dry bulk density of 1.72 g/cm³ initially had an effective permeability of 3×10^{-18} m², as defined by the flow rate of water into the dry column. The final permeability of 0.9×10^{-18} m² measured at 25°C appears to be a representative value for that column. Surprisingly, it is much lower than the value of 2×10^{-17} m² obtained by Pusch [PUSCH]. The difference may be accounted for by the slightly lower clay content (about 17%) and lower density (1.53 g/cm³) in Pusch's experiment compared to our experiment (22% and 1.59 g/cm³, respectively).

We do not believe the effect of normal groundwater (compared to the pure water used in most of our experiments) to be a major factor, because the salt in normal basaltic groundwater ($[Na^+] \sim 0.015M$) does not greatly affect the swelling of smectites [BROWN]. However, additional tests using groundwater at moderate temperatures are planned.

^{*}X-ray diffraction shows a basal spacing of 19 Å for the wet clay. Assuming a density of 2.52 g/cm³ for air-equilibrated clay with a basal spacing of 12 Å, a density of 2.65 g/cm³ for the sand, a dry bulk density of 1.64 g/cm³, and expansion of the lattice to a basal spacing of 19 Å, the porosity is estimated at 28% in the hydrated core.

Fig. I-10.

Expansion of Fresh and Altered 75% Sand, 25% Bentonite Mixtures in Water. Left: unaltered starting material. Right: same quantity of material from column 272-17, heated to 260°C. The materials have been mixed with water and allowed to settle. The layer on the bottom is sand. Material from unheated columns behaves like the starting material.

The permeability depends somewhat on the flow rate and the history of the column. At 25°C, an increase in flow rate causes an immediate increase in permeability, followed by a slow, irreversible decrease. The initial increase in permeability may be due to air in the column, hydrodynamic factors, or decreased swelling of clay against the inlet frit. It was not observed in pressurized systems, from which air was excluded. The irreversible decrease is probably due to movement of particles within the column. The effects observed are minor over the pressure range investigated.

In the absence of flow, or at low flow rates, the permeability does not change detectably with time. This contrasts with the results of Wheelwright et al. [WHEELWRIGHT], who reported a severalfold decrease in permeability over 30 days. Their observed decrease may have been due to continuous flow at high pressure differences across the column.

The clay has been altered rapidly at temperatures of 200°C and higher. Although mineralogically the clay is still a smectite, it is much less expandable than it was before being subjected to high temperatures. The low permeability of fresh bentonite-containing mixtures is due to the ability of bentonite to swell in water to many times its dry volume. The increased permeability of the columns at high temperatures is due to reduced swelling ability.

On the basis of preliminary X-ray diffraction data and the speed of reaction, it seems possible that the change is an ion-exchange reaction, with substitution of calcium ions or other cations for sodium ions. However, a sufficient source of cations is not evident. The sand consisted of quartz plus microcline, and was washed before being mixed with bentonite. Microcline could provide potassium or aluminum ions, but only after extensive reaction, and the alteration appears much too fast for that. Neither quartz nor microcline contains divalent ions. Furthermore, the basalt is not known to rapidly contribute divalent cations to solution at high temperatures [WOOD]. The bentonite contains some calcite, but apparently not enough to convert a large fraction of the clay to the calcium form (Table I-2). Analyses of the clay and accessory minerals by scanning electron microscopy, and bulk chemical analyses, are expected to resolve the question of what compositional changes may have occurred.

We also have several samples of bentonite treated hydrothermally at the University of Michigan in distilled water and in artificial basaltic groundwater. Some of the samples apparently have reduced expandability compared to the starting material. Attempts to quantify the changes are under way.

E. Recommendations

Backfill mixtures would be quite permeable if used in a repository at temperature of 200°C or above, at the tested compaction and concentration of bentonite. However, there is some doubt whether 25% would be a sufficient concentration of bentonite for high-temperature use at any degree of compaction. Filling of the pores by swelling of bentonite is the reason for low permeability at 25°C. Even at a high dry bulk density of 2.0 g/cm³, the bentonite would have to expand by 2.4 times to fill the pores, assuming a density of 2.87 g/cm³ for the basalt [LAGEDROST] and an estimated initial density of 2.52 g/cm³ for the air-dried bentonite (with montmorillonite hydrated to a basal spacing of 12 Å). Expansion of the bentonite lattice from 12 Å to 19 Å would not be sufficient to fill the pores, although the bulk expansion may be somewhat higher than the lattice expansion because of the effect of surface charges.

Regardless of the permeability of the material, the degraded material will have relatively little ability to expand to fill fractures or otherwise conform to minor changes in volume of the repository.

The mechanism and range of conditions at which degradation occurs need to be determined. More data are needed for groundwater at moderate temperatures. It should be established whether the phenomenon is general or specific to the tested clay. If it is a general phenomenon, other bentonite clays may degrade at high temperatures as well.

The temperature-time relation of the degradation needs to be explored to determine the range of conditions under which breakdown occurs and to determine whether the temperature dependence is due to a phase boundary or to kinetic dependence. It will be necessary to establish the long-term behavior of the materials to be used in a repository; the time-temperature dependence and mechanism are important to this evaluation.

To determine the physical properties of backfill mixtures, direct testing of hydrothermally and thermally altered materials is necessary. Major degradation of bentonite, as documented here, is not readily apparent with the usual mineralogical techniques. Changes may not be detected even by analytical electron microscopy or high resolution microscopy.

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II. TRACE-ELEMENT TRANSPORT IN LITHIC MATERIAL BY FLUID FLOW (N. C. Sturchio and M. G. Seitz)

A. Chemical Mobility during Hydrothermal Alteration of Volcanic Rock in an Active Geothermal System

Important additions have been made to the data set for the continuing study of chemical mobility during hydrothermal alteration of the rhyolite flow breccia of the Biscuit Basin Flow in Yellowstone drill holes Y7 and Y8. Most of the new data have been acquired by instrumental neutron activation analysis (INAA). There is now compelling evidence of significant mobility of many elements in the shallow portion of this high-temperature geothermal system. The more mobile elements identified so far include H, Li, B, C, O, Na, Mg, Si, K, Ca, Fe, As, Br, Rb, Sr, Sb, Cs, Ba, W, and U. The mineralogical sources and sinks for some of these elements have been tentatively identified.

B. Instrumental Neutron Activation Analysis

The INAA method used here is slightly modified from that of Jacobs et al. [JACOBS]. About 100 mg of each sample was sealed in ultrapure 5.0-mm-O.D. x 3.4-mm-I.D. silica glass tubes (from Heraeus-Amersil, Inc., Sayreville, NJ). Portions of the Stentor steel rock-crushing apparatus and a blank silica glass tube were also analyzed to evaluate their possible contributions to the sample elemental abundance data. A standard fly ash (NBS 1633a) was used as an internal standard for the elements K, Sc, Cr, Fe, Co, As, Se, Pr, Rb, Sr, Sb, Cs, Ba, U, La, Ce, Nd, Sm, Cu, Tb, Yb, Lu, Hf, Ta, W, and Th. A standard basalt (USGS BCR-1) was used as a standard for Na, due to the low Na₂O content in NBS 1633a (0.22 wt %) relative to that of BCR-1 (3.23 wt %).

Irradiation was done at the University of Missouri research reactor in Columbia, MO. A thermal neutron flux of 3.5×10^{13} n/(cm²·s) was used. Samples were rotated during irradiation to minimize the effects of any neutron flux gradient. After ten hours of irradiation on March 12, the samples were retained at the reactor for decay of short-lived nuclides until March 16, at which time they were shipped to Washington University in St. Louis, MO, for gamma-ray spectrometry.

Gamma-ray spectra were acquired for eight hours on each sample during the week of March 19-23, then again during April 9-13, using four lead-shielded Princeton Gamma-Tech Ge-Li crystal detectors interfaced with a Nuclear Data Model 6620 multichannel analyzer system. Spectral data were reduced using the computer programs of D. Lindstrom and R. Korotev [LINDSTROM]. Analytical uncertainties for elemental abundances are 2-5% (relative) for most elements.

C. Samples Analyzed

The samples analyzed consisted of portions of rock, glass, and mineral separates from the Yellowstone Y7 and Y8 drill cores, plus residues from evaporated thermal waters from Y7 (other data for these water samples were reported previously [STEINDLER]). Twenty-five powdered rock samples, six hand-picked hydrated glass separates, three hand-picked mineral separates, and two water residues were analyzed.

The predominant rock type analyzed is termed a rhyolite vitrophyre flow breccia. Rhyolite is the volcanic equivalent of granite, and compositionally is essentially a mixture of roughly equal amounts of SiO_2 (quartz), KAlSi_3O_8 (K-feldspar), and $\text{NaAlSi}_3\text{O}_8$ (Na-feldspar), with minor amounts of Fe, Ca, Mg, Ti, and P, and other elements in trace amounts (<0.1 wt %). Vitrophyre is a volcanic rock consisting of glass that contains some well formed crystals (phenocrysts); in this case, the phenocrysts are feldspars, pyroxenes, Fe-Ti oxides, quartz, zircon, and apatite. Vitrophyre represents an igneous rock system quenched in the liquidus phase volume. The term "flow breccia" indicates that the vitrophyre was fragmented during flow as it cooled and became less plastic. Thus, as seen in the drill core, the rock consists of >1 -cm fragments of vitrophyre in a matrix of crushed vitrophyre (glass shards, crystal fragments, etc.). The matrix is poorly sorted and not well packed; therefore, it is more porous and permeable than the relatively unporous vitrophyre fragments that it contains. The flow of thermal water through the rock is mainly restricted to the matrix. This is reflected in the fact that the matrix is usually much more extensively altered (to clays and zeolites) and contains more precipitated silica than the vitrophyre fragments.

The sampling strategy employed here is based on the assumption that if there is (1) no significant primary compositional difference between the vitrophyre fragments and the matrix material at a given level and (2) no significant primary compositional variation with depth in the vitrophyre, then any significant chemical mobility due to hydrothermal alteration should be evident in any compositional anomalies or trends observed along the length of the sampling interval. As a test of this basic assumption, vitrophyre fragments and matrix material were analyzed at 1.5- to 6-m (5- to 20-ft) intervals along the flow breccia unit in Y7 and Y8. Most of the vitrophyre fragments analyzed were relatively unaltered, but several completely altered fragments were also analyzed. The matrix material ranged from moderately altered and friable through completely altered and cemented.

D. Analytical Results

1. Vitrophyre and Matrix Samples

Results of the recent INAA work are listed in Tables II-1, -2, -3, and -4. These results indicate that the basic assumptions used in the sampling strategy appear to be valid. Although considerable interpretation of the data remains to be done, and more data collection is in progress, some of the evidence for chemical mobility in this data set is discussed below.

First of all, the assumption of primary compositional homogeneity may be evaluated by comparing the concentrations of the relatively immobile trace elements, Zr, Ta, the rare earth elements (REE), and Th. This is illustrated in Fig. II-1, a chondrite-normalized REE diagram. The following features are evident in the figure.

- (1) The REE concentrations in Y7 and Y8 vitrophyre samples are identical, and vary within a narrow range.
- (2) The REE concentrations in Y7 and Y8 matrix samples have the same relative abundances as the vitrophyre samples, but a slightly greater range that totally overlaps that of the vitrophyre samples.

Table II-1. INAA 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 ppm (except as designated)											
	Y7174BV	Y7196BV	Y7205BV	Y7211BV	Y7217BV	Y7220.3BV	Y7233.6BV	Y7239BV	Y8190BV	Y8194.5BV	Y8202BV	Y7190PM
Na ₂ O, wt %	2.82	2.94	3.04	3.10	3.19	2.95	2.93	3.27	3.86	4.18	3.78	2.82
Sc	6.45	6.61	7.30	6.94	6.95	6.90	8.22	6.75	6.75	6.74	6.92	7.03
FeO, wt %	2.68	3.05	3.21	3.08	3.12	3.23	5.62	3.10	2.99	2.91	2.87	3.23
Co	2.02	2.53	3.17	2.65	2.69	2.84	4.33	2.65	2.66	2.66	2.49	3.12
Br	2.4	1.4	1.6	1.4	1.5	1.4	-	1.5	-	-	-	1.8
Rb	190	170	160	160	170	170	140	160	130	120	110	140
Sr	110	140	100	140	120	120	180	120	140	60	150	150
Zr	460	380	390	360	370	390	460	400	440	350	430	390
Cs	6.6	6.0	4.7	4.9	5.1	5.0	2.5	5.1	228	223	250	5.0
Ba	970	940	900	910	890	800	1520	780	890	520	520	930
U	5.3	5.1	9.7	12.8	6.4	7.5	6.0	5.5	5.9	5.6	6.6	4.9
La	71	69	68	69	69	70	71	68	70	68	71	68
Ce	144	140	136	140	138	140	144	140	139	136	142	141
Sm	11.4	11.6	11.1	11.5	11.3	11.5	11.5	11.3	11.3	11.2	11.4	11.3
Eu	1.82	1.87	1.95	1.99	1.88	1.86	2.04	1.81	1.92	1.90	1.90	2.04
Tb	1.8	1.8	1.8	1.7	1.7	1.9	1.6	1.7	1.7	1.8	1.8	1.7
Yb	6.0	5.9	5.6	6.0	5.9	5.9	5.4	5.9	5.6	5.5	5.7	5.9
Lu	0.90	0.88	0.84	0.87	0.88	0.87	0.82	0.87	0.85	0.83	0.86	0.88
Hf	12.1	11.5	10.9	10.9	11.8	11.5	13.2	12.3	11.8	10.3	12.2	11.6
Ta	2.9	2.8	2.8	2.9	2.9	2.9	3.3	2.8	2.9	2.8	3.3	2.8
Th	21.4	20.7	20.3	20.7	20.7	21.0	23.9	20.4	21.2	19.9	22.0	20.2

^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.

Table II-2. INAA Analyses of Matrix Separates from Flow Breccia of Biscuit Basin Flow, Yellowstone Drill Holes Y7 and Y8

Constituent	Composition of Samples, ^a ppm (except as designated)											
	Y7174MX	Y7199MX	Y7205MX	Y7209MX	Y7211MX	Y7217MX	Y7220.3MX	Y7223MX	Y7226.6MX	Y7233.6MX	Y7239MX	Y8202MX
Na ₂ O, wt %	3.75	3.40	3.43	3.34	3.47	3.22	3.34	3.29	3.52	3.19	3.24	3.80
Sc	9.56	7.11	8.32	8.25	6.72	6.94	6.14	5.87	6.38	6.52	6.01	6.51
FeO, wt %	4.37	3.43	3.86	3.74	3.11	3.24	2.73	2.74	2.72	2.92	2.83	3.17
Co	4.54	3.35	3.68	3.59	2.84	2.96	2.58	2.42	2.46	2.69	2.68	2.96
Br	1.4	1.7	2.1	1.6	1.4	1.1	0.4	-	0.3	-	0.5	-
Rb	150	160	180	160	140	140	130	150	140	130	120	130
Sr	150	120	160	150	140	120	100	100	120	110	130	120
Zr	500	480	480	510	420	390	370	410	400	430	380	510
Cs	6.0	4.6	5.6	5.0	3.6	3.5	2.9	3.2	3.0	2.8	2.8	185
Ba	890	840	1010	1100	950	1010	970	930	960	1020	1190	970
U	6.2	18.6	35.3	22.4	16.2	8.4	13.5	10.6	7.0	5.9	5.4	6.4
La	74	72	85	82	67	66	63	67	65	64	62	64
Ce	151	143	167	164	135	133	126	133	132	128	126	131
Sm	12.9	11.9	13.6	13.3	11.1	10.3	10.3	11.0	10.7	10.6	10.1	10.6
Eu	2.57	1.94	2.28	2.20	1.89	1.80	1.72	1.55	1.84	1.76	1.69	1.80
Tb	2.0	1.9	2.2	2.2	1.8	1.7	1.7	1.8	1.8	1.6	1.7	1.8
Yb	5.5	6.1	6.9	6.4	5.3	5.3	5.1	5.6	5.4	5.5	5.2	5.4
Lu	0.81	0.91	1.03	0.97	0.81	0.77	0.76	0.83	0.82	0.80	0.76	0.81
Hf	12.7	12.0	13.3	14.1	11.0	10.5	9.8	10.1	10.5	10.7	10.2	12.9
Ta	2.7	2.8	3.3	3.3	2.6	2.6	2.5	2.7	2.6	2.6	2.5	2.7
Th	19.4	21.3	24.6	23.8	19.8	19.5	18.8	20.6	19.7	19.1	19.7	19.9

^aTwo-letter suffix in sample number:

MX = matrix

Numerical value between drill-hole number (Y7 or Y8) and suffix indicates depth in feet.

Table II-3. INAA Analyses of Hydrated Glass, Mineral, and Xenolith Separates from Flow Breccia of Biscuit Basin Flow, Yellowstone Drill Holes Y7 and Y8

Constituent	Composition of Samples, ^a ppm (except as designated)									
	Y7174GL	Y7196GL	Y7205GL	Y7217GL	Y7239GL	Y8194.5GL	Y7239CE	Y7239CT	Y8191.1MO	Y7189XE
Na ₂ O, wt %	2.41	2.45	2.57	2.64	2.93	4.41	0.45	0.51	0.84	2.66
Sc	3.97	3.76	3.78	3.75	3.75	4.06	12.0	0.81	0.03 ^b	34.8
FeO, wt %	1.64	1.60	1.59	1.55	1.57	1.63	13.6	0.36	0.04	15.0
Co	0.71	0.68	0.72	0.80	0.74	1.36	17.3	-	-	34.7
Br	-	-	-	-	-	-	-	0.31	-	1.0
Rb	200	200	190	200	190	150	270	46	24	40
Sr	30	30	50	40	-	30	-	19	-	290
Zr	370	360	330	360	350	360	220	13	-	390
Cs	5.0	4.5	4.6	5.2	5.7	336	8.5	3.01	56	6.3
Ba	890	870	860	820	730	490	100	220	35	440
U	5.8	5.4	6.8	5.9	5.5	4.8	3.4	1.42	0.7	0.8
La	74	74	75	75	74	62	102	3.63 ^b	0.32 ^b	40.1
Ce	145	144	145	145	144	124	207	7.0	0.8	85
Sm	11.5	11.4	11.5	11.6	11.5	10.0	23.9	0.70	0.05	11.0
Eu	1.00	0.98	1.01	1.01	0.98	1.19	2.26	0.06 ^b	-	3.56
Tb	1.8	1.8	1.7	1.8	1.8	1.5	4.5	0.13	-	1.9
Yb	6.0	5.8	5.9	5.9	5.8	5.2	19.1	0.53	0.03	5.3
Lu	0.91	0.90	0.90	0.90	0.91	0.82	3.0	0.08 ^b	-	0.80
Hf	10.1	10.0	10.0	10.3	10.1	9.7	3.0	0.44	0.11	8.6
Ta	3.2	3.2	3.2	3.2	3.2	3.1	0.8	0.10	-	1.8
Th	24.9	24.8	24.9	24.9	24.8	23.9	7.7	0.96	0.1	4.4

^aTwo-letter suffix in sample number:

GL = glass

CE = celadonite

CT = β -cristobalite

MO = mordenite

XE = xenolith

Numerical value between drill-hole number (Y7 or Y8) and suffix indicates depth in feet.

^bCorrected for contribution from silica tube.

Table II-4. INAA Analyses of Residues from Evaporated Yellowstone Thermal Waters^a

Constituent	Composition, $\mu\text{g/L}$	
	Y7200	Y7240
As	830	930
Br	22	33
Rb	150	170
Sb	27	27
W	400	500

^aAnalyses are of residue from 5.00 mL of sample evaporated at 75°C.

These features apply as well to the glass separates; however, the glass and mineral separates are discussed separately here.

If these close compositional similarities are taken to indicate primary compositional homogeneity, then anomalous concentrations or trends observed for other elements may be taken as evidence for mobility. Elemental mobility in such systems is due to leaching, dissolution, precipitation, crystallization, recrystallization, ion exchange, or adsorption processes involving the interaction of solid and liquid (and sometimes gaseous) phases. Several first-order anomalies and trends are evident in the data set.

Uranium concentrations in vitrophyre samples (with two exceptions) are fairly constant (5.1-7.5 ppm), but matrix U concentrations are generally much higher, reaching 35.2 ppm in sample Y7205 (sample from drill hole Y7 at a depth of 205 ft) as shown in Fig. II-2. At low concentrations, five of the Y7 matrix samples, and the Y8 matrix sample, match the vitrophyre samples in U concentration. These are interpreted as being representative of primary U concentrations in the matrix.

The fact that U does not correlate with Zr in the U-enriched samples indicates that the anomalous U is not contained in zircon. The highest U concentrations occur in a zone from Y7199 to Y7211. This zone coincides with a zone of boiling in Y7, as evidenced by deposits of bladed calcite in open fractures [KEITH-1978]. There is a possible connection between the anomalous U and the calcite. During boiling, dissolved CO_2 is released from the liquid to the vapor phase, thereby disturbing the dissolved carbonate equilibria, causing precipitation of calcite and an increase in pH. If U is in solution as a carbonate complex, then the sudden drop in pCO_2 and increase in pH during boiling could destabilize the U-carbonate complex and cause precipitation of a less soluble U-hydroxide phase. In this case, disseminated U-hydroxide should be present in the matrix samples having anomalous U, and would be revealed by an induced fission autoradiographic technique.

Fig. II-1. Chondrite-Normalized REE Diagram for Vitrophyre, Matrix, Glass, and Mineral Separates from Flow Breccia of Biscuit Basin Flow, Y7 and Y8 Drill Cores, Yellowstone National Park. Chondrite values from Haskin [HASKIN].

As shown in Table II-1, there appears to be a general trend of decreasing Ba with increasing depth in the Y7 vitrophyre samples (970 ppm at 174 ft to 780 ppm at 239 ft). This is also seen in the glass separates

Fig. II-2. Uranium Concentration vs. Depth in Vitrophyre, Matrix, and Glass Separates from Flow Breccia of Biscuit Basin Flow, Y7 and Y8 Drill Cores, Yellowstone National Park

(Table II-3), and possibly indicates more leaching of Ba from the glass with increasing depth (temperature). An exception to this is sample Y7233.6 in Table II-1 (1520 ppm), a vitrophyre sample that is almost completely altered to celadonite and clinoptilolite. Perhaps the clinoptilolite has preferentially incorporated Ba during alteration. In the matrix samples, Ba is generally higher than in the vitrophyre samples. This could also be related to the generally greater amount of clinoptilolite in the matrix relative to the vitrophyre.

Although Cs is not highly variable in Y7 vitrophyre samples (Table II-1), 4.7-6.6 ppm, except Y7233.6 with 2.5 ppm, it shows a general decrease with increasing depth in the Y7 matrix samples (Table II-2), 6.0 ppm at 174 ft to 2.8 ppm at 239 ft. However, Cs is very much enriched in the Y8 vitrophyre (Table II-1) and matrix (Table II-2) samples, 185-250 ppm. This difference is probably not primary, but is probably related to the alteration mineralogy. As shown in Table II-3, a mordenite separate from Y8 at 191.1 ft

has 56 ppm Cs, which is not sufficient to account for all the anomalous Cs in the Y8 samples. A logical possibility for the Cs host is analcime. Analcime has been identified as the host for the anomalously high Cs concentrations in samples from Y8 and other Yellowstone drill cores [KEITH-1983]. Also, trace amounts of analcime have been identified in the flow breccia samples, Y8185.3 and Y8187 [KEITH-1978]. Considering that analcime concentrates contain up to 4700 ppm Cs [KEITH-1983], then trace amounts of analcime in addition to the abundant mordenite could account for the high Cs concentrations in the Y8 samples.

2. Glass and Mineral Separates

The INAA data for glass and mineral separates are given in Table II-3. Major-constituent data for glass separates are given in Table II-5.

Table II-5. Major-Constituent Composition of Hydrated Glass from Flow Breccia of Biscuit Basin Flow, Yellowstone Drill Holes Y7 and Y8

	Composition of Samples, ^a wt %					
	Y7174 (8)	Y7196 (11)	Y7205 (6)	Y7217 (8)	Y7239 (7)	Y8194.5 (6)
Constituent:						
SiO ₂	71.5	70.8	71.9	71.6	70.8	68.9
TiO ₂	0.23	0.22	0.23	0.21	0.22	0.22
Al ₂ O ₃	11.4	11.1	11.2	11.1	11.2	11.1
FeO ^b	1.57	1.60	1.55	1.57	1.57	1.58
MgO	0.09	0.08	0.09	0.08	0.08	0.10
CaO	0.58	0.54	0.57	0.52	0.51	0.58
Na ₂ O ^c	2.41	2.45	2.57	2.64	2.93	4.41
K ₂ O	5.4	5.6	5.2	5.0	4.8	1.7
H ₂ O	6.8	6.9	6.9	7.4	7.7	10.2
CO ₂	0.04	0.04	-	0.07	0.07	0.40
Sum	100.0	99.3	100.2	100.2	99.9	99.2
Ratio:						
Na ₂ O/K ₂ O	0.45	0.44	0.49	0.53	0.61	2.59

^a All oxides except Na₂O, H₂O, and CO₂ analyzed by JEOL 733 electron microprobe; parenthetical values indicate numbers of spots averaged. Na₂O in glass separates measured by INAA. H₂O and CO₂ in glass separates measured by Perkin-Elmer model 240 CHN analyzer (I. Fox and P. Lindahl, analysts).

^b Total Fe as FeO.

^c INAA data for Na₂O in glass separates reveals a systematic error in electron microprobe Na₂O data [STEINDLER]; INAA data are more accurate.

The glass separates contain 6.8 to 10.2 wt % H_2O (measured as H by CHN analyzer). The H_2O content increases with increasing depth. Some of the H_2O in the Y7217, Y7239, and Y8194.5 separates may be attributed to incipient zeolitization of the glass. Most of the H_2O probably occurs as molecular water [BARTHOLOMEW]. However, no distinctions can be made with respect to bonding mechanisms from the available data.

Na_2O increases with increasing depth, and K_2O generally decreases with increasing depth, in the glass separates. Inasmuch as all the other major components of the glass (excluding H_2O) and the $(Na + K)/Al$ ratio remain constant, it is probable that the systematic variability in Na_2O/K_2O reflects an ion exchange process [TRUESDALL], as shown in Fig. II-3. Similar effects in hydrated rhyolitic glass have been reported by other workers [JEZEK, NOBLE, STEWART].

The celadonite vein separate from Y7239 (Table II-3) shows that Sc, Co, Fe, Rb, Cs, and the REE are significantly enriched relative to the vitrophyre in Y7239 (Table II-1). This suggests that these elements were all efficiently scavenged from the thermal water during celadonite growth. Some of the trace components are probably structural constituents of celadonite (Sc, Co, Rb, Cs), whereas others may be adsorbed. The abundances of the REE in this celadonite separate indicate relative enrichments of Sm, Tb, Yb, and Lu when

Fig. II-3. Alkali Variation vs. Temperature in Hydrated Glass Separates from Vitrophyre in Biscuit Basin Flow, Y7 and Y8 Drill Cores, Yellowstone National Park

compared to the REE in the vitrophyre, matrix, and glass separates (Fig. II-1). This may indicate fractionation due to the greater stability (mobility) of heavy REE halide and carbonate complexes relative to light REE complexes in aqueous solution.

The Y7239 cristobalite separate shows generally low concentrations of all trace elements analyzed (Table II-3). The FeO and REE concentrations in the cristobalite separate are all about 3% as large as those in the celadonite separate, indicating that about 3% of the cristobalite separate consists of intergrown celadonite. The appreciable Na₂O content of the cristobalite separate probably indicates the presence of some intergrown clinoptilolite (as also indicated by unpublished X-ray diffraction data provided by T. Keith, USGS). Thus, the Rb, Sr, Cs, and Ba concentrations may also be partly due to contributions from the intergrown celadonite and clinoptilolite.

The Y8191.1 mordenite vein separate shows very low concentrations of all elements analyzed, except for Na, Rb, Cs, and Ba (Table II-3). Of these, the high Cs and low Rb, Sr, and Ba concentrations relative to those of vitrophyre samples has an important bearing on the fates of these elements during alteration of vitrophyre.

3. Water Samples

Two thermal water samples (5.00 mL each) were evaporated at 75°C. The residues were analyzed by INAA and data are shown in Table II-4. The only elements for which reliable data were obtained are Na, As, Br, Rb, Sb, and W.

E. Further Work

More analytical data are being collected for some of the samples reported here (ICP-AES and oxygen isotopes by mass spectrometry). The U anomaly in Y7 will be further studied by obtaining ²³⁴U/²³⁸U and ²³⁰Th/²³²Th ratios, in addition to performing induced fission autoradiography, on selected samples. Unaltered samples of the Biscuit Basin Flow will be collected from surface outcrops and analyzed using the same methods, for comparison with altered samples. A series of samples of the pumiceous tuff in Y8 will be analyzed, because the data for Y7190PM (pumiceous tuff) indicate no significant primary compositional difference between the tuff and the vitrophyre. The bottom of Y8 is about 504 ft below the surface; thus, there is about an additional 300 ft of pumiceous tuff to be sampled. The alteration mineralogy of the tuff does not differ from that of the flow breccia in Y8 [KEITH-1978, -1983]; therefore, this extra sample interval will provide valuable information with respect to some of the composition anomalies and trends observed in the present data set. Apparent distribution coefficients will be calculated when more mineral separates have been analyzed.

Further analyses of the data, and implications for studies of hydrothermal alteration, ore deposition, nuclear waste isolation, and geothermal energy development, are also continuing.

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III. REACTION OF GLASS WITH WATER (J. K. Bates, T. J. Gerding, and D. F. Fischer)

In work for Lawrence Livermore National Laboratory (LLNL), ANL is developing a test procedure that will be used to provide licensing information for the Nevada Nuclear Waste Storage Investigations (NNWSI) Test Site repository location. Part of the program is to develop the test procedure (T1), part is to demonstrate that the test results provide the necessary information, and part is to perform actual testing. The scope, summary, uses, and limitations of the test have been given previously [STEINDLER-1984A]; however, the uses and limitations of the test are repeated herein.

The test is designed to provide reliable, reproducible data that can be used in the licensing of the NNWSI repository site. To facilitate achieving this goal, the test has been designed as a simplified controlled simulation, but not a duplication, of expected repository conditions. The procedures [STEINDLER-1984A] provide a worst-case water/waste package contact rate and provide artificial constraints to ensure reliability. Specifically, the test will provide the following:

- (1) Data on release of radionuclides and selected matrix elements from the waste package by means of solution analysis as a function of time. These data will be used to determine whether a constant release from the waste package can be established and what the limits of this release are.
- (2) Data on alteration of the waste form as a function of time. These data will corroborate those from the solution analysis to determine the degree of release that can be established and provide insight into the method of the waste form/water reaction. The test matrix is not extensive enough to provide a detailed mechanism of the release process directly.
- (3) A description of the interaction between the waste form and canister under the specific conditions necessary to aid a more detailed investigation of canister corrosion.
- (4) A description of the interaction between the released radionuclides and the repository rock under specific test conditions, to aid in interpreting more detailed radionuclide-migration testing.

Test limitations are as follows:

- (1) The test conditions are not an exact duplication of the repository conditions, and test results should not be taken out of context and used as such. However, in conjunction with parametric tests, it may be possible to use them for other purposes.
- (2) The test will not provide detailed canister-corrosion rates that can be used to measure canister integrity.

- (3) The test will not provide detailed radionuclide-migration information that can be used to predict transport through tuff. (Due to lack of Eh/pH control in the test, the radionuclide valence states may not be the same as in the repository.)

An initial vessel design and test procedure were developed [STEINDLER-1984B], and a series of nine preliminary tests was run to assess the utility of the test method and its ability to meet the specified uses and limitations. Based on this assessment, the vessel design and procedures were modified slightly and two prototype reaction vessels were built. Using the prototype vessels, two subsequent five-week tests were run.

Current effort in T1 development has been to assess, in detail, the results of both sets of tests to establish a final vessel design, to determine vessel construction and cost alternatives, and to finalize a test matrix so that actual waste package testing can begin. Additionally, parametric tests are being conducted to establish source term release from the waste form/package, and analog tests (T2) using tuff rock cores are in progress.

A. NNWSI Test 1 (T1) Development

The T1 test requires a vessel design that is easy to work with and compact, yields reproducible and interpretable data, and can be used in both the laboratory and the hot cell. It must also be amenable to manufacture within reasonable cost and time constraints. Finally, the results must be repository relevant as described in the uses and limitations listed above.

The preliminary vessel design [STEINDLER-1984B] was followed, using materials on hand, to produce the vessels used in initial testing. These vessels tested the design, provided a feeling for the type of data that would be produced, and revealed a need for modifications that would be necessary before long-term and hot cell testing could begin. The data produced are not necessarily representative of data that will be produced in the final Phase II testing program, because materials of construction have not been carefully controlled, and because procedural modifications have been made.

1. Summary of Preliminary Test Results

Nine preliminary tests have been completed and analyzed. Tests were run for six and twelve weeks using the test matrix shown in Table III-1. The tests are best interpreted by analyzing them in groups of six and twelve-week tests conducted using collection vessels of (1) tuff, (2) a planchet with no tuff, and (3) a planchet on top of the tuff. A detailed listing of results of preliminary T1 tests is presented in Table III-2; some data are incomplete.

a. Test 6

This test ran for six weeks using a tuff collection vessel. There was a reaction between the Type 304 L stainless steel (SS) components of both the waste package and the tuff support ring and the Type 303 SS of the reaction vessel. The reaction resulted in large amounts of Cr, Fe, Ni, and especially Mn in solution and in the formation of several reaction products, but it is not likely to have significantly affected the release from the glass

Table III-1. NNWSI T1 Tests

Test No.	Test Components			Test Period, weeks	Analyses
	Vessel	Waste Package	Liquid Collection		
<u>Preliminary</u>					
6	45-mL Parr	Glass, perfaplate	Tuff, tuff support ring	6	Solution, perfaplate, glass, tuff support ring
7	45-mL Parr	Glass, perfaplate	Tuff, tuff support ring	12	Solution, perfaplate, glass, tuff
9	22-mL Parr	Glass, perfaplate	Planchet	6	Solution, perfaplate, glass
10	22-mL Parr	Glass, perfaplate	Planchet	12	Solution, perfaplate, glass
13	22-mL Parr	Glass, perfaplate	Planchet	6	Glass
12	45-mL Parr	Glass, perfaplate	Planchet on tuff, tuff support ring	6	Solution
8	45-mL Parr	Glass, perfaplate	Planchet on tuff, tuff support ring	6 +2 +4 (12 total)	Solution Solution Solution, tuff
11	22-mL Parr	Glass, perfaplate	None, tinopal fluorescent dye		
16	45-mL Parr	None	Tuff, tuff support ring	6	Solution and tuff
<u>Subsequent</u>					
15	Prototype	Glass, welded perfaplate	Planchet on tuff, tuff support ring	5	Glass, perfaplate
14	Prototype	Glass, welded perfaplate	Vessel only	5	Glass, perfaplate

Table III-2. Description and Results of Preliminary T1 Testing

Solution Volume, mL	Analysis	Concentration, ng (total in solution), except as noted							
		Al	B	Ba	Ca	Co	Cr	Fe	Li
Test Components									
	J-13 water, ng/mL	<100	130	<10	13600	<20	<20	<10	49
	SRL 165 glass, element %	2.17	2.11		1.07			8.60	2.18
Test No. 6									
22.62	Vessel soak		1470	400	69500	300	9000	41000	12000
20.95	Vessel acid rinse	730		850	13000	350	10700	25000	900
	Total	730	1470		82500	650	19700	66000	12900
Test No. 7									
21.33	Vessel soak	2800	9400	500	222000		1650	15800	23500
20.13	Vessel acid rinse	1100	900	250	18000		9200	15900	1500
	Total	3900	10300	750	240000		10850	31700	25000
Test No. 9									
23.91	Planchet rinse				900			850	850
19.92	Planchet soak						320	400	
20.45	Planchet acid rinse						960	2650	
20.39	Vessel soak	1830	5300		15700		1100	8000	15900
20.11	Vessel acid rinse	1800			760		5000	9000	360
	Total	3630	5300		17360		7700	20900	17110
	Minus 0.9 mL J-13 water	3600	5200		5100				17100
	(NL) ₁ ^a	0.12	0.18		0.35				0.57
	(NL) ₁ ^a + 50%	0.18	0.27		0.53				0.86
Test No. 10									
21.17	Vessel soak	7600	13300	300	33900	370	1000		29600
20.39	Vessel acid rinse	2200	930		1800	240	3100	11600	1100
	Total	9800	14230	300	35700	610	4100	11600	
	Minus 1.8 mL J-13 water	9800	14000	300	11200				30600
	(NL) ₁ ^a	0.33	0.48		0.76				1.02
Test No. 12									
22.07	Vessel soak	840	1350		22000		550	2100	5500
20.88	Vessel acid rinse	1300			1700	200	2700	5000	6500
21.96	Planchet rinse								
20.83	Planchet soak								
	Subtotal	2140	1350		23700	200	3250	7100	2000
19.88	Waste package rinse	2600	975		3000			240	3000
	Total	4740	2325		26700	200	3250	7340	5000
Test No. 8									
21.77	Planchet rinse ^b				740				
19.82	Planchet soak							475	
20.20	Planchet acid rinse								
21.31	Planchet rinse ^c								
20.11	Planchet soak							300	
19.99	Planchet acid rinse								
20.97	Planchet rinse ^d								
20.00	Planchet soak							460	
20.21	Planchet acid rinse							300	
21.23	Vessel soak	1400	6100	400	743000	900	62000	330000	11900
20.34	Vessel acid rinse	1900	900	500	102000	700	49000	550000	750
	Subtotal	3300	7000	900	845000	1600	111000	880000	12650
17.06	Waste package rinse	800	1200		5600		200	11400	3100
	Total	4100	8200	900	850600		111200	891400	15750
Test No. 16									
10.73	Vessel soak + acid rinse - 0.9 mL J-13 water	1080	600		2250	200	2000	7615	

^aNormalized release rate (dimensionless).^bAfter six weeks.^cAfter eight weeks.^dAfter twelve weeks.

Table III-2. (Contd)

Solution Volume, mL	Analysis	Concentration, ng (total in solution), except as noted							
		Mg	Mn	Na	Ni	Si	Sr	U	Zr
Test Components									
	J-13 water, ng/mL	2130	<5	46700	28	30900	41	<1	<10
	SRL 165 glass, element %	0.48	2.25	7.64	0.71	25.29	0.13	0.99	
Test No. 6									
22.62	Vessel soak	2500	387000	84600	27000	32000	475	11	840
20.95	Vessel acid rinse	550	150000	7750	30000	17000	100	25	1650
	Total	3050	537000	92350	57000	49000	575	36	2490
Test No. 7									
21.33	Vessel soak	10200	360000	196000	16600	72500	1450	26	960
20.13	Vessel acid rinse	1130	139000	15700	700	8000		129	1200
	Total	11330	499000	211700	17300	80500	1450	155	2160
Test No. 9									
23.91	Planchet rinse		25000	5700				125	
19.92	Planchet soak		16700		1430			34	
20.45	Planchet acid rinse		45600		880			88	
20.39	Vessel soak	3500	500000	90000	3900	50000	350	734	260
20.11	Vessel acid rinse		165000	2400	2600	20000		784	400
	Total	3500	752300	98100	8810	70000	350	1765	660
	Minus 0.9 mL J-13 water	1600		56100		42200	300	1765	
	(NL) ₁ ^a	0.24		0.53		0.12	0.20	0.13	
	(NL) ₁ ^a + 50%	0.36		0.80		0.18	0.30	0.19	
Test No. 10									
21.17	Vessel soak	7200	930000	191000	4400	119000	550	85	275
20.39	Vessel acid rinse	500	216000	7500	3300	10200		1590	1100
	Total	7700	1146000	198500	7700	129200	500	1675	1375
	Minus 1.8 mL J-13 water	3900		114000		73600	480	1675	
	(NL) ₁ ^a	0.59		1.08		0.21	0.31	0.12	
Test No. 12									
22.07	Vessel soak	1300	88000	62000	9900	11000			150
20.88	Vessel acid rinse	330	79000		9400			140	2500
21.96	Planchet rinse								
20.83	Planchet soak		625		1500				
	Subtotal	1630	167000	62000	20800	11000		140	2650
19.88	Waste package rinse	660	12500	18000	8000			107	500
	Total	2290	179500	80000	28800			247	3150
Test No. 8									
21.77	Planchet rinse ^b		6750	15450					
19.82	Planchet soak		2400		1250				
20.20	Planchet acid rinse		160		1270				280
21.31	Planchet rinse ^c		300						
20.11	Planchet soak		2000		1150				150
19.99	Planchet acid rinse								
20.97	Planchet rinse ^d		500						
20.00	Planchet soak		460		540				
20.11	Planchet acid rinse								260
21.23	Vessel soak	15000	113000	234000	57000	108000	3600	25	1300
20.34	Vessel acid rinse	2000	167000	17000	40700	55000	650	53	1400
	Subtotal	17000	280000	251000	97700	163000	4250	78	2700
17.06	Waste package rinse	1200	36000	24000	700	16700		170	150
	Total	18200	316000	275000	98400	179000		248	2850
Test No. 16									
10.73	Vessel soak + acid rinse - 0.9 mL J-13 water	3000	118000	3500	10400	21450	64	15	750

^aNormalized release rate (dimensionless).^bAfter six weeks.^cAfter eight weeks.^dAfter twelve weeks.

or the overall behavior of the system. Additionally, a significant amount of sulfur was released from the Type 303 SS. This permeated the experiment and may have affected the glass reaction, but because some sulfur is always present in Savannah River Laboratory (SRL) defense glass, the results may not have been affected too adversely. Calcium sulfate, formed as round assemblages, was found in the bottom of the tuff cup.

The elements whose release is indicative of glass reaction are Li, U, and possibly Sr and B. Other elements are present in either the J-13 well water, the tuff, or the SS components. Improper treatment of the tuff could result in data for B, K, Ca, and Na that would be difficult to interpret, whereas SS reactions could produce large amounts of Cr, Mn, Fe, and Ni.

Normalized release rates $[(NL)_i]$ for the six-week period were calculated; however, they are only tentative because they do not take into account the solution that remained on the waste package and the fact that some equilibration occurred with the tuff that was saturated in J-13 well water. These $(NL)_i$ values are best used for comparative purposes, as discussed later.

b. Test 7

This test ran for 12 weeks using a tuff collection vessel. The waste package components have an appearance similar to that described for the six-week test except there was a greater coverage of $CaSO_4$ on the bottom of the tuff cup. Solution analyses, when compared with the six-week test, show an increase of all elements, with the soluble tuff components (Ca, Mg, Sr, Na) showing a greater increase than that observed for Li and B, which come mainly from the glass. Uranium is sorbed to the tuff, as shown by complete tuff dissolution.

It appears that both absolute release (B, Li) and interactive release (all other elements) can be obtained from this type of test.

c. Tests 9 and 13

These tests ran for six weeks using a planchet as the collection vessel. There was no tuff present. In both tests, the waste package had a typically reacted appearance, except that on the top surface of the glass there was evidence of leached layer formation. These layers were rich in Mn and Ni and were similar to layers formed on other SRL glasses. Various alteration products were noted that contain Si-, Al-, S-, and Cr-enriched SS components. These products were noted on both the glass and the SS surface in contact with the glass.

The elemental releases were within reasonable limits, ranging from 0.8 g/m^2 for Na and Li to 0.1 g/m^2 for U. The elements B and Si had low releases compared with Na and Li. The low Si value can be explained by alteration product formation, but the low B value is surprising. Normalized weight loss $[(NL)_{wt}]$ was $\sim 1 \text{ g/m}^2$. Very little solution remained in the planchet at the end of the experiment.

d. Test 10

This test ran for 12 weeks using a planchet as the collection vessel. No tuff was present. The waste package was, by visual appearance, somewhat more reacted than previous waste packages. The surface will be analyzed by secondary ion mass spectroscopy (SIMS).

Elemental releases of all elements but U were greater than they were during the six-week periods of tests 9 and 13. However, the rate of release of most elements decreased during the second half of the period, as is typically observed for SRL glasses in static or low-flow tests.

e. Test 12

This test ran for six weeks using a planchet placed on top of a tuff cup to collect the liquid that dripped from the waste package. The waste package had a typically reacted appearance, with a $(NL)_{wt}$ of $\sim 1 \text{ g/m}^2$. The solution analysis indicated that very little solution or cations remained in the planchet. The cations in the solution collected from the test vessel were present in amounts similar to those observed when using the tuff vessel only. Additionally, there was no buildup of cation concentration in the standing water remaining on the waste package, suggesting that either some type of "vapor phase" or aerosol transport occurred or that transport occurred along interconnecting pathways of thin liquid film. Somehow, there was transport of cations from the waste package to the tuff and the vessel walls.

f. Test 8

This test used a planchet placed on tuff as a collection vessel, and was terminated after 12 weeks. The planchet was replaced twice, after 6 and 8 weeks, and the test was continued each time. The waste package had a $(NL)_{wt}$ of $\sim 2 \text{ g/m}^2$ and a typically reacted appearance at termination. There was very little solution in any of the planchets and a similarly small amount of cations. After the 12-week period, solution from the entire assembly was analyzed. It contained constituents released from the glass and also provided evidence that the tuff pretreatment process had not been complete because of large amounts of Na, Ca, Mg, and Sr in solution. The U was detected mainly in the tuff. This again provided evidence of thin film or vapor phase transport.

g. Test 16

This was a six-week test in which J-13 water was introduced directly into a tuff cup. There was no waste package present. We expected that behavior similar to that noted in tuff/water equilibration experiments [OVERSBY] would be observed. Amounts of Al, B, Ca, Mg, Sr, and U in excess of that added to the system were found in solution, whereas lesser amounts of Na and Si were noted. The Ca, Mg, Sr, Na, and Si results are in variance with those of Oversby. The Ca, Mg, Sr could have come from soluble caliche that had not been removed by pretreatment, and Si values were subject to poor analytical sensitivity (this has been corrected), but the amount of Na was unexplainably smaller than expected. Low Na values in solution were not noted in other experiments where leachate contacted tuff.

2. Comparison and Interpretation of Preliminary Testing

The utility of the preliminary test procedure and vessel design is best judged by comparing the 6- and 12-week results of each test type (i.e., tuff, no tuff, planchet on tuff) separately and then by intercomparing the results of each test type. This is to determine whether the present uses and limitations of the test can be established. Additionally, changes in vessel design or procedures that result in improving the ease of operation are also considered.

a. Tests 6 and 7

In these tests, tuff was used as the collection vessel. Comparisons can be made between the 6- and 12-week runs of the behavior of the waste package, the appearance of the tuff, and analysis of solutions.

(1) Waste Package

The degradation of the waste package can be measured by the $(NL)_{wt}$ and by surface analysis of the glass. The weight loss measure is an established, easy, and precise way of measuring total release from the glass, and is complementary to surface analytical and solution analysis. The $(NL)_{wt}$ was not measured at 6 weeks; after 12 weeks it was 1.9 g/m^2 .

Visual observation of the 6- and 12-week waste packages showed little difference between the two. Detailed analysis by scanning electron microscopy (SEM) of the glass surfaces and cross sections revealed little difference in the surface appearance and no evidence of layer formation. This would be expected based on the 12-week $(NL)_{wt}$, which indicates any selective release mechanism would penetrate into the glass $< 1 \text{ } \mu\text{m}$. Analyses by SEM and energy dispersive X-ray (EDX) become effective tools for studying reacted layers only when the layer thickness is greater than 1-2 μm . A SIMS system is currently being set up, and should provide useful information about thin reaction layers.

(2) Solution Analysis

Solution analyses were done for all cations expected in the system except K and Cs. Results for Cr, Fe, Mn, and Ni are difficult to compare because their release is determined by SS corrosion that, upon visual examination, is not uniform between samples. A considerable amount of all the SS components was found in solution, and Mn was detected in especially large amounts.

The amounts of the other cations increased from the 6- to the 12-week test. The measured amount is governed by reaction of the glass, reaction of the tuff, and equilibration/dilution of the leachate with the J-13 water in the tuff. The effect of the last point is most important during the first six weeks of the 12-week test and depresses the values for all elements, especially B, Li, and Sr, because their release is mainly from the glass. However, after the tuff becomes saturated with leachate and if there is no reaction with the tuff, the amount of an element found in solution equals that released from the glass. Generally the amount of water necessary to

saturate a tuff cup is ~0.5-1 mL, so equilibration of the saturated tuff should occur at about six weeks. Therefore, solution data for the first six-week period cannot be expected to provide quantitatively interpretable values. Solution data must also be tempered by the possibility that all highly soluble caliche was not removed from the tuff. This would affect results for B, Ca, Na, Sr, and Mg.

However, releases calculated for the second and continuing test periods may provide useful data. Several elemental releases calculated for the second six-week period (Table III-3) are useful in later comparisons.

Table III-3. Data from the Second Six-Week Period, Test 7^a

	Concentration, ng (total in solution)						
	B	Li	Na	Sr	Si	Mg	Al
Tuff	8830	12100	77320	875	9430	6150	42724
No Tuff	8950	13590	58370	250	18100	2283	6100

^aStanding water on the waste package not included. Its effect would be minimized as test duration increases.

The release of uranium is a somewhat different situation. Analytical techniques for analyzing U are very sensitive and reproducible, and no U is analyzed in J-13 well water. This, and the fact it is a radionuclide, make U very attractive to study. However, some uranium is present in unreacted tuff. Three separate tuff samples were analyzed for U, providing an average value of 3.3 ± 0.2 μg per gram of tuff. The amounts of U detected in solution in both tests 6 and 7 were extremely low. Therefore, in test 7, a portion of the tuff most likely to have contacted the leachate was totally dissolved and analyzed; it contained 4.1 ± 0.2 μg per gram of tuff. This is a small but significant increase and suggests that total dissolution of the tuff is a possible means to analyze for certain elements.

(3) Tuff

The only apparent change to the tuff was a greater coverage of CaSO_4 present after 12 weeks than after 6 weeks.

When tuff is used as the collection vessel, the test can provide information about (1) the quantitative release of radionuclides from the glass, (2) the quantitative degradation of glass, and (3) the interaction of glass components with the tuff.

A quantitative measure of the release of the radionuclides doped into the glass can be obtained by combining them in solution with those determined by analyzing the tuff (using either dissolution and radiochemical separation or γ counting). This is possible because the radionuclides must come from the glass. A quantitative determination of other elements released

from the glass is possible if the tuff is dissolved, but the precision of these values would probably not be good because there would be small differences between large numbers and because the nonuniformity between 5-g tuff samples might be of the order of magnitude of the release from the glass. The elements most likely to give reliable results would be B, Li, U, and Sr.

The degradation of the glass can be measured by weight loss and by surface analytical techniques. Weight loss was shown to give numbers of good precision, and surface profiling with SIMS should provide elemental information.

The interaction of glass components with tuff can be obtained by ion beam profiling of the tuff or by careful analysis of solution results (Sec. III.A.3). Samples subjected to ion profiling could then be dissolved for total analysis or, perhaps, the ion profiling itself would provide quantitative values.

b. Tests 9, 10, and 13

In these tests, a planchet was used as the collection vessel. With no tuff present in the system, a more straightforward analysis of elemental release is possible. Those elements found in solution can come only from the glass or the SS. The effect of tuff on the release from the glass would be small, but must be determined. Comparative analyses can be made of the waste package and of the solution.

(1) Waste Package

Normalized weight loss was determined for one six-week test and was 0.81 g/m^2 . Visual and SEM analyses revealed little difference in the appearances of the two test components, but a more detailed analysis will be done with SIMS.

(2) Solution Analysis

Normalized release rates have been determined for elements that are not SS components (Table III-2) after accounting for standing water and for the contribution from J-13 water. The first six-week period of test 10 may have had a somewhat lowered release, because release from the entire surface does not occur until the entire surface has been wetted. Experiments using a fluorescent dye indicate that both the top and bottom surfaces reach volume equilibrium in about two weeks; thus, this lowered release should not have too much effect. Elemental trends are discussed in Sections III.A.1.c and d. In particular, release of most elements during the second six-week period of test 10 remained constant (Al, B, Ca, Mg) or slowed (Li, Na, Si, Sr). For uranium, there was a slight decrease in the amount detected after 12 weeks compared with 6 weeks.

Two data points do not make a statistically accurate curve, but the trend for most elements is, as expected, based on results from other SRL glasses. It may be useful to include this type of test in the Phase II test matrix because it is relatively easy to determine element release that comes only from the glass. The present analyses did not measure the

amounts of elements released from the glass that adhere to the perforated SS plate. This analysis might be useful for uranium, a significant amount of which was released from the reaction vessel only after an acid rinse.

c. Tests 8 and 12

In these tests, a planchet was placed on top of the tuff to collect the released solution. The testing was designed to provide a continuous test schedule using one waste package that could be periodically sampled. We anticipated that some liquid would collect in the planchet and, although liquid transport by convection and recondensation would occur, the cations would accumulate in solution. After each testing period the planchet would be removed and replaced with a new one, the solution in the planchet would be analyzed, and the test would continue.

This approach was made in test 12, which was terminated after 6 weeks, and in test 8, which was sampled after 6, 8, and 12 weeks. Comparisons were made of the 6- and 12-week waste packages, tuff cups, and solution analyses.

(1) Waste Package

Normalized weight losses were determined for both samples, 0.8 g/m^2 for 6 weeks and 2.2 g/m^2 for 12 weeks, indicating reaction of the waste package continued during the second 6-week period.

Visual observation of the waste package components indicate few differences, except that the tuff cup in the 12-week test had contacted the walls of the vessel and some interaction had occurred. Detailed surface analysis will be done with SIMS.

(2) Solution Analysis

The two tests were consistent in that in neither case was a significant amount of any element but Fe, Ni, or Mn found in the planchet. This suggests either that no dripping from the waste packages collected in the planchets, or that there was no dripping at all from the waste packages. In visual observation of the waste packages upon termination of the tests, large drops were seen several times at the bottom of the waste package, with release apparently imminent; in some cases a small amount of liquid was present in the planchet, although this could have resulted from condensation. Additionally, the waste package rinses indicated no increased concentration of cations in the water standing on the waste package. In both experiments the cations on the surface were similar and accounted for only a fraction of each element detected in total. Therefore, it seems highly likely that water does drip from the waste package.

Nevertheless, there is a process whereby the water and the cations transfer from the waste package or planchet to the cooler parts of the system, usually the vessel walls. This transport could be either some type of aerosol movement or diffusion along a thin liquid film that exists throughout the system. This will have to be studied further, but the ramifications are evident; those elements released from the glass will migrate to the cooler

parts of the repository unless they sorb selectively to some components. For uranium, tuff or SS seems to be a selective sorber, as in neither the 6- nor 12-week experiment is much U found in the vessel. However, on analysis of the vessel rim from the 12-week test, 4.1 μg of U on tuff was detected. This is greater than the amount of U found in nonreacted tuff.

A comparison of the solution results for the 6- and 12-week tests was not attempted because the pretreatment process for the latter (test 8) clearly left some highly soluble material remaining in the tuff; the detected levels of Ca, Mg, Sr, Na, and Si were unusually large. Anomalous results may also have been introduced due to the tuff contact with the vessel walls.

These six-week results are similar to the six-week results for the tuff (test 6); however, test 8 suggests that, whatever the transport mode, there is equilibration with the tuff with accompanying dilution of the J-13 water in the tuff. Thus, as in tests 6 and 7, the first six-week solution results do not give a total indication of release.

This test clearly did not achieve the desired results; however, it did produce valuable, although difficult to interpret, results. It provided information on degradation of the waste package, total release of radionuclides (as in tuff only), possible release of matrix elements (B and Li, because they appear not to interact with the tuff--see next section), and a measure of vapor phase or thin film transport.

3. Intercomparison of Results

The tests done with only the waste package give a good indication of selected elemental release, especially during the second six-week period when sample wetting and standing water effects are minimized. A comparison can be made with the second six-week period of the tuff-only test because, in this case, dilution effects become minimized. This comparison is shown in Table III-3. These results should give an indication as to whether any interaction occurs between released elements and the tuff and what type of solution/dissolution occurs in tuff under these conditions. However, the results must be tempered by the fact that, in some cases, there are small differences between large numbers.

The releases of B and Li in the two cases are essentially identical, indicating that little interaction occurs with the tuff, and that the two sets of experiments are providing consistent data. These elements are not expected to interact with tuff and, provided there is proper pretreatment, neither should be released by reaction with tuff. Sodium shows an increase due to reaction with tuff, which is expected. The alkaline earths, Sr, Mg, and Ca, each show an increase, which suggests a reaction of the tuff or dissolution of a soluble component not removed by pretreatment. Previous experiments [OVERSBY] suggest that, during equilibration of J-13 water with tuff at 90°C, these elements are depleted from solution. This is a discrepancy that may or may not be real. Silicon and aluminum seem to be held up in the tuff, but the Si values suffer greatly from detection sensitivity and the Al values must be verified in subsequent experiments. These results suggest that B and Li can be used to provide a reasonable measure of glass dissolution, whereas the other elements will be affected by tuff/leachate interactions.

Waste package degradation can be measured by $(NL)_{wt}$. All weight loss values are tabulated in Table III-4 and show that, with time, additional release occurs. The weight loss during the second six weeks is nearly the same as that observed during the first six weeks.

Table III-4. Normalized Weight Loss for All Tests

Test No.	Test Period, weeks	Surface Area, cm^2	Δ Mass, 10^{-4} g	$(NL)_{wt}$, g/m^2
14	5	12.23	11	0.90
15	5	12.20	11	0.90
			Avg	0.90
6	6	12.34	ND ^a	-
9	6	ND	ND	-
12	6	12.31	10	0.81
13	6	11.63	13	1.12
			Avg	0.97
7	12	11.88	23	1.95
8	12	15.35	34	2.21
10	12			
			Avg	2.08

^aNot determined.

Release from the waste package can also be compared with results of a set of simple tests [STEINDLER-1984A] done by dripping water on a sectioned piece of glass. The (NL) values measured in the present test are slightly larger than those from the simple tests ($<2X$), which is expected because the perforated SS allows more water to contact the glass. Thus, more release can occur before saturation is reached and release stops.

4. Conclusions from Preliminary Testing

The following major conclusions, directed toward assessing the utility of the test method, can be drawn from the preliminary testing.

- (1) General degradation of the glass can be ascertained by normalized weight loss measurements. This gives an easy, precise check on what happened during the experiment and can guide other analyses and aid in interpreting more sophisticated data.
- (2) Degradation of the waste package can be determined by surface analyses of the components. Analyses by SEM/EDX can be conducted to survey the extent of reaction and to identify the reaction products. The degree of reaction cannot easily be determined by SEM cross-section measurements, but should be amenable to study with ion-beam profiling techniques.

- (3) The release of radionuclides can be determined by analyzing the solution and dissolving and analyzing the tuff. Complete tuff dissolution is necessary because many radionuclides are expected to behave like uranium, which displays an affinity for tuff.
- (4) The release of Li and B (glass matrix elements) can be determined by analyzing the solution, provided sufficient time is allowed for J-13/leachate equilibration to occur. Such equilibration occurs within six weeks.
- (5) The degree that other elements (Al, Ca, Fe, Mg, Mn, Na, Si, and Sr) are released from the glass cannot be reliably determined when tuff is present, even by dissolution of the tuff. However, some indication of the interaction of these elements with the tuff can be obtained if the source term release from the glass is known.
- (6) The presence of tuff in the test does not appear to affect the degree to which the glass degrades. This is evident from weight loss measurements and from B and Li release during the second six-week period. However, considerably more testing is necessary to establish this point.
- (7) Separately designated collection vessels cannot be used to collect solution to be removed periodically for analysis. Some type of transport of water and cations appears to occur in the system. However, the use of this collection vessel approach (planchet on tuff) should provide valuable information on this transport process.
- (8) A new vessel design should incorporate greater clearance to manipulate test components, and the waste package needs to be sturdier to assure that the perforated SS rests flat and evenly on the glass.

It appears, within the limitations noted to be applicable, that this test procedure will provide the data required to meet its uses.

5. Summary of Prototype Test Results

To meet the recommendation noted in item (8) of the conclusions, and to make all components out of Type 304 L SS, minor modifications were made to the vessel design [BATES]. Two prototype vessels were constructed and two five-week tests were run to establish their performance. These two tests are described in Table III-1. Not all analyses have been completed; however, some results can be reported. These are summarized herein, and will be described in detail in a later report.

a. Test 15

This test ran for five weeks using a Type 304 L SS cap placed on top of a tuff cup. At the conclusion of the test, condensation was found on the sides and bottom of the test vessel, but no water was observed in the

SS or tuff cup. The bottom of the waste package was wet, but the top was dry. The glass had a typically reacted appearance, with circular areas visible on the top and bottom of the glass and flow patterns evident on the sides. The perflaplate had some rust-colored reaction products visible on the bottom piece near the welded areas. Weight loss from the glass was 0.9 g/cm^2 .

b. Test 14

This test ran for five weeks using only a waste package. The vessel and waste package at the conclusion of the test appeared the same as in test 15. We speculate that the top of the waste package was dry in these tests (it was wet in the preliminary tests) because (1) it takes longer from the time the vessel is removed from the oven until it is opened in the prototype tests; thus, more condensation can occur on the vessel walls during cooling, and (2) there is a tighter fit of the perflaplate on the top of the glass.

There was considerable reaction between the glass and the bottom perflaplate. This reaction occurred in the zone affected (discolored) by the welding process where there was contact with the glass. There were several pitted regions that were very Cr rich and contained a great deal of Fe and/or Cr silicate reaction product. This reaction product was on the glass and on the perflaplate.

This was surprising, so we reviewed all processes involving purchase, fabrication, and testing of the perforated canister. Analyses had been done previously (Sec. III.B) on the SS composition, excluding carbon, and all SS materials matched their certified values. A carbon analysis has revealed that the carbon levels are also as certified. The welding process was reviewed and is typical, if somewhat mild, for what would be done on an actual canister. The only suggestion of variance noted was the appearance of the as-received SS when viewed with the SEM; the grains are evident, which is definitely an unexpected situation.

We have submitted a perforated canister to D. McCright of LLNL for investigation and are testing the SS for sensitization ourselves. The supplier has been contacted to see if any abnormal steps were involved in processing. According to the specifications, none should have been. The reason for the reaction is still being investigated.

6. Phase II Testing

Based on results and observations made in the preliminary and prototype tests, a test matrix consisting of 11 separate tests has been established for Phase II testing. The main purpose of the Phase II test is to measure the release of elements from the waste package in the presence of tuff. Tuff is used in the system despite the fact it causes problems for analysis and interpretation. Duplicate tests are stopped at 13-, 26-, 39-, and 52-week periods and provide complete information on the system.

To aid in interpretation of the main battery of tests and to provide additional replication, a test is conducted without tuff in the system. This procedure provides a source term for element release in the absence of tuff

and allows the test to be continued indefinitely. Also, to provide replication, aid in interpretation, and study the effect of vapor phase or thin film transport, a test is included where the tuff vessel is covered with a SS cap. This test also is sampled periodically and can be continued indefinitely. The sampling procedure would involve taking the waste package and tuff cup (if included) out of the used reaction vessel and placing them in a new one. This would require two additional reaction vessels, but it is possible that the start of these tests could be delayed for 13 weeks to permit reuse of vessels from the first tests.

A blank(s) would also be included. The purpose of a blank is usually to identify any effects of the nonreactive or constant elements in a test. In the present case, a blank could be just the test vessel itself (this does not make much sense because SS components cannot be interpreted anyway), the tuff cup (perhaps best studied in a parametric test), the canister without glass (again, SS components cannot be interpreted), or the canister without the glass dripping into a tuff cup (SS components). At this point, the exact blank to be used is undefined.

The analyses would provide the following data:

- (1) Total radionuclide release by analysis of the solution and dissolution and analysis of the tuff.
- (2) Total (B, Li) release by solution analysis assuming no interaction with the tuff. It may be possible to determine total Cs release because tuff contains only 2 ppm Cs, but this would have to be investigated. Release of all elements from the glass can be determined from the no-tuff experiments.
- (3) Degradation of the waste package by weight loss and surface analyses.
- (4) Corrosion of SS components and the SS/glass interaction by surface analysis.
- (5) Migration in tuff using the ion microprobe technique. This sample would then be available for total dissolution.
- (6) The interaction of cations with tuff by a vapor phase or thin film transport reaction.

7. Fabrication and Materials Options for Phase II Vessel Assembly

Cost and availability of the test vessels and components were obtained from the ANL Central Shops and from Parr, Inc., Moline, IL. The vessel design was that described in the prototype tests (Sec. III.A.5). The only difference in the vessels suggested by the two bidders, to simplify production, was in the outside parameters of the vessel. The Parr vessel was patterned after its small acid digestion bomb, but with a modified top piece. This vessel was judged more difficult to handle and close, especially

in a hot cell. The ANL and Parr cost estimates were identical, but Parr anticipated an eight-week delivery, whereas ANL delivery would begin immediately at a rate of at least one vessel per day. Therefore, we suggest that the vessels be made at ANL. The waste package holder requires special forms to standardize production and to meet specifications, and these have already been made at ANL. The vessel and waste package holder costs are given in Table III-5.

Table III-5. Cost of Producing a Phase II Test Vessel and Holder^a

Component	Cost, \$		
	Material	Labor	Total
Type 304 L SS Reaction Vessel and Closure	30	300	330
NPT Feedthru (needed for machining)	10		10
Waste Package Holder	10	75	85
			425
ANL Overhead Charge			100
			525

^aBased on a production run of 40 vessels.

B. Parametric Testing

1. Source Term Tests

Parametric tests are being conducted to measure the source term release from the glass only, and from the waste package with differently aged canister materials. These tests are being attempted in Teflon containers so that analyses and interpretation can include all glass components. A series of tests was stopped when it became obvious that the vessels were leaking and no water was being retained. The series was restarted using reduced-leak vessels (not leak free) and these vessels have retained water through the first six weeks of testing. A complete description of these tests will be provided in a subsequent report.

2. Glass Production Methods

The waste form to be studied in Phase II and related parametric testing is designed as a right circular cylinder ~1.6 cm in diameter and ~2 cm in height. These dimensions provide the proper surface area so that, with the necessary flow rate and drop size, a measurable volume of solution can be collected within a six-week period. The flat ends of the cylinder will be cut with a diamond saw so that there is opportunity for water to collect between the glass and the perforated SS end caps. The circular portions of the cylinder are to be as cast, smooth, and somewhat stressed to simulate a fracture that would occur in a poured glass canister. However, they should be representative of the bulk glass.

To produce such waste forms, the following procedure is used:

- (1) SRL 165 glass frit is modified by the addition of U, Cs, and Sr and melted/homogenized using established procedures.
- (2) The melt is heated at $\sim 1100^{\circ}\text{C}$ and then poured into a Pt 5% Au mold that was polished before use with a $0.03\text{-}\mu\text{m}$ Al_2O_3 slurry and placed completely in a firebrick and preheated in the 1100°C oven for three minutes. The firebrick and mold reach a temperature of $\sim 700^{\circ}\text{C}$ and have a dull red glow.
- (3) The firebrick is immediately transferred to a furnace heated to 500°C and remains in the furnace for 15 minutes.
- (4) The door to the oven is opened and the oven is turned off. The glass cools at a rate of $\sim 200^{\circ}\text{C/h}$ for one hour and then the mold is removed from the firebrick and allowed to air cool to ambient temperature.
- (5) The glass is removed from the mold by tapping the mold gently with a plastic mallet.
- (6) The glass is cut to the proper size using a low concentration diamond blade and an Isomet saw with water as the cutting fluid.
- (7) The glass is cleaned using Materials Characterization Center (MCC) procedures.

Because there is concern about the nature of the glass surfaces, several cast sections were analyzed for surface topography and composition. These samples were cast in one of the molds received in January 1984, and the samples are being used in the parametric tests described in Section III.B.1. They include the first and sixth samples cast as well as three other samples. Generally, both top and bottom sections were investigated. Descriptions are given below.

- (1) This is the first specimen poured for use in the parametric tests, but the second sample actually poured. The top section has a fairly smooth surface with some raised regions that correspond to forming marks in the mold. There are also clumps of Fe- and Ni-rich spinels. The spinels are not uniformly spread throughout the surface. The bottom section has no spinels, but does have some protrusions of $\sim 1\text{-}5\text{ }\mu\text{m}$ diameter. The top surface is very smooth with no spinels.
- (2) This is a miscellaneous sample in which a section was taken from the top of the sample. Both the smooth surface and corresponding cross section were investigated. The smooth surface has very few spinels. In the cross section, spinels are observed only at the surface. There are none evident in the interior region of the sample. No spinels were observed on the cut faces.

- (3) Another miscellaneous sample was investigated. The origin of the sample is not known, but it shows a moderate number of spinels, some protrusions, and some holes that seem to be mainly associated with the protrusions. The hole size is $\sim 1-2 \mu\text{m}$.
- (4) This is the bottom section of a sample that was cast into a mold that had been heated at 500°C instead of 700°C . The smooth surface had a substantial number of spinels.
- (5) This is the sixth sample cast for parametric testing. There is not much difference between it and the first casting. There are some mold marks, some holes, some protrusions, and on the top part quite a few spinels. The bottom has far fewer spinels.

Two samples cast in an earlier mold were also investigated. The mold was little used and produced a sample with some spinels and a fairly smooth surface. The second sample was cast from the same mold, but after many castings and reshaping had been done. There are a few spinels and the surface is very rough and scratched with many holes.

Because the MCC is considering casting some samples in SS molds, to be used in Phase II testing, there is some concern that the glass might wet or react with the SS, causing the surface to be unacceptable for testing. To anticipate some of the problems that may occur, some SRL 165 frit (no U, Cs, or Sr) was cast into a small Type 300 SS ring that had been polished. The ring was in air and at ambient temperature during casting. The mold released fairly easily from the glass, but the glass had contacted the mold only in a small region. This region was obvious on both the mold and the glass where the wet area had a different appearance. In one spot the glass stuck to the mold. The wet region has rims from the SS spinning operation and many holes. The non-wet region is smooth but has some pits, protrusions, and flakes. The wet region shows some density differences when viewed with the Robinson back-scattered electrons detector. Analyses were taken of the non-wet glass, the wet glass, and the dense region of the wet glass. These show that, over the entire wetted region, there is an enrichment of Cr, whereas the dense region is enriched in Fe, Cr, Mn, and S, and somewhat less Na. The reacted SS was also briefly investigated. The wet region looks definitely reacted and the composition shows a slight decrease in Cr. A more thorough investigation would be required for any positive assertions.

Conclusions from these investigations are that the glasses cast in the Pt 5% Au mold have surfaces that are smooth but marked with some small holes and protrusions. Spinel occurs at the surface and seems to be concentrated more at the top than at the bottom of the casting. The amount varies from heavy to light coverage and seems to be greater at the top than at the bottom.

Glass waste packages produced in the manner described above would be easy to produce, would be consistent in size and surface finish, and could be used in testing. However, the MCC will be providing glass samples of PNL 76-68 composition to use in commercial waste glass testing. At this time, MCC is considering other production methods including taking cores from larger castings, smoothing the surfaces by a quick anneal at $\sim 500^\circ\text{C}$, and then attempting to introduce stress into the glass by cooling it quickly to room temperature.

This method will not produce an as-cast surface, but should provide a smooth reproducible surface that we hope will be stressed. Tests are currently being conducted at ANL to see whether this production method can be used for SRL glass, because a consistent method of glass production is desired.

3. Analysis of Stainless Steel Components

The Phase II test apparatus contains Type 304 L SS components supplied from four different batches. These components include the test vessel, the perforated sheet used in the waste package, and both 0.035-in.-dia and 0.0625-in.-dia wire used as supports and in construction of the waste package. Because preliminary testing indicates a reaction occurs between Type 304 L and Type 303 SS components, it is possible that some reaction could occur between Type 304 L SS components of different compositions. Thus, it was necessary to analyze the various Type 304 L SS components for major element (Si, Mo, Cr, Mn, Fe, Ni, and Cu) composition. Additionally, these analyses serve to check the certification provided by the suppliers.

The analyses were done using a Princeton Gamma Tech System III X-ray analyzer with quantitative capability. An NBS certified SS sample was used as a standard for Si, Mo, Cr, Mn, Fe, and Ni, whereas Cu was analyzed using Fe as the scaling standard. This sample provides adequate standards for Cr, Mn, Fe, and Ni because the composition of these elements is great enough to produce reasonable statistics in the energy peaks. However, the errors in Si and Mo are greater because they are present in the sample to a lesser degree.

Analyses were done on six samples. These are listed in Table III-6 and include the components noted above, a test coupon received from LLNL, and the SS sheet as received. Up to three areas of each sample were analyzed, but replicate samples were not analyzed. Spectra were taken with a beam current of 4×10^{-9} A for 300 s. Some fluctuation in the beam current occurred over this time period and introduced error into the analyses. If the beam current drifted to more than 4×10^{-9} A, the total weight percent of the analyzed component was greater than 100%, whereas a drift to less than 4×10^{-9} A caused a deviation to less than 100%. As long as all elements were affected equally, a normalization of the results to 100% should provide satisfactory results. This has been done for the results given in Table III-6, but the total non-normalized weight percent for each analysis is also given. Also included in the table are the certified compositions as provided by the supplier.

The results indicate that, for the major elements, Cr, Fe, and Ni, the deviation between the certified and analyzed values is generally less than 2%. For the minor elements, Si, Mn, and Cu, the deviation is greater, but is still generally less than 20%. However, for Mo, the certified values, when given, are substantially less than the analyzed results. The Mo peak is easily observed in the spectra, which suggests Mo is present in the samples at the analyzed levels.

It is also of interest that the compositions of Cr, Ni, and Cu in the punched perplate are different than those in the as-received plate. These

Table III-6. Analysis of Type 304 L Stainless Steel Components Used in the Phase II Test Apparatus^a

Sample	Composition, wt % ^b							Total ^d
	Si	Mo	Cr	Mn	Fe	Ni	Cu ^c	
LLNL Test Coupon	0.49	0.64	18.73	1.74	70.33	8.67	0.23	100.82
ANL Sheet, As Received ^e	0.48	0.97	17.75	1.31	70.08	9.11	0.30	100.60
	0.51	0.28	18.15	1.33	69.91	9.22	0.36	
ANL Sheet, After Punching	0.64	0.76	18.77	1.44	69.50	8.15	0.73	99.99
ANL Hex Stock ^e	0.45	1.20	19.32	1.78	66.68	10.29	0.28	98.38
	0.37	0.33	19.50	1.58	67.39	10.41	0.22	
ANL 0.035"-Dia Wire ^e	0.48	0.50	18.23	1.38	69.06	10.35	0.00	97.44
	0.45		18.69	1.65		10.28		
ANL 0.0625"-Dia Wire ^e	0.54	0.90	18.64	1.57	67.95	10.23	0.16	100.84
	0.26		18.50	1.61		10.62		
NBS Standard Sample 160 A	0.605	2.83	18.74	1.62	61.54	14.13	0.174	

^aAnalyses by quantitative EDX. Carbon analyses were conducted for the ANL stock; values ranged from 0.015 to 0.029 wt %, which is within the limits for Type 304 L SS.

^bNormalized to 100%.

^cCu analyzed using Fe as a scaling standard.

^dTotal of non-normalized element weight percent.

^eData in second row are certified compositions.

differences are greater than the statistical error determined for triplicate analyses and are believed to be real. However, analyses of different samples need to be performed to confirm this observation.

Finally, the Cr composition of the as-received sheet is below the prescribed level for Cr in Type 304 L SS (18-20%). However, the certified value, 18.15%, is within the limits and the difference between the two values is attributed to analytical error.

C. NNWSI Test 2 (T2) Development

The T2 test procedure will use a tuff rock core into which a waste package has been placed. The flow through the rock core will be as natural as possible. This test will be far less controlled than T1, but is designed to determine whether the waste package reactions and vapor phase or thin film transport observed in the T1 test will occur in a somewhat more realistic environment.

Tuff cores (5 x 2-1/2 in. right circular cylinders) have been taken from a large piece of tuff and have been machined to a smooth finish. A core has been sectioned across its axis, and a volume has been machined from its center. The core was heated in deionized water (DIW) for three days at 90°C, and soaked in J-13 water for a week. It was then placed in a Teflon jacket and sealed in a SS container. The outside of the jacket was pressurized to produce a tight fit between the tuff and the Teflon. Inlet and outlet ports were maintained at both ends of the apparatus. The tuff core was saturated and the entire system was placed in an oven at 90°C.

Water into the system was provided by a heated source and line. In this fashion, we hope that vapor will contact the upper core surface evenly. This method of introducing water was chosen over the dripping of J-13 well water onto one spot on the surface, because it should produce an even flow through the core.

The flow through the core has been set at ~1 mL/d, based on expected worst-case flow in the repository, and can be controlled by changing the temperature/pressure of the water source. The flow characteristics and composition of outlet water are being monitored to see if the core has been preheated adequately enough to remove highly soluble material.

A previous experiment, using a solid core, showed that considerable anion content existed in the water even after 30 days of flow. However, the core in this experiment had not been pretested in 90°C DIW. We anticipate pretesting the present core for 30 days. After that time the waste package will be introduced into the core and the experiment will begin. Three separate experiments are planned with durations of 3-, 6-, and 12-month periods.

The waste package will be like that used in the present experiment, perforated Type 304 L SS and SRL 165 glass frit doped with ^{152}Eu , ^{133}Ba , ^{137}Cs , Sr, Cs, and U. This will allow easy identification of movement of three types of glass components from the waste package to and through the surrounding tuff; ^{152}Eu is representative of rare earth fission products and actinides, ^{133}Ba is representative of alkaline earth components, and ^{137}Cs is representative

of elements easily leached from the glass. This glass has been prepared with radiotracer levels determined from previous experiments, and long-term testing should begin shortly.

D. Quality Assurance Plan

A preliminary quality assurance plan was prepared and submitted to LLNL for comments. Application of the plan to the program is ongoing, with special attention being focused on data traceability and instrument calibration.

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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 flow-sheets for removing and concentrating transuranic elements (TRU) in Hanford current acid waste (CAW) and dissolved sludge waste (DSW) by two extraction systems. One of the extractants to be tested is dihexyl-N,N-diethylcarbamoylmethylphosphonate (DHDECMP); the other extractant is octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (O ϕ D[IB]CMPO). Both extractants will be diluted by ~30 vol % tributyl phosphate (TBP) in a normal paraffinic hydrocarbon (NPH) mixture of C₁₁-C₁₄ chain length.

A study was done at Rockwell Hanford Operations (RHO) that showed a substantial cost advantage in 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. For commercial waste to qualify as nonTRU waste, the alpha-activity concentration must be less than 100 nCi/g; there is no prescribed limit, at this time, for military waste. Therefore, we are to study reducing 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 must define other elements of the process, such as (1) process flexibility, (2) equipment, (3) safety, and (4) availability and cost of the solvent inventory and makeup.

After the flowsheets are computed--using literature data and information supplied by E. Philip Horwitz et al., Separations Group, Chemistry Division, ANL--two countercurrent laboratory tests of the O ϕ D[IB]CMPO extraction of TRU from DSW will be performed. The extraction scheme will be 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 latter test will contain radioisotopes of americium, plutonium, neptunium, and technetium.

A final report will be issued at the conclusion of the program in July 1984. At that time, RHO management will decide whether the process should be thoroughly tested and scaled up--we assume by ANL.

B. Progress

Work this quarter centered on computing conceptual flowsheets for TRU removal by both TRU-extraction (TRUEX) solvents (0.2M O ϕ D[IB]CMPO/1.4M TBP/NPH and 0.4M DHDECMP*/1.2M TBP/NPH), from both feeds (CAW and DSW), to both levels of decontamination (100 and 1000 nCi/g). An informal letter report, sent to RHO on March 21, 1984, included these flowsheets (including the number of requisite stages and the relative flows and the mass balances for all process streams) and discussion of the following items:

*Added as the ~86% material. The other 14% consists of neutral species with properties much like those of TBP.

- Potential suppliers of DHDECMP and O ϕ D[IB]CMPO and estimated unit prices of extractants
- Evaluation of extractant inventory and extractant loss
- Physical properties of extractants
- Aqueous phase solubilities and partitioning of extractants
- Diluent properties and phase compatibility in TRUEX systems
- Chemical and radiolytic degradation of extractants
- Process flexibility
- Process equipment for solvent extraction
- Process safety
- Recommendations for additional research and development

The informal report and the data collected from the two countercurrent experiments to be run in April 1984 will be the bases for the final report that will be drafted in late May 1984 and published as an ANL topical report in late July. There has been nothing uncovered so far that makes the use of the O ϕ D[IB]CMPO TRUEX process untenable, but the use of DHDECMP appears far less attractive. There are many issues still not resolved in this process that must be known before pilot plant tests of TRUEX can begin:

- Radiolysis and hydrolysis of the solvent under realistic process conditions and variability.
- Physical characteristics of the extractant and the TRUEX solvent that are important to the process, to solvent makeup, and to quality control analyses.
- Effects of all possible variations in the feed composition on the process. These variations in the feed composition will require possible modifications of process conditions and development of process control procedures and analytical methods to test feed and solvent compositions.
- Solvent losses due to aqueous phase solubility and entrainment. The extent and consequences of disproportionate losses of the extractant and TBP are important variables; means to analyze for both species in the solvent and to correct compositional changes must be studied.
- Dissolution of the sludge and regulation of the nitric acid and oxalic acid concentrations of the DSW.
- Effects of temperature on third phase formation and distribution ratios under process conditions.

- Benefits and methods of noble metal recovery from the feed before solvent extraction (to decrease the likelihood of noble metal scum formation during extraction and of precipitation of the metals during stripping with dilute nitric acid/hydroxylammonium nitrate).
- Effectiveness of solvent washes for the removal of acidic decomposition products. If conventional Na_2CO_3 or NaOH strips are not sufficient, then methods that will work must be devised.
- Means of eliminating the split scrub for the O ϕ D[IB]CMPO flowsheets. For example, it may be possible to use a single $\sim 0.5\text{M}$ HNO_3 scrub.

This list will no doubt grow after we gain experience with the countercurrent flowsheet.

Work during the next quarter will center on initiating the laboratory countercurrent experiments to test the O ϕ D[IB]CMPO flowsheet and on completing the topical report for this program. The scope of this program may be expanded to study TRU removal from other possible Hanford waste streams.

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, J. E. Parks, D. J. Raue, L. N. Ruppert, C. G. Wach, and A. A. Ziegler)

Current project efforts are oriented 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 late July 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 recently announced delay in the shipment of the initial LWBR fuel rod will afford POB the opportunity to expand the previously planned training of project personnel to provide 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. E. Fagan, R. A. Benson, T. F. Cannon, J. C. Hoh, and C. G. Wach)

Work associated with the full scale shear facility (FSSF) was concentrated on mechanical improvements to facility equipment, continued testing of the shear computerized operating procedure (OPRFSS),** writing of associated documentation, and other facility-related preparations for the EOL campaign. Disposal of solid radioactive waste produced during pre-validation rod (VR) tests and VR processing was initiated.

Modifications to the FSSF (Cell M-3) pneumatic cutter used to sever the tang from the fuel rod were made after some difficulty had been experienced in cutting the VR tang. Adjustments to lower the cutting blades and improve visibility during cutting were completed. Subsequently, several simulated reflector- and seed-size rod plenums were transferred into the FSSF and their tangs successfully removed without difficulty. All other shear systems remain in a state of readiness for the EOL campaign.

*Analytical Chemistry Laboratory (ACL), ANL.

†Chemical Technology Division Computer Section.

‡Grid-Rod-In-Pile.

**A "master" program that executes a procedure by calling individual "slave" programs in the correct sequence. Tasks performed by the slave programs include display of text on the video terminal, reading of sensors, data storage, and equipment control.

To test changes made to POBSYS* system software, and for the purpose of operator training, the shear computerized operating program was used in the simulated shearing of a full-length fuel rod (rod "S"). Several minor programming errors (bugs) were fixed by POB programmers during the shearing, and debugged OPRFSS procedure sections were retested. Overall operation of the program proved satisfactory, and OPRFSS is considered ready for EOL operations.

The data collected in the processing of rod "S" was used to test the report-generation program, which uses data files generated by OPRFSS to produce a comprehensive data summary report for a given fuel rod. A programming error showed up when the data obtained from the shearing of the last segment (S-17) was being compiled, but it was located and corrected, and the program was retested and found to be satisfactory.

Documentation for the FSSF operating procedure has been completed. The final OPRFSS document consists of a printed copy of individual, serialized procedural steps preceded by an introduction, which includes a brief description of the FSSF, the intended applicability and use of the procedure, and a list of reference documents. The procedure steps include overlays (slave programs) that describe what the computer system is doing to satisfactorily perform a given step. An appendix to the procedure contains maintenance procedures, sample copies of data summaries and computer-generated data reports, and hard copies of computer displays that are not shown in the procedure text. Copies of this document will be distributed for formal approval early next quarter.

During fuel rod shearing operations, the comminuted fuel is collected in either 3-in.- or 6-in.-long aluminum cans, depending on segment length or weight. Approximately 100, 6-in.-long aluminum sample cans were prepared for use in EOL operations. Cans were sorted by weight, saving those cans that weighed less than 10 g for EOL use; reducing the weight of aluminum loaded into the dissolver is desirable because of nitrate solubility limits in the high acid ($13.5M \text{ HNO}_3$) solutions used for the primary dissolution at the dissolver. The selected sample cans were leak-checked, washed in Freon, rinsed with distilled water, oven-dried, then sealed in plastic bags and placed in storage. They will be labeled and reweighed immediately prior to use.

An effort is being made to dispose of low-level radioactive waste created during testing of the shear and dissolver systems. About 22 kg of sheared thorium pellets and 4.5 kg of sheared (hulls) and whole Zircaloy cladding scrap were produced during shearing tests. The thorium contains small slivers of Zircaloy cladding that were produced during shearing; such slivers may be pyrophoric, i.e., will support combustion if ignited. Cladding hulls that were produced during the shearing of sections of thorium-filled cladding have been separated from the bulk of the sheared thorium. This form of Zircaloy

*An ANL-written system of programs and files used in operating the FSSF, the two units of the dual dissolver system (DDS), and the eight electronic balances associated with these systems.

is not pyrophoric, but to be conservative and to conform with federal regulations on packaging pyrophoric radioactive materials, the thorium and Zircaloy sections will all be blended into a cement-water slurry that, when allowed to solidify, will both immobilize the waste and put it into an inert form.

B. Dual Dissolver System (DDS)

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

The mechanical repair and installation of a number of equipment items associated with the dual dissolver system (DDS) were completed this quarter as part of the post-VR cleanup, and in preparation for the POB EOL campaign. The dissolver computerized operating program (OPRDDS)* was upgraded with the addition of (1) a series of piping and instrumentation (P&I) diagrams intended to aid in monitoring the dissolver operating status, (2) steps for the decontamination of used gas and solution sampling equipment, and (3) modified blend tank weighing operations.

1. Mechanical Work

The dissolver system 2 (DS2) tantalum vessel, which incurred a broken drain line during the dissolution of one of the VR segments, was remotely removed from its DS2 station. The practicality of untried vessel removal procedures was verified, as the remote operation proceeded smoothly, though slowly. The damaged DS2 vessel was removed using the bag-out system of the Cell M-1 dissolver alpha enclosure and placed in storage for later examination. Selection of a replacement vessel from the two remaining units (of an original group of four) was to be made based on the original evaluation of radiographed weld regions by the ANL Quality Assurance Division. A recent radiographing of welds in the drain lines of both the spares showed them to be sound, and both units are considered fully usable; however, one of them, showing slightly thicker girth and longitudinal weld regions, was selected over the other.

The transfer into Cell M-1 and remote installation of the replacement vessel proceeded extremely well, with a few new helpful experiences gained. Revised procedures for the removal or installation of DDS vessels were written as a result of the DS2 vessel replacement.

The waste dissolver solution storage system in Cell M-1 was readied for EOL service with the installation of the repaired Magnetrol† liquid level probe and the waste solution transfer pump. The liquid level probe for waste tank 1 (WT1) had been received from the vendor with a cracked Kynar‡ plastic protective sheath, which was apparently damaged during shipment. The probe was repaired by the vendor, and subsequent testing showed it to be sound. The waste transfer pump was in need of a discharge-side check valve alignment, which was done out-of-cell. Both items of equipment were remotely installed without difficulty, are functional, and stand ready for EOL use.

*A "master" program similar to that defined in Section V.A.

†Magnetrol International, Inc., Downers Grove, IL.

‡Registered trademark of Pennwalt Corp., Philadelphia, PA.

During post-VR testing of upgraded operating procedures, the power supply console for the Validyne* DDS pressure transducers failed. A faulty capacitor was discovered and replaced at the Chemical Technology Division (CMT) instrument shop. The repaired unit has since been reinstalled and is ready for use. Onsite recalibration of the associated pressure transducers was recommended by instrument shop personnel, and has since been completed by POB personnel. A previously ordered spare power supply console was received and is available for the EOL campaign.

Each of the nine blend tanks, nineteen dissolver solution filter housing assemblies, and fifteen gas sampling cylinders used during VR segment dissolutions has been readied for reuse. Results of analyses by the Analytical Chemistry Laboratory (ACL) indicate successful acid reflux decontamination of blend tanks (the criterion is less than 100 μg U maximum allowable in the second reflux solution) and acid rinse of filter assemblies; the gas sampling cylinders were cleaned by means of a five-minute purge with dry air. All items are in storage awaiting use during EOL operations.

2. Work on Computerized Procedures

Modifications designed to upgrade and refine OPRDDS continued. Written specifications for POB programmers have been completed, and the development of associated software has been initiated for (1) an automated blend tank weighing procedure, (2) air purge of used gas sampling cylinders, and (3) reflux decontamination of used blend tanks.

The control display program, CONDSP,[†] which displays DDS sensor values on the video terminal at the operating station and provides operator access to process control (PC) states (computer commands that selectively coordinate the operation of multiple dissolver system components), was restructured for easier monitoring of all sensors by the operator. A software interlock program was written and implemented to prevent simultaneous operation of the CONDSP and OPRDDS programs, to avoid conflicting operation of DDS components.

Each of the two Cell M-1 operating stations has two video terminals for use during fuel sample dissolution, a VT-100[‡] for use with OPRDDS and a GIGI[†] (General Image Generator and Interpreter) for graphic display of information, which now includes the display of P&I diagrams. The P&I diagrams, recently computerized for use on the GIGI, consist of five basic graphic formats designed to provide a visual schematic display of dissolver component status and, therefore, a verification of correct PC-state operation and related process activity. The five formats include (1) dissolver cooling, (2) off-gas, (3) blend tank evacuation, (4) reagent and solution transfer/sampling,

*Validyne Engineering Sales Corp., South Holland, IL.

[†]A program that controls the ON/OFF status of DDS valves, pumps, and blowers upon operator command, as opposed to the automatic commands of OPRDDS.

[‡]Digital Equipment Corp., Maynard, MA.

and (5) dissolver pressurization. Interfacing the OPRDDS procedure with the P&I program has been completed, and testing intended to coordinate individual OPRDDS steps and corresponding P&I graphics has been initiated.

C. Scrap and Waste Disposal
(R. E. Nelson and A. A. Ziegler)

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. Essentially all approvals from DOE-CH and the storage site operator (R-H) have been received. Final approval has also been received from the Nuclear Regulatory Commission (NRC) for shipment of the LWBR-POB waste in packages conceptualized in developing this plan.

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. Current emphasis is on item (3), as described below by subcategory of effort.

1. Design/Drawing and Fabrication Status

Design work and the preparation of drawings necessary to fabricate the planned components for the conversion of the liquid dissolver solution into a cemented waste form and the necessary containment packages required to house and ship this waste were completed, concluding this phase of effort. All components, except for the shielded radwaste casks, have been fabricated and assembled, including the dual mixing stations and handling/loading items. Except as noted, this concludes the planned fabrication phase of effort for the scrap/waste system.

2. Procurement Status

All planned procurements for the scrap/waste system have been completed except for the radwaste casks. However, two prototype casks were fabricated and received for evaluation, per contract.

3. Evaluation of Radwaste Casks

Two prototype radwaste casks underwent initial examination that included the checking of welding, verification of dye penetrant testing of the welds, and dimensional checks. Subsequently, tests with a radiation source were made. A cobalt source was placed inside the casks, and external radiation readings were taken in a specific pattern around the cask walls, including the top and bottom, to verify that the lead thickness and lead pouring technique used by the vendor were adequate. The tests results,

supported by computer modeling test results, showed the design to be adequate. Some modification in quantities of lead filling in the two prototype units is required; therefore, the two units are being returned to the vendor for upgrading.

Permission has been given to the cask vendor to fabricate the remaining 48 units per upgraded specifications, but contingent on approval of a complete manufacturing and quality verification plan, which has not yet been received.

4. Assembling and Testing of Components

a. Mixing Stations

Two mixing stations have been assembled and bench tested, and are ready for in-cell installation. Installation of these units is planned for April 1984, to be followed by in-cell testing in May 1984.

b. Remote Drum Cover Seating Device

The "remote drum cover seating device" for the 55-gal drums (the outer container for the waste package) has been assembled and bench tested. This device accommodates the out-of-roundness of the drums in seating the cover properly. Remote testing is planned next quarter.

c. Remote Drum Ring Closure Device

The "remote drum ring closure device" has been assembled and bench tested satisfactorily. This device expands the drum closure ring so that it can be remotely placed around the drum and drum cover.

5. Irradiation Test of the Feed Dispensing System

This test is discussed in Section V.G.3.

6. Miscellaneous Tasks

A service request was initiated to have the ANL Carpenter Shop fabricate 12 reusable wooden boxes, which will be used as part of the necessary restraint for the 55-gal waste drums within the metal (M-3) bins during transport to the waste storage facility; each box holds one drum. The wooden boxes have been fabricated. Foaming of the void area in the boxes must be completed before they are ready for use; this work is planned for early next quarter.

Sketches are being prepared to facilitate the design and fabrication of two feed dispensing stations, which will include trays and splash-shield features.

About 15 L of low level liquid radioactive waste was disposed of through ANL Reclamation - Waste Management Operations. This liquid was produced in testing of the prototype single-unit dissolver and the dual dissolver system.

D. Computer System and Data Management

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

An integrated computer system is being developed for use by the LWBR-POB Analytical Support Project. This system, known as POBSYS, will provide automatic data acquisition, various monitoring functions, and several degrees of automated control for the equipment, instrumentation, and procedures by which ANL will process and 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 has 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; this work includes changes referred to in other parts of Section V.

1. Hardware

a. Description

The newly available PDP-11/73** processor was evaluated as a replacement for the central processor of the PDP-11/23-PLUS** system. The new processor operates at three to five times the speed of the present system and doubles the program memory size. Steps to procure the new PDP-11/73 processor have been initiated. When replaced, the old PDP-11/23 processor will be stored as a spare for the ACL PDP-11/23 system used for analytical operations, also referred to as GAMMA.

b. Recent Progress

Installation of an expansion backplane assembly, which was necessary for the installation of other on-hand components on the PDP-11/23-PLUS system, was completed during the quarter. At the same time, an additional memory was installed, thereby increasing system capacity from 256K to one megabyte. The additional capacity was found to be necessary to improve the multiple, simultaneous operations of the FSSF and the DDS during EOL operations. A board with four additional terminal lines was installed to provide interfaces to the FSSF and DS1 and DS2 work station printers. A clock/calendar board, to provide an accurate and automatic time setting for use during system startup, was also installed.

*Chemical Technology Division Computer Section.

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

‡Science Applications, Inc., Schaumburg, IL.

**Digital Equipment Corp., Maynard, MA.

The high speed DECnet network interface board was tested and installed, and is now fully operational. This interface provides a 19.2 kilobaud link between the PDP-11/23-PLUS (in Bldg. 200) and the VAX-11/780 (in Bldg. 205) computers. The only significant hardware malfunction was the failure of the disk controller on the PDP-11/23-PLUS system. The ANL Electronics Division (EL) replaced the faulty controller with its spare unit, located and sent the defective board out for service, and reinstalled the original board after it was repaired. The EL personnel also performed preventive maintenance on the controller disk drive fans. The response of EL to POB service needs has been excellent.

2. Software

a. Description

No changes were made to overall software systems concepts during the quarter. Progress toward completing these systems is described below.

b. Progress

Implementation of POB software required effort in five areas, as follows: (1) PDP-11/23 operating systems maintenance; (2) modifications and enhancements to POBSYS to meet requirements revised during FSSF and DDS testing; (3) completion and testing of OPRFSS and OPRDDS, the computerized operating procedures for the FSSF and DDS, respectively; (4) analytical systems; and (5) report-generation programs.

(1) Operating Systems Maintenance

The operating system software package (RSX-11M V4.1),* previously installed on the POB and ACL PDP-11/23 minicomputers, has functioned well. DECnet network software for the PDP-11/23-PLUS system was regenerated to incorporate the high speed link to the VAX system, and to provide for a future direct link between the two PDP systems. Software written to use the new calendar/clock board was completed and installed. Plans were made to install the new RSX-11M-PLUS* operating system software on the PDP-11/23-PLUS system. This new operating system provides improved functionality and is designed to run on larger systems (such as the 11/23-PLUS and 11/73 models).

(2) POBSYS Testing and Modifications

Functional testing and improvement of POBSYS have continued during its use in the development and testing of procedures for the FSSF and the DDS. During this quarter, the following changes were made to the procedure-independent portion of POBSYS: the Variable Send-Data (VS) software (which links individual POBSYS programs into an integrated system) was extended to handle twice the message traffic as in the past; a method for displaying system alarm messages in the alarm box on the operations

*Digital Equipment Corp., Maynard, MA.

video terminal was implemented; and minor maintenance of software components (i.e., bug fixes) continued, although very few system problems were detected during this time.

(3) Development of OPRFSS and OPRDDS

Development, testing, and changes to POBSYS involving OPRFSS and OPRDDS are discussed in Sections V.A and V.B.

Changes made during the quarter to OPRDDS and associated DDS software in response to requests resulting from dissolution of the VR included (1) a reduction in the number of manual steps requiring operator sign-off and (2) modification of the in-cell sample bottle weighing routines to allow use of either of two Mettler (300-g capacity) balances. Work on the P&I diagrams was completed, and automatic startup and switching of graphics were incorporated into OPRDDS. The P&I diagrams use color graphics at a GIGI video terminal to display the operational status of DDS control components (e.g., valves, pumps, blowers). The automating of post-dissolution operations, consisting of sample gas cylinder purging and blend tank decontamination, was initiated with the writing of associated software.

(4) Software System for Analytical Processes

All programming associated with automation of the alpha/gamma spectrometer has been completed, and this system is now considered fully operational for the EOL campaign.

(5) Report-Generation Programs

Data processing procedures were written in preparation for generation of analytical reports. The procedures serve to produce an organized file of processed fuel rod data containing averaged values and uncertainty ranges for rod gas analysis, rod gas isotope analysis, and dissolver off-gas analysis. Development of specifications for the EOL analytical reports continued during the quarter. Report-generation programs for the alpha and gamma spectrometry results were completed during a previous quarter [STEINDLER].

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 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

*Analytical Chemistry Laboratory (ACL), ANL.

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, analytical results from the destructive assay of the VR were compiled, reviewed, and transmitted to BAPL. Preparation of a document describing the computation of individual results and estimating uncertainties associated with the results was begun. This document is intended to serve not only as a report covering the processing of the first irradiated fuel rod of the EOL campaign, but also as a guide to understanding and interpreting results from future processing of rods. These later results will be generated by identical computational procedures using computerized report-generation programs. For the sake of efficiency, preparation of specifications for the report-generation programs has been proceeding in parallel with the statistical analysis and documentation of the VR data. The logical structure of the report-generation programs was laid out in consultation with project programmers. Specifications were completed for program sections relating to fission gas measurements and were started for the remaining sections addressing uranium analyses and fission-product-monitor determinations.

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. Analytical work related to the processing of the VR was finished early this quarter. During the latter portion of the report period, analytical effort in support of the LWBR-POB project was reduced to that required only to maintain the POB-dedicated equipment and facilities in a state of standby readiness until receipt at ANL of the next irradiated fuel rod, currently scheduled for late July 1984.

Analyses performed during this quarter for the destructive assay of the VR included

- (1) chemical and radiometric measurements on the last few samples from dissolution of segments from the rod,
- (2) determination of uranium in samples generated during the decontamination of blend tanks for reuse in DDS operations,
- (3) screening of dissolution filters by gamma counting for ^{137}Cs to verify the absence of undissolved fuel material on the filters, and
- (4) cleanup of the ACL/POB facilities and disposal of waste from processing the VR.

Effort related to item (1) in this list was merely an extension of work described last quarter and is not discussed further in this report. The uranium determinations in item (2) were performed by spiking the blend

*Analytical Chemistry Laboratory (ACL), ANL.

tank decontamination rinse solutions with 10 µg NBS-993 uranium (^{235}U) and subjecting uranium fractions isolated from the solutions to mass spectrometric isotope dilution (MSID) analysis. Samples obtained from each of the nine blend tanks were analyzed and all showed acceptably low levels of uranium (<100 µg U) in the blend tank after decontamination.

The gamma-counting survey (item 3) of each of the dissolver transfer line filters required adaptation of the counting system to handle the relatively high levels of activity associated with the filters; the activity is mostly from ^{125}Sb , a radioactive daughter product of the tin in the Zircaloy that has dissolved. To obtain reasonable detector dead-time levels, the total count rate from the detector was reduced by increasing the sample-to-detector distance by means of an extension to the sample positioning shelf. Several positions on the extended shelf were calibrated, and the optimum position for each filter sample was used in counting the sample. Measurable amounts of ^{137}Cs fission products were found in every filter, but in no case did the levels indicate the presence of significant amounts of undissolved fuel material. In the worst case (segment A-02), ^{137}Cs on the filter samples corresponded to only 0.02% of the ^{137}Cs in the segment; in all other cases the ^{137}Cs on the filters was 0.01% or less of that in the segment.

The aluminum sample can containing segment A-09, the Zircaloy stub section of the VR, was also counted to estimate its ^{137}Cs content. No special effort was made to account for gamma-ray absorption by the aluminum can or for other factors that would affect the counting system calibration for a sample of this type. Thus, the screening analysis for fuel material in this segment can be considered only semiquantitative. Nevertheless, the extremely low level of ^{137}Cs activity found by this screening process, less than 0.0006% of the ^{137}Cs found in the thorium and binary fuel-bearing portion of the rod, demonstrated convincingly that this segment contained a negligible amount of fuel.

Cleanup of the ACL facilities and disposal of the radioactive waste from processing of the VR (item 4) was accomplished through normal procedures except for the treatment of intermediate- or high-level waste solutions. These solutions were of two types: (1) acidic solutions, which included unused portions of the dissolver solution samples submitted for analysis and samples prepared for gamma counting of fission product monitors, and (2) strongly basic solutions containing high concentrations of aluminum nitrate as well as fission products and thorium; these solutions accumulated from the hexone extraction procedure used to isolate uranium from the dissolver samples for subsequent purification and mass spectrometric analysis. The acidic waste solutions were combined and transferred to Cell M-1 for inclusion with the acidic waste solutions generated during operations with the DDS. For the basic solutions, a small-scale cementation procedure was developed, which allowed the conversion of the solutions to a solid form (cement) directly in their storage containers in the analytical cell (Cell K-3), and subsequent disposal of the solidified wastes by ANL Reclamation - Waste Management Operations.

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

The upgrading of shielded-cell facility-related systems and equipment and facility operations continued this quarter, as reported below.

1. Facility

a. Manipulators

Two master/slave (M/S) manipulators were removed from Cell M-1 (DDS) for repair in January. One incurred an untracked wrist cable during the VR operations and the other had a broken tape on the slave arm (in-cell part of the manipulator), which was caused by overstressing the tape when the slave arm was being used at its extended limit. During removal, both manipulators were surveyed by Health Physics, Occupational Health and Safety Division, and found to be free of contamination, thus demonstrating that the plastic booting, which covers the entire in-cell portion of the manipulator (the slave), is effective in preventing contamination of the slave during operations with radioactive materials in the cell. Repairs of both manipulators were completed and the units reinstalled in Cell M-1. A third M/S manipulator in Cell M-1 had a broken electrical plug, replacement of which was accomplished without removal of the manipulator.

One of the two M/S manipulators in Cell A-4 was also removed to install new tape. This cell is being refurbished by POB personnel so that the ACL may conduct a short-term project for the Savannah River Laboratory. Repairs on this manipulator were completed, and it was reinstalled in the cell.

Troubleshooting and repair of the bridge-mounted polar manipulator located in the corridor behind the ACL cell (Cell K-3) were also completed. A problem with this electrical manipulator had been traced to a faulty component in the magnetic-amplifier power supply.

b. Booting

Multiple boot failures that have occurred during operations over the past six months have required that manipulator booting be redesigned. The booting, which consists of a vinyl sheath covering the slave portion of the manipulator, serves a twofold purpose: (1) protect the manipulator from radioactive contamination or attack by acid fumes within the cell enclosure and (2) prevent unfiltered supply air from entering the cell enclosure or, in the event of ventilation failure, backflow of contaminated cell air into the operating area. (The cell wall penetration provided for the manipulator slave is normally sealed so that essentially no inward leakage occurs between the operating area and cell enclosure.)

Newly designed replacement boots incorporate a new, unique, rotating joint feature. The replacement boot consists of two sections connected by the rotating joint, which allows the lower section to rotate independently of the fixed, upper section. The new joint relieves stress by allowing rotation at the boot joint when applying azimuth rotation to the manipulator. This ability to rotate eliminates the stress previously applied to the boot seams in the old single-piece design. Following installation on the six manipulators in Cell M-1, testing of the new design proved it to be superior in terms of ease of manipulator operation.

Because of the superior performance of the new boot design, fabrication of new boots for all remaining POB cells was initiated. At present, new booting has been completed for the DDS cell (Cell M-1) and the FSSF cell (Cell M-3), and is 75% complete for the ACL cell (Cell K-3). All boot fabrication should be completed early next quarter.

c. Cell Ventilation

Replacement of the torn and damaged boots in Cell M-1 revealed a new problem within the cell when it was discovered that the alpha enclosure was operating at a high negative pressure of 0.9 in. of water as compared with the design negative pressure of 0.25 to 0.4 in. of water. A recent adjustment of the cell exhaust blowers had been made to bring the cell exhaust up to design specifications for the new stack radiation monitoring system (located in M-Wing, Room MA-001). This adjustment was made while the boots were in a torn condition and, under these conditions, the boots allowed sufficient in-leakage of makeup air to keep the negative pressure in the cell at its previous low level. When the torn boots were replaced, this large in-leakage of air was cut off, resulting in the high negative pressure in the alpha enclosure. (Prior to the boot change, but after the increase in ventilation air flow, no change in the alpha enclosure negative pressure had been detected because the torn manipulator boots had allowed the large in-leakage of air.) Work is underway to achieve a negative pressure level within design specifications by replacing one of the existing Lexan panels that form the alpha enclosure with a panel containing a bank of three additional intake filters. This work is to be completed next quarter, after which the ventilation situation will be reviewed.

d. Cell Entries

Several times, POB personnel entered the Cell M-1 alpha enclosure to install the new manipulator boots and to remove equipment in need of repair by hands-on effort, as opposed to doing it remotely, which would have required about ten times the effort. Entries were made with the support of Health Physics personnel who measured background and contamination levels in the alpha enclosure to determine if hands-on work was feasible. The general background radiation level in the enclosure was found to be 20 mR/h, whereas the interior of the enclosure had a general contamination level of only 2 mR/h beta/gamma and 5000 dpm alpha, smearable. The entries were made using respiratory protection and double paper suits. The outer layer of protective clothing (the outer paper suit) was removed upon exiting the alpha enclosure. During four entries in February, each about one hour in duration, the six manipulator boots at the Cell M-1 shielding windows were replaced, and balance #4 (2000-g capacity) and the can-out transfer hatch were bagged out of Cell M-1 for decontamination and repair. Suited entries into Cell M-1 were then made in March to reinstall the repaired equipment. These operations were carried out safely and without any untoward problems; radiation surveys by Health Physics detected no gross contamination tracked out of the enclosure.

e. Cell-Door Interlock System

Work was begun and completed on the installation of a cell-door interlock system to prevent inadvertent opening of cell doors while a high level radiation condition exists in the cell. This system is the second part

of a facility safety upgrade program that was begun about three years ago and is expected to be operational in time for the EOL campaign. The system requires that a key be used to bypass the interlock to open the door of a cell that has a high gamma radiation level, as is necessary during transfer of material between cells. The system will provide added safety during the EOL campaign and the post-EOL cell cleanout phase. A preliminary test of the system showed that some of the radiation monitors were wired incorrectly. The monitors have since been rewired, and a final test of the system is scheduled for early April.

2. Archive Sample Storage

The archive samples collected during the VR processing, which are currently stored in Cell M-1, were weighed several times this quarter to determine any change in the solution evaporation rates. The sample solutions, which are contained in borosilicate glass bottles with vented polyethylene caps, are being monitored to determine if they will reach dryness before they are disposed of in one or two years.

Three weighings of the archive samples were performed at about 30-d intervals. The average daily weight loss per sample at the first weighing was about 20 mg/d. The second weighing, which took place 72 days after the samples were generated, showed a much lower average daily weight loss of only 2 to 3 mg/d. The most recent weighing took place 33 days after the previous weighing, or about 105 days after the samples were generated. Contrary to the expected decrease in evaporation rate as the samples become increasingly concentrated, 40 of the 44 samples showed an increase of 1 to 2 mg in the daily average weight loss. The other four samples, which consist of two pairs of samples, showed a marked decrease in their evaporation rates. An attempt to explain this difference in the evaporation rates at this time would be speculative. A check of the dissolver operations process log is planned to determine if these two pairs of samples might be different from the other 40 samples. We have not yet estimated how long it would take to reach dryness.

3. Support Work for the Waste Treatment System

Irradiation and testing of a Master-Flex pump* were conducted to determine its suitability for use in the Waste Treatment System. The pump was operated for 23 h at a flow rate between 11 and 13 mL/min. During the time the pump was operating, it was exposed to a gamma field of 1×10^6 R/h for 5 h. This radiation exposure (estimated to be about nine times the projected exposure for the EOL campaign) had no effect on pump operation, and the silicone rubber tubing used in the pump showed no signs of deterioration.

A new device for lifting and moving waste cans was designed and built this quarter. This can lifter will replace the vacuum cup lifter that had originally been intended for this use. During preliminary testing with the proposed waste cans, we discovered that, when a can was jogged while being lifted with the vacuum cup, the lid was easily dislodged and the can itself dropped. The new lifter holds the can by its rim and does not depend on the holding ability of the friction lid.

*Cole-Parmer Instrument Co , Chicago.

4. Miscellaneous

Background readings were taken in all POB cells in the open area outside the alpha enclosure. Cell M-1 (DDS) was the highest with a background of 20 mR. This is understandable inasmuch as all the waste from the VR campaign is stored in this cell. Background readings in Cell M-3 (FSSF) and Cell K-3 (ACL) were ~2 mR and <2 mR (after waste removal), respectively.

A cleanup of the cave corridor, after VR processing was completed, was undertaken during this quarter as part of an effort to improve house-keeping around the cave area. An accumulation of contaminated tools and equipment, much of which was obsolete, was removed from the corridor and disposed of as solid radioactive waste. The reuseable tools and equipment were sent to ANL Reclamation - Waste Management Operations for decontamination.

H. Radiation Monitoring Systems

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

A multipurpose, automated, stack monitor system was installed during the previous report period to monitor 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 under R. Fergus, Group Leader. The overall task was coordinated by Frank Marchetti, ANL Occupational Health and Safety Division.

The stack monitor system was used to monitor effluents from the VR dissolution, during the last quarter, but most of the data obtained during the VR dissolution was evaluated, and some further calibration of the system was done this quarter. Some discrepancies in data were found that will necessitate further system calibration; however, in general, overall operation of the automated stack monitor system was good.

The system has four stations that monitor effluents from the four shielded cells involved with the processing of the LWBR fuel, i.e., Cell M-3 (FSSF), Cell M-1 (DDS), Cell K-1 (waste treatment), and Cell K-3 (ACL). Each cell ventilation system is designed with dual (high- and low-flow) exhausts; therefore, separate gas sampling lines are provided in each of the ducts. A computer controlled valve allows selection of which of the two sample lines is used with the monitoring station during a given period. At each station are one or more detection elements, as appropriate. Each element measures a specific gas characteristic: particulate solids are trapped on a filter disk, which is subsequently checked (counted) for activity levels; ⁸⁵Kr is detected by a Pilot B scintillator;* radioactive iodine is detected using a charcoal cartridge with a NaI gamma detector; and ²²⁰Rn (thoron) is detected using a simulated Lucas-type cell[†] and photomultiplier tube, which are located between the filter and charcoal cartridge.

In reviewing the operation of the radiation monitoring system, the focus was on the release of ⁸⁵Kr, which occurs in Cells M-1 and M-3. Analysis of the data from Cell M-3 is complete; further work is needed on the data from

*Harshaw Chemical Co., Hinsdale, IL.

[†]ANL-designed zinc-sulfide lined container.

Cell M-1. Some calibration tests were made to verify the analysis of cell data obtained during the VR run; we anticipate that further calibration tests will be needed.

1. Gas Release in the Shear Cell (M-3)

Knowledge of the amount of ^{85}Kr gas released during fuel rod shearing is needed to complete the material balance on a given fuel rod campaign. Information on this release was obtained using the automated stack monitor system. To check the system, a Geiger-Muller (G-M) tube monitoring system was used in parallel with the computerized stack monitoring system. The G-M system was itself checked by the release of VR plenum gas samples that had been analyzed independently by the ACL. The check between the G-M system and the ACL procedure was good, with results of 7.2 mCi and 7.0 ± 0.5 mCi, respectively. The check between the G-M system and the automated stack monitor system showed that the automated system was low by a factor of 2.7. (Additional testing with new G-M tubes was conducted, as described in Sec. V.H.3.) Using the G-M data to determine the ^{85}Kr concentration factor, the total amount of ^{85}Kr released during puncturing and shearing of the rod was found to be 113.5 mCi. Of this, 7.2 mCi was released from the fuel rod by the plenum puncture and 106.3 mCi was released during shearing of the fuel rod. An analysis of data from ^{85}Kr releases in both the low- and high-flow ducts of Cell M-3 showed that about 93% of the ^{85}Kr released during the shearing operation was drawn into the low-flow exhaust duct attached to the head of the shear, and about 7% was exhausted by the high-flow exhaust duct, which draws gas from the cell as a whole.

2. Gas Release in the Dissolver Cell (M-1)

Initially, only a partial analysis was done on the ^{85}Kr gas release in Cell M-1. There were three reasons for this. First, the gas release data are not needed to complete the material balance, as was the case in Cell M-3. This is because the ACL can determine the amount of ^{85}Kr released in the dissolvers by analysis of the dissolver gas samples. Second, the way in which the data were taken made analysis difficult. The problem was largely procedural, in that data were taken in two separate locations and the procedure was not fully coordinated. The procedures for taking ^{85}Kr release data are being revised so that this problem will be corrected for the EOL campaign. Finally, the results exhibited a flaw similar to that seen in the case of Cell M-3, in which the ACL and G-M results were in good agreement, whereas the computer results were low by a factor somewhat greater than two. In the case of Cell M-1, the ACL and computer results were in good agreement, but the G-M results were high by a factor of 2.4. Thus, it is important to analyze the data from Cell M-1 in more detail. The analysis of the Cell M-1 data will be completed during the next quarter.

3. Calibration Tests

For the calibration tests, the two G-M tubes were in their original locations in the two M-1 stacks where they had been during the VR run. Two new G-M tubes were mounted in the M-3 stacks; the tubes were selected for radiation response characteristics similar to those of the first two G-M

tubes. Thus, when a known amount of ^{85}Kr , determined by ACL, was released in Cell M-3, we expected that the ACL and G-M tube values would agree and that the computer results would be low by a factor greater than two. To the contrary, the calibration tests showed good agreement between the ACL values and the computer results, whereas the G-M tube results were high by a factor of 2.4. Further calibration tests are planned to resolve these contradictions.

Before the additional calibration tests for the radiation monitoring system are carried out, the gas flow probes for the computer system will be recalibrated. These probes could be contributing some additional error to the data, because they were not calibrated at the same time that the gas flow in each stack was measured. This is suspected to be a problem because gas flow fluctuates significantly with time. When the probes are recalibrated, the computer probe reading and the gas flow measurement (using a Pitot tube at the stack exit) will be taken simultaneously to eliminate this possible source of error.

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

One of several options is being examined to keep track of the fissile material inventory during the EOL campaign; ^{233}U is the main constituent of interest. As proposed, a separate notebook would be set aside for each of the two waste tanks, as they present special problems with many liquid additions and withdrawals and with evaporative losses. Use of the computer to calculate the waste tank notebook data is being evaluated. One computer alternative would be to write a FORTRAN program to process the notebook data, and such a program was outlined. A second alternative would be to use a spreadsheet program such as the DIGICALC* program, which is available on the VAX computer. If it can be used, the spreadsheet program would be the more convenient alternative because the data are entered, the calculations are done, and the results are shown on a single screen. This program is being reviewed to see if it can handle the calculations that are needed.

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*WHY Systems, Inc., Redmond, WA.

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