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NUCLEAR TECHNOLOGY PROGRAMS
QUARTERLY PROGRESS REPORT

October-December 1983

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ABSTRACT

The radiolytic production of nitric acid or ammonia in a nuclear waste repository can potentially cause degradation of bentonite-based backfill materials. This potential is being evaluated, and experiments regarding the transformation of bentonite under hydrothermal conditions to albite, quartz, and paragonite are reported. The analysis of active geothermal systems as natural experiments in the transport of trace elements in lithic material is discussed. In addition, a summary of a literature review regarding the interaction of humic substances with heavy metals is reported. New prototype vessels for evaluation of the reaction of nuclear waste glass with water are being tested, the need for which was indicated by the results of preliminary testing. Also, a program studying the applicability of natural basaltic glass as an analog for nuclear waste glass is under way. Two extraction systems for the separation of transuranic elements from high-level waste are to be investigated. Work has included identification of mathematical relationships for calculating material balance and development of procedures for a literature survey of the extractants.

Full-scale equipment and systems for the destructive analysis of full-length irradiated fuel rods from the Light Water Breeder Reactor are being developed, installed, tested, and qualified. A full-scale shear facility, dual dissolver system, and other systems and facilities are included.

SUMMARY

Modification of Backfill Materials under Repository Conditions

Questions have been raised about the ability of bentonite-based backfill materials to hold up to the hydrothermal conditions and heavy irradiation expected adjacent to waste canisters in a high-level nuclear waste repository. In this report, two potential causes for degradation of bentonite are considered: radiolytic formation of nitric acid and transformation under hydrothermal conditions to albite, quartz, and paragonite.

Gamma irradiation of air in a repository is expected to produce nitric acid, or ammonia if the system becomes sufficiently reducing. Either is potentially harmful to bentonite under some circumstances. The radiolytic yield of nitric acid under ^{60}Co gamma radiation was measured at 200°C and found to be 2.2 molecules per 100 eV. If nitrogen is free to diffuse through a repository, the total production of nitric acid in the immediate vicinity of the canisters over the lifetime of the gamma-active elements is estimated

to be on the order of 0.5 mol/L of pore space, or about 40% of the cation exchange capacity of the clay. Montmorillonite, the active component of bentonite, is unstable in acid solution; experimentally, an irreversible loss in swelling ability was found to take place. At sufficiently high concentrations of acid (greater than or equal to the ion exchange capacity of the clay), the clay was transformed into amorphous material.

Nitric acid or ammonia formed by radiolysis may diffuse away from the canisters or react with basalt, and therefore, do no harm. However, montmorillonite has a very high surface area and is very reactive to acids. More experiments are needed to assess the possible consequences of radiolytic fixation of nitrogen.

Montmorillonite is unstable in hydrothermal environments, and may be partly transformed in a repository to illite, muscovite, or paragonite. A synthesis of the literature on the smectite-illite-muscovite transformation suggests that, because addition of potassium is required for the transformation, the availability of potassium is the limiting factor in the transformation. The rate of fluid flow and, consequently, the permeability of a rock formation are determining factors in the persistence of smectites over geologic time.

In hydrothermal experiments reported here, after 96 days at 360°C in groundwater, calcite impurities in bentonite dissolved and potassium in the bentonite was partially exchanged for calcium. After 92 days at 460°C in groundwater, transformation of montmorillonite to albite, quartz, and possibly paragonite was observed. Under the same conditions, basalt was partly altered to form a potassium-rich, iron-rich smectite and possibly illite.

Conversion of smectite to albite, quartz, and paragonite is assumed to occur at lower rates at lower temperatures. Because addition of sodium is required for the transition, the availability of sodium is expected to be the limiting factor in a basalt repository. Flow calculations based on measured permeabilities of mixtures containing 25 % bentonite suggest that, during the thermal period of the repository, groundwater may supply enough sodium to allow partial conversion of montmorillonite. The resulting volume loss could be detrimental to the permeability of backfill material. Use of a higher proportion of bentonite in the backfill would help to limit the rate of conversion.

Trace-Element Transport in Lithic Material by Fluid Flow

Work reported this quarter is in two distinct tasks. The first task is to analyze natural geothermal systems to gain an understanding of rock-water interactions that are important in moving trace elements in crustal material. This task uses active geothermal systems as natural experiments that are of a size ($1 \times 10^6 \text{ m}^3$) and duration (1×10^3 to 1×10^6 years) unattainable in normal laboratory practice.

The second task is to understand the role natural organic molecules in groundwater play in mobilizing heavy metals such as neptunium and americium. Reported this quarter is a summary of a review of the technical literature on the interaction of natural humic substances with heavy metals.

The combination of analyses of field situations together with laboratory experimentation, exemplified by these two tasks, allows us to develop an understanding of trace-element migration processes directly applicable to natural settings.

Reaction of Glass with Water

Preliminary testing of the Nevada Nuclear Waste Storage Investigations Phase II test procedure has been completed. Analyses of solutions and test components suggest that modifications to the vessel and procedure should be made. Thus, two prototype vessels of a new design have been built and are being tested. If these new reaction vessels are satisfactory, actual waste package testing will be initiated.

A new program studying the applicability of natural basaltic glass as an analog for nuclear waste glass has begun. Both hydration and MCC-1/MCC-2 tests are in progress. Initial hydration testing indicates that basaltic glass reacts similarly to glasses with defense waste compositions, forming analcime and gyrolite on the surface. However, the basaltic glass reacts at a slower rate than the defense waste glass.

TRU Removal from High-Level Waste

The objective of this program is to develop a series of conceptual flow-sheets 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 one is octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide.

Initial work has been to identify the proper mathematical relationships to calculate material balance in the flowsheets, develop a methodology to use the new Questel Telesystemes substructure searching computer system to perform a literature survey on the two extractants under study and on their analogs, contact potential suppliers of bulk quantities of these extractants, and make preparations for the laboratory part of the program.

Light Water Breeder Reactor Proof-of-Breeding Analytical Support

This project involves the destructive analyses of 16 or 17 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. Systems reported upon include: (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, and (8) radiation monitoring systems. 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

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A. Physical and Radiological Investigations

(R. A. Couture and D. L. Bowers*)

1. Introduction

Backfill in a high-level nuclear waste repository in basalt is expected to be exposed to moist air at high temperatures. Unless a heavily shielded canister is used, the vapor will be exposed extensively to gamma radiation, and reactive radiolysis products will be produced. This report deals with radiolysis of air and the effects of radiolysis products on bentonite in backfill.

Irradiation of air efficiently produces oxides of nitrogen. In the presence of liquid water, nitric acid is formed; in the presence of water vapor and bases, nitrates are formed. At some time the oxygen may be entirely consumed by reaction with basalt. Nitric acid can also be produced from nitrogen and water in the absence of oxygen [WRIGHT]. In this case, small amounts of ammonium ion and, presumably, hydrogen gas are also produced [WRIGHT]. Ammonia may also be produced by reaction of nitric acid with basalt. The effects of nitric acid and ammonia on the backfill must be considered.

The possible production of nitric acid in a repository has been considered in detail from data in the literature [STEINDLER-1984A]. That review should be consulted for a more complete discussion of the radiolytic chemistry of nitrogen. Reported values for the radiolytic yields of NO_2 lie between 0.4 and 7.7 molecules per 100 eV. Values for the radiolytic yield of nitric acid of 2.9 and 1.9 molecules per 100 eV have been reported. It was also estimated in [STEINDLER-1984A] that 0.001M HNO_3 is thermally stable at 200°C.

If air is free to diffuse or move through a repository, a significant amount of HNO_3 may be generated. No data on radiolytic fixation of nitrogen at high temperature have been found in a literature search. Consequently, experiments were done to determine whether the radiolytic yield is high enough to cause alteration of clay in the backfill.

The experiments were done by irradiating bentonite, water, and air in sealed containers at 200°C. The clay and water were then analyzed.

2. Methods

Samples of clay were sealed in fused quartz vessels with distilled water and air and irradiated in a ^{60}Co facility at 200°C. Other samples were, and are still being, irradiated in air at room temperature. Although the total dose was lower than expected in a repository, the gas/solid ratio

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was kept high in some samples to increase the ratio of radiolysis products to clay. The dose to the gas phase, per unit mass of clay, is comparable to the maximum expected in a repository.

Envirogel 200, a commercially available bentonite, was used. The sand and silt fractions were removed by sedimentation in water. The clay suspension was then dried in vacuum at about 80°C.

The samples were heated to 200°C and irradiated with ^{60}Co gamma rays for 1024.5 hours at dose rates of 5×10^4 to 7.5×10^4 rad/h. Samples of bentonite and basalt were also given a dose of 1×10^6 rad/h at room temperature, and are still being irradiated. Table I-1 shows the experimental conditions. The relative humidity was calculated at 200°C from the amount of water present and the volume of the container. A relative humidity of 100% signifies that liquid water was present.

After irradiation some of the samples were analyzed. About half the samples have been retained for later analysis if necessary. Added to the samples were 1 mL of water and measured quantities of 0.0093M NaOH, and the samples were back-titrated with 0.0025M HCl using an automatic titrator. The end points of the titration were determined with Gran plots. The samples

Table I-1. Experimental Conditions in Clay-Vapor Radiolysis Experiments

Sample	Mass of Clay, mg	Mass of Water, g	Volume of Gas, cm^3	Relative Humidity	Dose, rad
1	0.44	0.0995	9.4	1	$(6 \pm 1) \times 10^7$
2	0.86	0.0998	8.9	1	$(6 \pm 1) \times 10^7$
3	2.05	0.1042	10.2	1	$(6 \pm 1) \times 10^7$
4	1.92	0.1007	8.9	1	$(6 \pm 1) \times 10^7$
5	0.70	0.0581	9.0	0.82	$(6 \pm 1) \times 10^7$
6	0.65	0.0609	9.4	0.82	$(6 \pm 1) \times 10^7$
7	2.45	0.0553	9.1	0.77	$(6 \pm 1) \times 10^7$
8	2.65	0.0627	10.4	0.77	$(6 \pm 1) \times 10^7$
9	0	0.1005	9.0	1	7.7×10^7
10	0	0.1020	9.7	1	7.7×10^7
11	0	0.1467	10.2	1	7.7×10^7
12	0	0.1332	8.8	1	7.7×10^7

were then filtered and the liquids analyzed for anions by ion chromatography and for cations by inductively coupled plasma (ICP) atomic emission spectroscopy. The alkalinity of the clay was determined by titration with acid and was found to be $(2.75 \pm 0.08) \times 10^{-4}$ eq/g. The concentration of acid consumed by the clay is $[\text{NO}_3^-] - [\text{H}^+]$; the concentration consumed by dissolution of the clay is defined here as this quantity less the alkalinity of the clay.

3. Results

The results are presented in Table I-2 and Fig. I-1. Considerable acid was generated; the acid concentration in the undiluted samples was about 10^{-2}M . The figure shows the amount of nitrate produced and the amount of acid consumed by the clay. The nitrate analyses are accurate to about $\pm 0.4 \mu\text{mol}$. A large fraction of the acid produced was consumed by attack on the clay. The cation exchange capacity of the clay was not measured, but is typically about 1 meq/g. The dashed line in the figure shows the estimated cation exchange capacity of the clay and demonstrates that, in the samples containing less than 1 mg of clay, the amount of acid consumed exceeds the exchange capacity. Thus, there has been an attack on the clay structure, resulting in consumption of H^+ and release of cations. In the samples with higher clay/acid ratios, the amount of acid consumed is about equal to or slightly less than the cation exchange capacity of the clay, and attack on the clay is less complete.

Table I-2. Water Analyses after Irradiation

Sample	Mass of Water, g	Mass of Clay, mg	Amount Dissolved, μmol								Alkalinity of Clay, ^a μeq
			H^+	NO_3^-	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	
1	0.100	0.443	0.75	1.6	0.2	<0.4	0.15	0.13	0.4	<0.2	0.122
3	0.104	2.05	0.56	2.5	1.2	0.75	0.21	0.25	0.6	<0.2	0.56
5	0.058	0.695	0.94	1.9	0.6	<0.4	0.12	0.19	0.5	0.17	0.19
7	0.055	2.46	0.45	2.2	3.0	0.70	0.15	0.20	1.8	0.17	0.68
9	0.100	0	1.51	1.9	0.3	<0.4	0.01	0.06	0.5	<0.2	0
10	0.102	0	1.57	1.6	0.0	<0.4	0.006	0.02	0.2	0.16	0

^aAt 2.22×10^{-4} eq/g.

The analysis for cations is approximate, because of the small sample size and because the samples were filtered after titration. However, the analyses clearly show that uptake of H^+ by the clay is accompanied by release of large amounts of Na^+ , and smaller amounts of K^+ , Ca^{2+} , and Mg^{2+} ions. These observations are consistent with substitution of H^+ for the exchangeable cations, and possibly with partial dissolution or leaching of the clay structure.

The clay from samples 1 and 7 was analyzed by X-ray diffraction, and the results are as follows.

Fig. I-1.

Amount of Nitrate Produced and Acid Consumed as Functions of the Mass of Clay. The Xs show acid consumed by dissolution of clay; dots show acid consumed by dissolution and alkalinity of clay, as defined in the text. Dashed line shows the assumed cation exchange capacity of the clay.

Clay from sample 7 retained its identity as a smectite mineral. However, it has a reduced ability to expand in water. The moistened sample has a basal spacing of 19 Å, as determined with a diffractometer. Unirradiated material expands in water to a basal spacing of well over 50 Å, possibly over 100 Å. The difference in expandability is easily verified by wetting a sample under a microscope. We attempted to restore the expandability of the clay by exchanging the exchangeable ions for Na^+ . The sample was treated overnight with 0.5M NaCl solution on the diffractometer slide. Then the solution was replaced with progressively more dilute solutions; finally, the sample was washed thoroughly for a prolonged period with deionized water. No change in expandability was detected with X-ray diffraction. Thus, the change appears to be irreversible.

A Debye-Scherrer powder diffraction pattern of clay from sample 1 showed only a weak basal spacing and a broad diffuse band, indicating amorphous material. Expansion of the lattice with ethylene glycol vapor did not improve the pattern. Thus, it appears that an excess of acid has largely destroyed the clay structure, leaving a much less expandable clay. The amorphous material is also apparent from the physical properties of the clay. Amorphous material has cemented the clay together, making the clay very difficult to disperse.

The radiolytic yield of nitric acid (GHNO_3) can be calculated from the analyses and the dose to nitrogen in the two blank samples (samples 9 and 10). From the nitrate analyses, yields of 2.8 and 2.2 molecules per 100 eV are calculated; the titrations are more accurate and give values of 2.23 and 2.14 molecules per 100 eV. Therefore, we assign 2.2 molecules per 100 eV as the best value for GHNO_3 at 200°C.

4. Discussion

In a tightly sealed system, the maximum possible amount of acid generated is limited by the concentration of nitrogen in air, which is about 0.04 g·atom/L of pore space at 200°C. However, we assume that gas will be

free to diffuse into the backfill from adjacent rooms, through imperfect seals. Assuming an adequate supply of nitrogen and water vapor in a gas-filled repository, and assuming G_{HNO_3} equals 2.2 molecules per 100 eV, the total production of nitric acid would be 0.55 mole per liter of pore space at a dose rate of 2×10^5 R/h over the lifetime (30-year half-life) of the gamma emitters. For backfill with 25% bentonite and 30% porosity, this is equivalent to over 40% of the cation exchange capacity. This number is approximate, as the radiolytic yield may depend on unknown factors that were not tested. However, it is apparent that the possible production of so much acid in a repository needs to be considered carefully.

We expect that, in the absence of liquid groundwater, NO_2 and NO will diffuse away from the canisters and possibly escape from the repository altogether. However, it is also possible that the gases will react with clay in the backfill. Montmorillonite has an extremely high accessible internal surface area, and hydrolysis of NO_2 by interlayer water would acidify the clay. In a mixed vapor-liquid system, nitric acid would dissolve in liquid water. The alkalinity of nonflowing, basaltic groundwater would be nearly two orders of magnitude too low to neutralize the estimated amount of acid.

The presence of an appreciable amount of nitric acid may have a considerable effect on the hydrothermal alteration of backfill. Hydrogen-ion-exchanged montmorillonite is thought to be unstable and rapidly reactive at room temperature [BROWN]. Theoretically, montmorillonite should be unstable in acid solution with respect to kaolinite or pyrophyllite. Our experiments at 200°C appear to confirm the breakdown of montmorillonite in acid solution. The amount of acid produced may be sufficient to adversely affect the stability of montmorillonite in backfill material.

In a repository, nitric acid may react in the presence of basalt to form ammonia; or ammonia, instead of nitric acid, may form radiolytically. As far as we know, the conversion of nitric acid to ammonia by basalt has not yet been studied. We are uncertain whether the rate of conversion from an oxidizing environment to a reducing environment in a basalt repository will be rapid enough to affect the outcome of radiolysis. It is probable that there will be a large reservoir of air in relatively cool parts of the repository, not immediately adjacent to canisters.

The possible formation of ammonia instead of nitric acid is also a potential problem because the ammonium ion behaves geochemically like potassium. Substitution of NH_4^+ for Na^+ in montmorillonite could lead to loss of expandability of the clay, by a process analogous to formation of illite.

5. Recommendations

It will be necessary to study the partitioning of HNO_3 , NH_3 , and possibly other radiolysis products, between bentonite and vapor or vapor plus liquid, to determine whether reaction of these products will have a significant effect on bentonite. The effect on the mineralogy and physical properties of bentonite also needs to be determined.

We recommend hydrothermal studies on the reaction of backfill mixtures with HNO_3 and NH_3 . In licensing, it may be necessary to determine the effects of production of at least as much as 0.04 mole per liter of pore space.

6. Acknowledgments

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B. Mineralogical and Hydrothermal Investigations

(D. R. Peacor, E. J. Essene, J. H. Lee, and L.-C. Kuo)*

1. Introduction

The primary concern regarding high level nuclear waste disposal is the long-term stability of the potential backfill materials under repository conditions. Because the backfill-host rock system represents a special diagenetic environment, reactions between these materials and groundwater can best be understood by conducting hydrothermal experiments under the specific physical/chemical conditions to be found at the repository. On the other hand, such experiments inevitably suffer a difficulty in simulating the time involved in nuclear waste storage (over 1000 years). This is especially true in the present case because the backfill materials we are dealing with are clay minerals (smectite, illite) and basalt. Therefore, although experiments can be conducted at unrealistically high temperatures to determine the mode of degradation of these materials, the rate of these reactions as a function of temperature must be understood by investigating the diagenetic sequences in natural geologic systems in which clay minerals are important phases.

In this report, we present data on hydrothermal experiments that may be indicative of the possible mode of backfill degradation, and synthesize a comprehensive review of smectite-illite-muscovite transition in a natural diagenetic environment to permit insight into the rates of this transition at temperatures similar to those anticipated in the repository.

2. Smectite-Illite-Muscovite Transition in Diagenetic Systems

Extensive studies have been devoted to an understanding of the nature of diagenetic reactions in argillaceous and clastic sediments. Comprehensive reviews have been published [e.g., KISCH-1983, SINGER]. Additional references have been given [LARSEN]. These studies are concerned, in part, with mineralogical/chemical changes in the clay minerals, smectite and illite, in response to increasing temperature (to about 300°C), geologic time, solution chemistry, and physical factors such as permeability and porosity, which in turn relate to rock/water ratios and fluid flow.

a. Nature of the Transition

The most important mineralogical processes during diagenesis of sediments are (1) the progressive conversion of detrital smectite into mixed-layer illite/smectite (I/S), which eventually approaches pure illite, [ARTRU-1968 -1969, BOLES, BURST-1959 -1969, CARRIGY, DUNOYER de SEGONZAC-1964 -1966 -1969, ESLINGER, HOWER, KARPOVA-1969 -1971, MUFFLER, PERRY-1970 -1972, POWERS-1959 -1967, STEINER, TEODOROVICH-1967 -1970, WEAVER-1959 -1971]

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and (2) the successive transition of illite to muscovite; from polytype: [ARTRU-1969, DUNOYER de SEGONZAC-1969, FREY-1969 -1970, GAVRILOV, KARPOVA -1966 -1967 -1969, LEWIS, LOGVINENKO, MAXWELL, VELDE]; from chemistry: [KARPOVA-1969, KOSSOVSKAYA]. In chemical and structural terms, illite is derived from smectite by (1) substitution of K in interlayer sites with concomitant loss of other cations (Ca, Na) and H₂O layer, and (2) substitution of Al for Si in tetrahedral layers. The transitions continue as illite transforms to muscovite with further substitutions of K + Al for Si plus a vacancy, with concomitant changes including increasing ordering (from a 1M₁ to a 2M structure) and a further decrease in H₂O and a loss of expandable layers. Thus, smectite-illite-muscovite transition can be considered as a continuous process with a gradual decrease in expandability and cation exchange capability.

b. Controlling Factors of the Transition

Weaver suggested that the K needed for the transitions is produced from breakdown of detrital K-feldspar and/or mica [WEAVER-1967]. This interpretation was supported by Hower and others, who observed a gradual disappearance of K-feldspar with increasing depth in Gulf Coast sediments and suggested that K-feldspar may also be the Al source [HOWER]. The possible importance of the K supply from the nearby shale formations during sandstone diagenesis was stressed by [WEAVER-1971]. On the other hand, [BOLES] proposed that the Al component of illite during the smectite-illite transition is entirely supplied from smectite layers and, therefore, some smectite must be consumed to form I/S. This implies that the smectite-illite transition can proceed without Al supply from the solution. However, the supply of K (or other interlayer cations) is critical to the smectite-illite transition (or breakdown of smectite into a nonexpandable phase), and these ions must be primarily from pore solution because their amounts are lower in smectite than in illite (or other nonexpandable phases).

The kinetics of the smectite-illite transition has been studied experimentally in the temperature range of 150-400°C by [EBERL-1976] who reported an activation energy of around 20 kcal/mol for the I/S transition, indicating the breaking of chemical bonds in tetrahedral/octahedral layers. It is important to note that this transition is more effective in K-saturated than in Na-saturated smectite. Furthermore, [EBERL-1978] showed that the inhibitory strength of monovalent ions for the smectite-I/S transition follows the order, Li, Na, Cs, and K, and that of divalent ions the order, Ca, Mg, Sr, and Ba, which is positively correlated to the magnitude of dehydration energy of these ions. This is because a higher negative charge in smectite layers is required to incorporate a cation with higher hydration energy into the interlayer site. However, this does not mean that Ca-smectite is the most stable, because all divalent cation-saturated smectites (except Ba-smectite) produced rectorite/smectite in 400°C runs, which manifests another mechanism of collapse of the expandable structure. Indeed, [EBERL-1977] showed that, when reacted with pure water, Na-smectites typically break down into paragonite-bearing assemblages, whereas K-smectite typically produces I/S. The inhibition of the smectite-I/S transition by Na, Ca, and Mg ions in the solution has been demonstrated [ROBERTSON].

The importance of fluid flow on the rate of these transitions has been stressed by [LEE-1984A,B,C], who found that, in a shale to slate transition in the Martinsburg Formation at Lehigh Gap, Pennsylvania, the entire range from illite to muscovite is present at a constant temperature (about 250°C) for a long geological time, even though I/S and illite are unstable relative to muscovite and the ions necessary for the illite-muscovite transition are available.

c. Temperature Ranges of the Transition

Temperature ranges of the smectite-illite transition have been inferred from various field studies [BOLES, BURST-1969, DUNOYER de SEGONZAC -1970, ESLINGER, FOSCOLOS, HOWER, MUFFLER, PERRY-1970 -1972, STEINER]. Most of these results indicate a temperature of about 100°C for the onset of I/S formation [e.g., FOSCOLOS, PERRY-1970]. Lower temperatures have also been reported, e.g., 60°C [BOLES, HOWER]. Complete conversion of smectite to illite is estimated to occur at temperatures as low as 200°C, from experiments of Khitarov and Pugin (1966) and Sabatier, as quoted by [DUNOYER de SEGONZAC -1969, HILTABRAND]. The temperature range for the transformation of illite to muscovite is large (about 100-350°C). Oxygen isotope thermometry of coexisting quartz and illite from the Belt Series [ESLINGER] indicates that 50% of the illite of the <0.5- μ m size fraction would have been converted from the 1M_d to 2M polytype at a temperature of about 290°C. Coal-ranks (for detailed reference citations: [KISCH-1974]) and illite crystallinity [KUBLER-1964 -1967, WEAVER-1967, WEBER-1972A,B] (for detailed reference citations: [KISCH-1983]) are widely used as indicators of temperature and, thus, of the degree of burial metamorphism (increasing depth, time, temperature) in a diagenetic sequence, and confirm this approximate temperature range.

3. Experimental Results

Table I-3 documents the mineralogical/chemical changes in the hydrothermally treated smectite, illite, and basalt as compared with the corresponding starting materials. The detailed findings in each run product are as follows.

a. Smectite

The product of run BN685 shows essentially the same characteristics as those of runs at 300°C; i.e., the absence of calcite peaks and the increase in d(001) value of the smectite (Fig. I-2). We suggest that the extensive exchange of Ca for K occurred in the smectite interlayer due to the increase in Ca concentration in the solution by calcite dissolution, whereas the structure of the smectite remained stable during the time period of the experiment.

The XRD pattern from run BN454 (Fig. I-2) shows the presence of strong albite peaks, an increase in the relative amount of quartz versus smectite, and the appearance of a 10-A phase. Because the original solution is rich in Na but poor in K, we suggest that this 10-A phase is paragonite, a Na-rich mica. The possible reaction can then be written as:

Table I-3. Conditions and Results of Hydrothermal Experiments^a

Run No.	Temperature, °C	Elapsed Time, days	Rock/Fluid Ratio	Mineralogical Changes
BN685	360	96.5	0.36	Disappearance of calcite Ca-K exchange in bentonite
BN454	460	92	0.45	Disappearance of calcite Formation of albite+ quartz+paragonite
IL680	360	96.5	0.42	Appearance of kaolinite
IL455	460	92	0.52	Appearance of kaolinite
BS681	360	96.5	0.54	Appearance of smectite+illite
BS450	460	92	0.47	Appearance of smectite+illite

^aAll experiments conducted at 30 MPa (300 bar) total pressure.

Fig. I-2. XRD Patterns of Hydrothermally Treated Bentonites and the Starting Material, (a) Starting Material, (b) BN685, (c) BN454

It should be noted that the Mg ion might form Mg-chlorite by introduction of Na^+ or by reaction with albite:

The first reaction is consistent with the observations of [WOOD], who measured the ionic concentrations in the solution reacting with the Wyoming bentonite as a function of time and found that (1) the concentration of Na in the solution decreases as reaction proceeds; (2) the concentration of K in the solution increases, indicating the absence of illite or K-feldspar in the reaction products; and (3) the solution after reaction becomes acidic (pH = 5.34 after 616 hours). The most important consequences of these reactions are (1) the partial dehydration of smectite; (2) the significant loss of the volume of solids (47% of the original volume for the first reaction); (3) the irreversible collapse of a 14-Å, expandable structure to a 10-Å, nonexpandable structure (or partially to a 14-Å, nonexpandable chlorite structure); and (4) the acidization of the resultant solution.

Figure I-3 illustrates the SEM images of the typical assemblage of the run product BN454. Quartz occurs as recrystallized, euhedral aggregates masking the surface of the partially reacted smectite plate. Albite crystals are relatively coarse and are sparsely distributed. Paragonite is characterized by a platy morphology.

b. Illite

Figure I-4 shows the XRD patterns of runs IL680 and IL455 and of the starting material. The only noticeable difference is the appearance of a 7-Å phase in these run products. This phase may be septechlorite, which is formed from smectite interlayered with illite, or kaolinite formed at the expense of feldspar. It appears that the relative amount of feldspar in the 460°C run is slightly smaller than in the 360°C run and in the starting material.

Fig. I-3.

SEM/EDX Characterization of the Run Product BN454. Note the occurrence of quartz (aggregates of gray, euhedral crystals), albite (white, discrete grains), and paragonite (indicated by arrows).

Fig. I-4. XRD Patterns of Hydrothermally Treated Illites and the Starting Material, (a) Starting Material, (b) IL680, (c) IL455

c. Basalt

The only difference in XRD patterns between runs BS681 and BS450 and that of the starting material is the appearance of a weak but definite peak corresponding to about 14 Å, indicating the production of smectite clay as the alteration product. This is confirmed by SEM observation in which feathery clay flakes are clearly observed (Fig. I-5). Under TEM, however, both 10-Å (illite) and 14-Å (smectite) lattice fringe images were observed (Fig. I-6). The 10-Å phase, tentatively suggested as illite, is discrete in occurrence. The amount of this phase is perhaps too small to be detected by XRD.

Fig. I-5. SEM Photograph of the Run Product BS450 Illustrating the Occurrence of Feathery Clay Flakes (surrounded by arrows). Most of the granular particles are plagioclase crystals.

Several energy dispersive spectra were taken for smectite grains. These are characterized by the high Si, K, and Fe concentrations with subordinate Na, Mg, Al, Ca, and Ti, a condition very similar to the chemistry of the immiscible glasses [STEINDLER-1984B]. Although this may not represent true smectite chemistry, because the grains are too small to obtain a contamination-free spectrum, it clearly indicates the close relationship between these clays and immiscible glasses and, in turn, the high reactivity of the immiscible glasses.

4. Discussion

The most important result of our hydrothermal experiments is that bentonite degrades into albite + quartz + paragonite rather than I/S when reacting with the groundwater in the repository. This result confirms the

Fig. I-6. TEM Lattice-Fringe Images of (a) the Run Product BS681 Showing the Occurrence of Discrete Illite Grains and (b) the Same Sample Showing the Occurrence of Illite and Smectite Grains. No interlaying between smectite and illite was identified.

observations of [WOOD] and defines the mode of degradation of the bentonite backfill under the repository conditions. Therefore, the next important question is: will this reaction occur at repository temperatures in geologic time?

Observations on natural diagenetic systems reveal that the smectite-illite-muscovite transition is influenced by (1) temperature, (2) fluid chemistry, (3) permeability of the sediments, and (4) time. The smectite-illite transition is complete at temperatures of about 200°C, and the illite-muscovite transition at temperatures approaching 300°C. A source of K (and perhaps Al) is required for such transitions. The presence of alkali and alkaline earth cations other than K tends to impede the smectite-illite transition. In the absence of K, however, other modes of transition may occur. Rectorite-smectite and paragonite-albite-quartz assemblages may be derived from smectite when Ca and Na, respectively, are the dominant cations in the solution. The rate of K (and Al) supply depends critically on the effective permeability of the sediments. Metastable smectite, I/S, and illite may remain largely unaltered at the temperatures given above if the sediments are essentially impermeable. Therefore, the degradation of bentonite under repository conditions depends greatly on the availability of Na because, once enough Na is accumulated, bentonite will degrade at repository temperatures (100-300°C) in geologic time.

The amount of Na available can be calculated by assuming that the flow of groundwater through the backfill material obeys Darcy's law:

$$u = - \frac{\kappa}{\mu} \frac{dP}{dx}$$

where

u = flow rate,

κ = permeability,

μ = dynamic viscosity of the fluid, and

dP/dx = pressure gradient across the backfill column.

We adopt permeabilities for bentonite-quartz mixtures measured by [COUTURE-1984] and dynamic viscosities of water at 30 MPa (300 bar) and different temperatures from [SCHMIDT]. The calculations are summarized in Table I-4. These results suggest that the rate of bentonite degradation may be too high to permit the use of a bentonite-quartz mixture as the backfill material. We point out that (1) the permeabilities used were the highest ones measured by [COUTURE-1984] (we expect that swelling of the bentonite will occur upon water saturation and permeability will greatly decrease) and (2) the permeabilities will be greatly reduced if higher proportions of bentonite are used. To further evaluate the availability of Na to the bentonite backfill, permeabilities under water-saturated conditions in the pure bentonite or bentonite-quartz mixture with high bentonite proportions (for example, 80%) are desired. As stressed above, whether or not the bentonite is stable in geologic time depends critically on the effective permeability of the backfill column.

5. Hydrothermal Experiments in Progress

In addition to the set of one-year experiments [STEINDLER-1984B], two sets of three-month experiments are now in progress. The experimental conditions are summarized in Table I-5.

The first set of three-month experiments involves using the basalt-bentonite mixtures with various proportions as the starting material. The major purpose of these experiments is to explore the mineralogical/chemical changes during hydrothermal reaction. It is conceivable that the mode of degradation of bentonite may be modified by the glass in the basalt, which is highly reactive. The results should allow insight into the controlling factors of bentonite alteration. If the characteristics of the run products with different basalt proportions are essentially identical, then the alteration of bentonite is suggested to be unrelated to the basalt (or glass) content. In contrast, if the basalt (glass) content is of vital importance in influencing the bentonite degradation, then the mineralogical/chemical features of the alteration products should show some correlation with the basalt content.

Table I-4. Calculated Rates of Bentonite Alteration as a Function of Temperature and the Size of Quartz Sand^a

Parameter	Alteration Rate		
	100°C	200°C	300°C
Permeability/Dynamic Viscosity (κ/μ), $\frac{\text{cm}^2}{\text{bar}\cdot\text{s}}$	1.05×10^{-5} (2.81×10^{-5})	2.13×10^{-5} (5.67×10^{-5})	3.12×10^{-5} (8.33×10^{-5})
Flow Rate (μ) ^b , cm/s	7.35×10^{-7} (1.96×10^{-6})	1.49×10^{-6} (3.97×10^{-6})	2.18×10^{-6} (5.83×10^{-6})
Na supply, ^c mol/($y\cdot\text{cm}^2$)	2.72×10^{-4} (7.25×10^{-4})	5.51×10^{-4} (1.47×10^{-3})	8.06×10^{-4} (2.16×10^{-3})
Rate of Bentonite Alteration, ^d mol/($y\cdot\text{cm}^2$)	3.58×10^{-4} (9.54×10^{-4})	7.25×10^{-4} (1.93×10^{-3})	1.06×10^{-3} (2.84×10^{-3})
Rate of Bentonite Alteration, ^e g/($y\cdot\text{cm}^2$)	0.13 (0.35)	0.27 (0.71)	0.39 (1.04)

^aMain entries are calculated for 25% bentonite (200 mesh) + 75% quartz (80-140 mesh) ($\kappa = 3 \times 10^{-14} \text{ cm}^2$); parenthetical entries are calculated for 25% bentonite (200 mesh) + 75% quartz (20-80 mesh) ($\kappa = 8 \times 10^{-14} \text{ cm}^2$) [COUTURE-1984].

^bCalculated by assuming a pressure gradient of 7 kPa/cm (0.07 bar/cm) [COUTURE-1984].

^cAssumes groundwater with 270 ppm Na.

^dAssumes 1 bentonite reacts with 0.76 Na^+ .

^eAssumes Na-bentonite with a formula weight of 366.0.

It is also very likely that the reactivity of the immiscible glasses in the basalt is a function of particle size [COUTURE-1983]. After collecting the data on this current set of experiments, we will carry out additional experiments on some mixtures with small basalt particle size.

The second set of three-month experiments uses K-saturated bentonite as the starting material. As discussed earlier, the source of Al for smectite-illite transformation is subject to debate. If Al is supplied by groundwater, then it is expected that bentonite will not degrade in these experiments even though K is added, because there is no Al in the solution. On the other hand, illite will form in these experiments if Al is available from smectite. The K-saturated bentonite can form illite even if distilled

Table I-5. Hydrothermal Experiments in Progress^a

Run No.	Temperature, °C	Rock/Fluid Ratio	Starting Material
BB-41	300	0.97	25% bentonite +
BB-44	300	0.11	75% basalt
BB-62	400	0.48	
BB-69	400	0.17	
BH-D4	300	0.87	50% bentonite +
BH-C5	400	0.82	50% basalt
BQ-D7	300	0.59	75% bentonite +
BQ-C1	400	0.97	25% basalt
KBN-A2	300	0.46	K-saturated
KBN-B8	400	0.45	bentonite

^a All experiments conducted at 30 MPa (300 bar) total pressure.

water is used as the solution [EBERL-1976]. This set of experiments, therefore, serves as a check on the results of [EBERL-1976]. The nature of such a transformation, if it has occurred, will be better understood by using STEM/AEM techniques.

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II. TRACE-ELEMENT TRANSPORT IN LITHIC MATERIAL BY FLUID FLOW (M. G. Seitz, N. C. Sturchio, D. Livermore,* and S. Boggs, Jr.†)

A. Chemical Mobility during Hydrothermal Alteration in an Active Geothermal System (N. C. Sturchio)

1. Introduction

Investigative efforts have been directed toward the mobility of radionuclides in rock-water systems, the stability of backfill materials, and the reaction of waste glass with water. A serious drawback that applies to some experimental data is that they cannot be confidently extrapolated from experimental time scales (hours or days) to those of concern in nuclear waste isolation (10^3 - 10^6 years). This can lead to severe compromise in the accuracy of predictions based on these data.

However, unique opportunities do exist to observe the effects of high-temperature water-rock interactions over long time scales in natural systems. For example, hydrothermal alteration in an active geothermal system may be regarded as a natural "experiment" in such interactions over time scales of 10^3 - 10^6 years and size scales unattainable in normal laboratory practice. Valuable information pertaining to the time-integrated effects of chemical mobility may be gained through careful study of such a system, thereby enabling verification of geochemical models, and allowing more accurate predictions be made. For this reason, a study of the chemical mobility during hydrothermal alteration of volcanic rock from the active high-temperature geothermal system at Yellowstone National Park is now under way.

2. The Yellowstone Samples

In 1967-1968, 13 research holes were drilled in thermal areas of Yellowstone National Park by the U.S. Geological Survey [WHITE]. Depths of the holes ranged from 65.5 to 331.4 m, and temperatures up to 237.5°C were recorded. Temperature variation with depth was found to be close to the boiling-temperature curve. Vertical water pressures exceeded 110% of hydrostatic pressure in 12 holes; a value of 147% was found in one of them. The environment explored by these holes is generally characterized by extreme gradients in temperature and water pressure.

The stratigraphy of Yellowstone National Park consists predominantly of rhyolitic ash-flow tuffs and rhyolite flows, minor basaltic flows, and interbedded volcanoclastic sediments [CHRISTIANSEN]. Siliceous sinter and travertine deposits are also common at or near the surface in areas where thermal water has emerged. Detailed studies of rock core samples from the Yellowstone drill holes have concentrated on the mineralogic consequences of hydrothermal alteration [e.g., HONDA, BARGAR, KEITH]. These studies have revealed that the major products of hydrothermal alteration at Yellowstone

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are clays, zeolites, and silica minerals. Minor amounts of carbonates, oxides, sulfides, and other phases have also been noted. Processes involved in the hydrothermal alteration of these rocks include dissolution, precipitation, and ion exchange. The temperature and composition of the thermal water is an important factor in determining the products of alteration. Many of the rocks in the drill cores contain abundant volcanic glass, which is highly reactive under the conditions at depth, and commonly is found to be completely replaced by clays and zeolites, whereas coexisting primary plagioclase, oxide, and other phases are not strongly affected.

For the purpose of the present study, a suite of core samples from drill holes Y-7 and Y-8 were chosen. The hydrothermal mineralogy and alteration sequence of these cores has been studied in detail by T. Keith and others of the U.S. Geological Survey (USGS) [KEITH]. This existing information will facilitate study of the chemical processes involved during hydrothermal alteration. The samples being studied here are from the rhyolitic flow breccia unit, at -52.7 m to the bottom of the hole at -73.8 m in Y-7, and from -55.2 to -62.8 m in Y-8. Measured temperatures in the flow breccia range from 110 to 140°C in Y-7 and 160 to 170°C in Y-8. The primary lithology of the flow breccia is relatively simple, consisting mainly of fragments of rhyolitic vitrophyre of various sizes in a porous matrix of millimeter-scale glass and mineral fragments. The vitrophyre (before alteration) consisted of glass containing phenocrysts of plagioclase, clinopyroxene, orthopyroxene, magnetite, ilmenite, quartz, sanidine, apatite, and zircon. During alteration the glass is replaced by clays (smectite and illite groups) and zeolites (mainly clinoptilolite and mordenite). Pore space and fractures are filled with hydrothermal precipitates of clays, zeolites, and silica minerals (mainly betacristobalite and opal). Clinopyroxene is altered to clays and minor chlorite. Plagioclase, magnetite, quartz, and sanidine remain virtually unaltered, although magnetite is locally oxidized and some chemical changes probably have occurred within the feldspars.

The strategy being employed in this study is to acquire compositional data on a wide range of elements in the thermal water, the unaltered glass, the clays and zeolites replacing the glass, and the clays, zeolites, and silica minerals precipitated in open spaces within the rock. The acquisition of these data requires meticulous separation of the various phases in rock, necessary because this is the only approach that can yield realistic hydrothermal distribution coefficients. Additional bulk analyses of vitrophyre clasts and matrix are also being acquired. The principal analytical tools being used are: electron microprobe, inductively coupled plasma (ICP) atomic emission spectrometry, and instrumental neutron activation analysis. Other more specific techniques are applied as needed.

3. Preliminary Results

The Yellowstone samples described above were acquired from the USGS, Branch of Igneous and Geothermal Processes, Menlo Park, California, during 18-21 October 1983. During November and December 1983, sample preparations and data collection were initiated. Sample preparations will be described elsewhere. The data collected to date are reported here.

a. Analysis of Thermal Water

Table II-1 gives ICP analyses of two samples of thermal water from the Y-7 drill hole (from J. M. Thompson, USGS). The sample numbers indicate the depth (in feet below the surface) at which the sampling was done. Samples were collected in September 1980, using a down-hole in situ sampler of USGS design. The samples were filtered through 0.45- μ m filters and acidified with HCl (to maintain cations in solution) shortly after collection by USGS personnel. These data are in close agreement with unpublished

Table II-1. ICP Analyses of Yellowstone Waters^a

Constituent	Concentration, μ g/L	
	Y7-200 ^b	Y7-240 ^c
Al	430	300
B	3230	3680
Ba	14	12
Be	<5	<5
Ca	1780	6350
Cd	<10	<10
Co	<10	<10
Cu	<5	<5
Fe	240	82
K	83 ^d	93 ^d
Li	1160	1190
Mg	17	72
Mn	17	20
Mo	840	1160
Na	400 ^d	440 ^d
Ni	<20	<20
Pb	<100	<100
SiO ₂	360 ^d	369 ^d
Sn	<100	<100
Sr	<5	<5
Ti	<5	<5
V	<10	<10
Zn	35	140
Zr	<10	<10

^aAnalysis by E. A. Huff, Analytical Chemistry Laboratory, ANL.

^bSample from 60-m (200-ft) depth.

^cSample from 73-m (240-ft) depth.

^dmg/L.

USGS analyses that were performed several years ago, especially regarding the major ions, Si, Na, and K [THOMPSON]. This indicates that no major compositional changes have occurred in these samples since that time. Additional data for these samples will be acquired by instrumental neutron activation analysis for the elements, Na, Fe, Sc, Cr, Co, Rb, Cs, La, Ce, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Th, U, Br, Sb, As, and W. The compositional data for the water samples will be integrated with that from the rock samples when data collection has been completed.

b. Electron Microprobe Analysis of Glasses, Clays, and Zeolites

(1) Analytical Methods

The instrument used for the analyses reported here is a fully automated JEOL 733 Superprobe at the Department of Earth and Planetary Sciences, Washington University, St. Louis, Missouri. All analyses were done using an accelerating potential of 15 kV, sample currents of 10-31 nA, and beam diameters of 10-30 μm (to minimize sample volatilization and ion migration). Samples were in the form of polished thin sections and were carbon coated prior to analysis. Count data were collected by wavelength-dispersive crystal spectrometers and reduced on line by the method of Bence and Albee [BENCE], using the empirical correction factors of Albee and Ray [ALBEE]. The relative analytical uncertainty (2σ) of this method, as determined from replicate analysis of mineral standards, is 3% or less for oxides present in concentrations of 8 wt % or more, and 6% or less for oxides present in concentrations of 1 to 8 wt %.

(2) Results

Table II-2 is a condensed version of the analytical results for glass, clay, and zeolite phases in three representative samples of the hydrothermally altered volcanic rocks being studied. Data are reported in terms of the arithmetic mean, $\bar{X}$, of a number of spot analyses, along with the standard deviation, σ , about the mean. The σ values indicate the degree of compositional variability within the phase analyzed and whether that variability exceeds analytical uncertainty.

Glass compositions were fairly consistent with respect to SiO_2 , TiO_2 , Al_2O_3 , and MgO . The low oxide sums indicate 8-9 wt % water of hydration. Concentrations of FeO , CaO , Na_2O , and K_2O show significant variations within and between samples. However, the compositional variation within glass in least altered areas of sample Y7-239 encompassed the range of variation in glass remnants in highly altered areas of the sample. Figure II-1 shows a microprobe traverse across such a remnant in this sample, indicating only minor compositional variation. Intersample variations are greater than intrasample variations, possibly indicating primary compositional differences in the samples.

Analyses of the clay minerals in samples Y7-239 and Y8-190 show significant differences between vein precipitates and glass replacement clays in each sample. In sample Y7-239, the vein precipitate is lower in TiO_2 and higher in MgO than the glass replacement clay. In sample Y8-190, the vein

Table II-2. Electron Microprobe Analyses of Glasses, Clays, and Zeolites in Hydrothermally Altered Volcanic Rocks from Yellowstone National Park

<u>Glasses</u>						
Sample Number	Y7-196		Y7-239		Y8-190	
Spots Averaged	5		7		5	
Beam Current, nA	31		30		31	
Beam Diameter, μm	30		30		30	
Concentration, wt %	Mean, $\bar{X}$	Std Dev, σ	Mean, $\bar{X}$	Std Dev, σ	Mean, $\bar{X}$	Std Dev, σ
SiO ₂	70.3	0.5	70.8	0.4	69.6	0.7
TiO ₂	0.21	0.01	0.22	0.01	0.21	0.01
Al ₂ O ₃	10.9	0.1	11.2	0.1	10.8	0.1
FeO ^a	1.54	0.09	1.57	0.05	1.31	0.13
MgO	0.08	0.004	0.08	0.01	0.07	0.01
CaO	0.61	0.04	0.51	0.05	0.97	0.05
Na ₂ O	1.43	0.09	1.61	0.22	2.43	0.16
K ₂ O	6.05	0.14	4.80	0.16	1.96	0.08
Sum $\bar{X}$	91.2	0.6	90.8	0.5	87.3	0.8

<u>Clays</u>				
Sample Number	Y7-239 ^b		Y7-239 ^c	
Spots Averaged	5		4	
Beam Current, nA	16		17	
Beam Diameter, μm	10		10	
Concentration, wt %	Mean, $\bar{X}$	Std Dev, σ	Mean, $\bar{X}$	Std Dev, σ
SiO ₂	52.2	1.8	49.8	1.8
TiO ₂	0.31	0.07	0.53	0.03
Al ₂ O ₃	10.0	0.9	9.94	0.54
FeO ^a	18.7	1.0	19.1	1.4
MgO	1.85	0.09	1.46	0.01
CaO	0.42	0.11	0.55	0.09
Na ₂ O	0.14	0.06	0.26	0.11
K ₂ O	7.22	0.38	7.28	0.61
Sum $\bar{X}$	90.8	2.4	88.9	2.9

(contd)

Table II-2. (contd)

<u>Clays (contd)</u>						
Sample Number	Y8-190 ^b		Y8-190 ^c		Y8-190 ^d	
Spots Averaged	3		2		3	
Beam Current, nA	17		17		16	
Beam Diameter, μm	10		10		10	
Concentration, wt %	Mean, $\bar{X}$	Std Dev, σ	Mean, $\bar{X}$	Std Dev, σ	Mean, $\bar{X}$	Std Dev, σ
SiO ₂	52.1	0.6	52.8	0.3	48.0	0.5
TiO ₂	0.02	0.00	0.51	0.02	5.12	0.67
Al ₂ O ₃	11.4	0.3	13.8	0.7	11.1	0.9
FeO ^a	19.2	0.8	13.3	0.8	17.4	0.5
MgO	1.97	0.01	1.30	0.11	0.81	0.16
CaO	0.29	0.05	0.25	0.04	0.35	0.10
Na ₂ O	0.27	0.03	0.23	0.01	0.11	0.04
K ₂ O	6.64	0.15	6.47	0.47	8.27	0.50
Sum $\bar{X}$	91.9	1.1	88.6	1.8	91.2	1.0
<u>Zeolites</u>						
Sample Number	Y7-239 ^e		Y7-239 ^f		Y8-190 ^f	
Spots Averaged	3		4		3	
Beam Current, nA	10		10 or 15		10	
Beam Diameter, μm	10 or 20		10		10 or 20	
Concentration, wt %	Mean, $\bar{X}$	Std Dev, σ	Mean, $\bar{X}$	Std Dev, σ	Mean, $\bar{X}$	Std Dev, σ
SiO ₂	71.2	0.6	70.9	0.5	68.5	1.5
TiO ₂	0.04	0.01	0.08	0.08	0.23	0.15
Al ₂ O ₃	12.6	0.2	12.8	0.1	13.7	0.2
FeO ^a	0.09	0.01	0.05	0.05	0.65	0.16
MgO	0.02	0.01	<0.01	-	0.12	0.04
CaO	0.44	0.03	0.45	0.12	2.06	0.05
Na ₂ O	2.21	0.23	2.16	0.12	2.08	0.25
K ₂ O	7.48	0.56	7.79	0.34	4.67	0.08
Sum $\bar{X}$	94.1	0.1	94.2	0.4	91.9	1.0

^aTotal Fe as FeO.^bCeladonite in vein.^cCeladonite replacing glass in and near hydration cracks.^dCeladonite "bud" within clinoptilolite that replaces glass.^eClinoptilolite in vein.^fClinoptilolite replacing glass.

Fig. II-1. Microprobe Traverse of a Glass Remnant in Hydrothermally Altered Volcanic Rock from Yellowstone National Park. (Symbols: unpatterned area - hydrated perlitic glass; stippled area - celadonitic clay; horizontally lined area - clinoptilolite.) Each "X" indicates the position of a spot analyzed by the electron microprobe (beam current - 31 nA; beam diameter - 30 μm). The wt % ratio of $\text{Na}_2\text{O}/\text{K}_2\text{O}$ at each spot is (1) 1.65/4.75; (2) 1.53/5.21; (3) 1.47/5.29; (4) 1.59/5.12; and (5) 1.54/5.04. These data indicate that the glass composition across this area varies within the range of glass in less altered areas of the sample.

precipitate is lower in TiO_2 and higher in MgO as well, but also lower in Al_2O_3 and higher in total Fe than the glass replacement clay. A very interesting result is the high TiO_2 content of the celadonite "buds" within the glass-replacing clinoptilolite in sample Y8-190. This may imply significant small-scale mobility of Ti, which is generally regarded as one of the most immobile of elements during hydrothermal alteration.

Zeolite analyses are notoriously difficult due to the volatilization and ion-migration effects of the electron beam. Whereas the stoichiometry of the Y7-239 clinoptilolites appears to indicate reliable

analyses, the oxide sums are higher than they should be, because zeolites contain 10-20% H₂O. The oxide sums for the Y8-190 analyses are more reasonable, but the poor stoichiometry indicates a less reliable analysis. We will attempt to correct the analyses for H₂O, assuming a reasonable stoichiometry. The zeolite data reported here should be considered as preliminary data only, and subject to refinement.

4. Further Work

Acquisition of trace-element compositional data from unaltered glass; clays and zeolites replacing glass; and clays, zeolites, and silica minerals precipitated in open spaces is in progress. When complete, the entire data set will be interpreted in terms of the specific mechanisms that govern chemical mobility (i.e., the magnitude and range of transport of the elements) during hydrothermal alteration in this system. The implications of these results for nuclear waste isolation, hydrothermal ore deposition, and geothermal energy exploration will be explored.

B. Review of Natural Organic-Radiochemical Interactions

(S. Boggs, Jr.^{*} and D. Livermore[†])

A review, completed this quarter, described the understanding found in technical literature of the interactions between natural humic substances and radiochemicals. This review is in support of an experimental program to investigate the influence of humic substances dissolved in water on the mobility of radioelements. The review and its findings are summarized here.

1. Introduction

The formation of water-soluble complexes of humic substances with metal ions is of particular interest because complexing can increase concentrations of these ions in soil waters and other natural waters far above the concentrations that could be expected based on their normal solubilities. Responsible scientists are concerned about the possibility that complexing of radioelements by humic substances may enhance the mobility of these elements and promote their entry into the biosphere. The anticipated program to study the interaction of humic substances with heavy metals has special pertinence to the siting of radioactive waste repositories; therefore, it is important that we develop a fuller understanding of the ability of dissolved humic substances to form complexes with dangerous radioelements such as the actinides. We may then be able to take adequate precautions to prevent these radioelements from becoming mobilized in organic-rich groundwaters.

2. Distribution and Characteristics of Dissolved Humic Substances

Humic substances are the major organic constituents of soils and sediments. They also occur in small concentrations in natural surface waters

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and groundwaters. They form through breakdown of plant and animal tissues by chemical and biological processes that tend to produce complex chemical structures that are more stable than the original material from which they were derived [SCHNITZER]. One of the more important characteristics of humic substances is their ability to form water-soluble and water-insoluble complexes with metal ions and hydrous oxides and to interact with clay minerals and various organic compounds such as alkanes, fatty acids, and toxic organic substances such as pesticides.

3. Interaction of Humic Substances with Metals

Most investigations of metal-organic complexing have been concerned with the stability of metal-organic complexes, and particularly the effects on stability of environmental variables such as pH, Eh, metal ion and organic carbon concentration, and ionic strength. The complexing behavior of numerous metals has been studied, including Al^{3+} , Ba^{2+} , Ca^{2+} , Cd^{2+} , Co^{2+} , Cr^{3+} , Cs^+ , Cu^{2+} , Eu^{3+} , Fe^{2+} , Fe^{3+} , Hg^{2+} , Mg^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Ru^+ , Sr^+ , and Zn^{2+} . The organic substances of principal interest in complexing studies are humic and fulvic acids, which occur in soils, sediments, fresh and marine surface waters, and groundwaters. Most investigators extract humic substances from soils for use in experimental complexing studies because soil humics are the simplest humic substances to extract in large quantities, and they are commonly assumed (perhaps incorrectly in some cases) to be similar in character to those found in natural waters. The characterization of humic substances from soils is extensive but by no means complete [SCHNITZER]. Only a few studies have attempted to characterize humic substances from groundwaters [MEANS, THURMAN].

The types of interactions that occur between metal ions and the organic acids found in natural waters range from complexing reactions to the formation of colloids [MORTENSON]. Many complexes between humic substances and metals have been reported to be chelates. To identify metal-humate chelates, investigators examine the ratio of metal cations complexed per mole of organic material and then compare the types of functional groups found in humic and fulvic acids to those present in other organic acids that have simpler structures and are known to form chelates. The formation of simple complexes and chelates can occur by ion-exchange and surface absorption reactions [MORTENSON]; however, the various processes involved in the formation of metal-humic complexes and the characteristics of the complexes are still poorly understood.

Most investigators who have analyzed and studied the functional groups of humic and fulvic acids conclude that phenolic OH and carboxyl groups [of both phenolic (C-ring) and aliphatic (C-chain) character] are two of the most important functional groups involved in complexation and chelation of metal ions [SCHNITZER]. Knowledge of these functional groups has been applied in modeling studies to investigate metal-organic complexing under natural conditions using organic acids of known composition. Salicylic and phthalic acids (Fig. II-2) have been used in such studies as structurally simple analogs for humic substances. Both salicylic acid and phthalic acid are bidentate ligands (a ligand that has two active functional groups per molecule) where the former acid contains one carboxyl and one hydroxyl group and the latter contains two carboxyl groups. These organic acids of known composition can thus be used to simulate the chelation tendency of humic and fulvic acids, which are not easily characterized chemically.

Phthalic Acid

Fig. II-2.

Structure of Phthalic and Salicylic Acids

Salicylic Acid

4. Complexing of Soil Humic Substances with Radionuclides

Several published studies have examined the effects of soil humic matter on radionuclide complexing and mobility. These studies reveal two opposing tendencies in radionuclide behavior in the soil environment. Under some conditions, certain radionuclides appear to form soluble complexes with the soil humic substances that promote radionuclide mobility in the soil-water system. Other radionuclides, or the same radionuclides under different environmental conditions, apparently can form either insoluble complexes that become bound to soil particles and thereby prevent removal of the radionuclides from the soil, or radiocolloids that precipitate and reduce solubilization.

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III. REACTION OF GLASS WITH WATER

(J. K. Bates, T. J. Gerding, P. L. McDaniel*, and D. F. Fischer)

A. Nevada Nuclear Waste Storage Investigations (NNWSI) Test Development

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 Test Site repository location. Part of the program is to develop the test procedure (T1), part is to demonstrate that the test results will provide the necessary information, and part is to perform actual testing. The scope, summary, and uses/limitations of the test have been reported previously [STEINDLER]. Current effort is to assess the results of experiments done using the T1 test procedure and actual test apparatus and to suggest modifications to the test. Additionally, parametric tests are being conducted to establish source term release from the waste form; analog type tests (T2) using tuff rock cores are in progress.

1. Test 1 (T1) Development

Six tests, using the T1 procedure and apparatus described previously [STEINDLER], have been completed. A description of the test format is given in Table III-1. The initial six-week tests (Nos. 5, 6, and 8) have been analyzed, whereas the 12-week tests have been terminated but not analyzed. A second series of six-week tests has been initiated; some of those have been terminated but not analyzed, and some are still in progress.

The procedure for stopping a test and performing analyses depends on the individual test, and on the test components. A general procedure is outlined below, and each individual test follows the steps that are appropriate. The steps followed to terminate a test and analyze the components are:

- (1) On the assigned date, without adding a new drop of water, carefully disconnect the feedthrough, remove the vessel from the oven, and immediately place it in an ice bath covering the lower 1/2" of the vessel.
- (2) When the vessel has cooled, remove the closure fitting and weigh the vessel.
- (3) Carefully, without contacting the inside vessel walls with the waste package, open the vessel and remove the lid and waste package. Note the location of condensed water and the appearance of the waste package.
- (4) Carefully, without contacting the inside vessel walls, remove the stainless steel (SS) collection planchet and/or tuff collection vessel.
- (5) Weigh the separated components when possible.

*Student research participant from Boise State University, Boise, ID.

Table III-1. NNWSI T1 Tests

Test No.	Test Components		Tuff ^c	Test Period, ^d weeks	Observations
	Vessel ^a and Fittings	Glass ^b Surface Area, cm ²			
6	45 mL	12.33	CV	6 (stopped)	Water was observed on the top and bottom of the waste package, the underside of the lid, the top of the condensate converter, the top rim of the tuff cup, and the sides and bottom of the stainless steel (SS) vessel. Parts of the sides and all of the bottom of the tuff cup were damp.
9	22 mL SS planchet		None	6 (stopped)	Water on top and bottom of the waste package and one large drop forming on the bottom. There were a few small droplets in the planchet. Most of the water had condensed around the upper 1/3 of the SS vessel. The planchet contacted the sides of the vessel when it was withdrawn.
8	45 mL SS planchet	11.87	CV	6 (sampled)	Water on the top and bottom of the waste package with some water in the planchet. Some water was present on the interior walls of the SS vessel.
	New planchet			+2 (sampled)	Similar.
	New planchet			+4 (stopped)	
7	45 mL	12.94	CV	12 (stopped)	Water on top and bottom of waste package, above and below the condensate diverter, on the sides of the vessel, and in the bottom of the vessel. The tuff was damp in spots.
10	22 mL		None	12 (stopped)	Waste package wet top and bottom with little drops of water on the top of the perfla-plate. There was no water on the lid, condensate diverter, or vessel sides; there was >1 mL in the bottom of the vessel. It was not realized that a SS planchet was present in the vessel until deionized water had been added as part of the processing procedure.
11	22 mL Tincal fluorescent dye		None	In progress	

(contd)

Table III-1. (contd)

Test No.	Test Components		Tuff ^c	Test Period, ^d weeks	Observations
	Vessel ^a and Fittings	Glass ^b Surface Area, cm ²			
12	45 mL		CV	0 (stopped)	Repeat of test No. 6.
13	22 mL		None	6 (stopped)	Repeat of test No. 9.
14	45 mL	None	CV	In progress	No waste package - J-13 contacting only a tuff vessel.
15	22 mL	None	None	In progress	J-13 being collected in a SS planchet with no tuff collection vessel.
16	45 mL	None	CV	In progress	J-13 being collected in a SS planchet with a tuff collection vessel present.

^aAll vessels were constructed of Type 303 SS and were cleaned ultrasonically in EtOH. Canisters were made of perforated Type 304 L SS. The bottom canister was welded to two supporting rods that were welded to the condensate converter. The top canister fit snugly between the supporting rods but was not welded in place. The welded assembly was cleaned in 8M HNO₃ to remove welding deposits, then rinsed with deionized water and cleaned ultrasonically in EtOH. Hole size was 1/8".

^bThe glass was SRL 165 frit with added Cs, U, and Sr. It was made in two separate batches and cast using a tapered Pt 5% Au mold. Up to three sections of glass were cut from each casting.

^cTuff was prepared by soaking for 7 hours in J-13 water. Tuff collection vessels (CV) were placed on SS spacers so they did not rest on the bottom of the vessel. Prior to starting the experiment, 0.5 mL of J-13 water was added to the bottom of each vessel.

^dTest temperature was 90°C.

- (6) Cover the bottom part of the vessel with a clean lid and weigh.
- (7) Either place the waste package aside to air dry or rinse the waste package with deionized water (DIW), collecting the rinse in a clean, tarred liquid polyethylene (LPE) container.
- (8) Rinse the SS collection planchet with DIW, collecting the rinse in a clean, tarred LPE container. Acidify the solution and submit it for inductively coupled plasma emission (ICP) analysis.
- (9) Add ~15 mL of DIW to the reaction vessel, cover, and heat overnight at 90°C. Transfer the rinse to a clean, tarred LPE container; acidify and submit it for ICP analysis.
- (10) Soak the reaction vessel in acidified DIW for 5 minutes; transfer the solution to a clean, tarred LPE container and submit it for ICP analysis.
- (11) Analyze the remaining components as appropriate.

These procedures were followed in analyzing the completed tests, and the results are given in Table III-2. Tests 6, 9, and 8 were all six-week tests, but used different test components. Test 8 used a SS planchet to collect the liquid, which was sampled periodically. After six weeks the planchet was removed, a new SS planchet was inserted into the test vessel, and the test continued. After six weeks very little liquid was present in the planchet. Most of the liquid had condensed on the sides of the test vessel. This condensation was not unexpected because calculations [STEINDLER] had indicated that, over a six-week period, temperature gradients on the order of 0.001 - 0.1°C could cause evaporation. However, we expected that salts (those elements released from the waste package) would remain in the planchet and be readily collected by rinsing the planchet. Such a release/collection scenario does not appear to have occurred in test No. 8; after the six-week period only small amounts of Ca, Mn, and Na were rinsed from the planchet. Subsequent soaks and acid rinses of the planchet produced only SS components in solution.

The test was continued, and after two additional weeks the SS planchet was removed and replaced. Analysis of the rinse, soak, and acid wash solutions from this planchet again showed only SS components.

The test was continued for an additional four weeks and terminated, but the solutions have not yet been analyzed.

Test 6 was a six-week test in which J-13 water dripped over the waste package and was collected in a tuff cup. Upon termination of this test, the waste package and tuff cup were carefully removed from the reaction vessel. Additional DIW was added to the reaction vessel, and it was allowed to soak overnight at 90°C. This solution was removed and the reaction vessel was rinsed with acid. Thus, two solution analyses were done for this test.

The results indicate that most elements present in the glass, tuff, SS, and J-13 water are detected in solution. During this test 1.4 mL of J-13

Table III-2. Tl Test Results

Test Number and Analyzed Solution	Analysis No.	Time, weeks	Solution Volume, mL	Total Amount in Solution, ^a ng																
				Al (30)	B (30)	Ba (10)	Ca (30)	Co (10)	Cr (10)	Fe (10)	Li (10)	Mg (5)	Mn (5)	Na (50)	Ni (20)	Si (500)	Sr (5)	Ti (5)	U (0.5)	Zn (5)
6																				
Vessel Soak	TF-4	6	22.62	-	1470	450	69500	300	5000	41000	12000	2500	387000	84600	27000	32000	475	-	11	840
Vessel Acid Rinse	TF-5		20.95	730	-	400	13000	350	10700	25000	900	550	150000	7750	30000	17000	100	-	25	1650
9																				
Planchet Rinse	TF-11	6	23.91	-	-	-	900	-	-	850	850	-	25000	5700	-	-	-	-	125	-
Planchet Soak	TF-13		19.92	-	-	-	-	-	320	400	-	-	16700	-	1430	-	-	-	34	-
Planchet Acid Rinse	TF-15		20.45	-	-	-	-	-	960	2650	-	-	45600	-	880	-	-	-	88	-
Vessel Soak	TF-12		20.39	1830	5300	-	15700	-	1100	8000	15900	3500	500000	90000	3900	50000	350	-	734	260
Vessel Acid Rinse	TF-14		20.11	1800	-	-	760	-	5000	9000	360	-	165000	2400	2600	20000	-	-	784	400
8																				
Planchet Rinse	TF-1	6	21.77	-	-	-	740	-	-	-	-	-	6750	15450	-	-	-	-	-	-
Planchet Soak	TF-6		19.61	-	-	-	-	-	-	475	-	-	2400	-	1250	-	-	-	-	-
Planchet Acid Rinse	TF-7		20.20	-	-	-	-	-	-	-	-	-	160	-	1270	-	-	-	-	280
Planchet Rinse	TF-10	+2	21.31	-	-	-	-	-	-	-	-	-	300	-	-	-	-	-	-	-
Planchet Soak	TF-16		20.11	-	-	-	-	-	-	300	-	-	2000	-	1150	-	-	-	-	150
Planchet Acid Rinse	TF-17		19.99	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
LPE Blank	TF-2		19.52	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
LPE Blank	TF-3		19.74	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Planchet + LPE Blank	TF-8		19.77	-	-	-	-	-	-	950	-	-	600	-	950	-	-	-	-	200
Planchet + LPE Blank	TF-9		20.06	-	-	-	-	-	-	700	-	-	-	-	-	-	-	-	-	-
DJW	TF-18		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
J-13 (1.4 mL)	J-13		1.4	-	182	-	19000	-	-	-	70	3000	-	65000	39	43000	57	-	-	-

^aThe numbers in parenthesis are the reporting limits for each element in ppb, reported as 3X the detection limit or 10X the standard deviation of the baseline noise.

water had been added to the reaction vessel, 0.5 mL at the beginning of the test and 0.9 mL during the test. (The total amount of each element contained in 1.4 mL of J-13 water is indicated in Table III-2). Additionally, some elements are released into solution from contact with tuff and the stainless steel components. There are no elements released solely from the glass, but B, Li, and U, plus Cs if it had been analyzed, can be attributed to release from the glass. The Co, Cr, Fe, Mn, and Ni in solution can be attributed mainly to release from SS components.

We note that more Al, B, Ba, Ca, Li, Na, Si, U, and Zn are detected in solution than can be accounted for by J-13 water. Of these elements, Al, B, Ca, and Na releases could have been increased as a result of interaction with tuff [OVERSBY]. However, because the tuff was pretreated by soaking it in J-13 water, it is likely that the B does not come from the tuff. Thus, the detected B, Li, U, and Zn can be attributed to release from the glass.

Test 9 was terminated after six weeks; it contained no tuff and used a SS planchet for solution collection. Thus, the planchet analysis can be compared to the results from test 8 (six weeks), whereas the vessel analysis can be compared to the results from test 6. There was considerable liquid condensation on the vessel walls, and when the planchet was removed there was some contact with this condensation. Also, the planchet was in direct contact with the bottom of the vessel throughout the test period.

Results of the planchet analysis of test 9 are similar to those of test 8 except for small amounts of Ca, Li, and U detected in the planchet rinse. This could be due to nonevaporated salts, or could be due to the incidental contact when the planchet was removed. Results of the vessel analysis of test 9 for B, Li, Sr, and Zn (glass components) are not much different from those of test 6, considering that in test 6 the solution was collected in a tuff vessel instead of a SS planchet. Measured release of U is greater in test 9 than in test 6 but, as reported elsewhere [LLNL], U is strongly sorbed onto tuff.

Although these results are from three rather complex tests with no replication, some useful generalizations can be made.

- (1) The release of B, Li, U, and Zn detected in solution (and likely Cs) can be attributed to glass degradation. When the measured releases (test 6) are normalized and compared to previously reported results [STEINDLER], there is reasonable agreement considering the differences between the two experiments.
- (2) Large amounts of Cr, Fe, Mn, and Ni were detected in tests 6 and 9. Solutions TF-4 and TF-5 had an obvious flocculent precipitate that had to be filtered prior to ICP analysis. Some degradation of SS components occurred and analysis of all test components is in progress to pinpoint the cause of the reaction.
- (3) Evaporation of solution during the test carried salts from the collection vessels (both tuff and SS) to other (cooler)

parts of the test vessel. Such aerosol phase transport of all species was unexpected but has been observed (not reported) previously [FOURNIER].

- (4) Uranium appears to interact with the tuff and does not undergo aerosol transport. Analysis of the tuff collection vessel may indicate where the uranium has sorbed.

These observations could have important ramifications in determining waste package behavior, and they must be confirmed by additional testing. However, they suggest several modifications that should be made to the test apparatus and procedure. A description of a modified test apparatus has been submitted to LLNL [BATES]. This apparatus is slightly larger to allow the waste package and test components to be more easily removed, has shelves to mount the waste package and collection vessels, and, because it is machined to design specifications, has an angled lid instead of a drip cap.

The procedure has been modified to recognize apparent aerosol transport. For periodic testing, instead of replacing just the SS planchet, the entire reaction vessel will be replaced. The waste package (and tuff if necessary) will be transferred to a new reaction vessel and the test continued. This procedure may produce altered results if aerosol transport to the waste package is significant.

2. Parametric Testing

a. Source Term Tests

Parametric tests are being done to measure the source term releases from the glass only, and from the waste package with differently "aged" canister material. Because Tl reaction vessels are difficult and expensive to fabricate, Teflon reaction vessels are being used. These are MCC-1 vessels (deep threads - Saville parts #561, #501) to which a threaded SS fitting has been added at the top as a drop feedthrough. A series of 16 tests has been in progress for eight weeks. However, it has become clear that for tests involving small amounts of water, as is the case for the Phase 2 test, extreme care must be taken to develop leak-free vessels. This matter is being addressed (it appears solvable), but it is likely that the source term tests will have to be repeated.

b. Accelerated Testing

It would be useful if some method of accelerating the Phase 2 test could be developed. Such a method is not obvious, because even accelerated test methods for leach testing have not been universally agreed on, and because the Phase 2 test poses some unique problems in that it is an intermittent-flow test that periodically reaches saturation.

(1) Types of Alteration

When glass reacts with water (vapor), basically three processes occur: hydration, devitrification, and dissolution.

- Hydration is the exchange of mobile cations in the glass with water. The resultant product is a glass matrix that remains mainly intact, but is "saturated" with water. This is generally called a gel layer, and it may or may not impede further hydration of the glass. This layer remains amorphous and its formation can be diffusion limited or affected by alteration-product formation. It will occur during both liquid and vapor contacts.
- Devitrification is the nearly isochemical in situ rearrangement of the glass network to form crystalline phases. A devitrified layer may form between the hydrated layer and the glass surface and may impede further hydration-layer formation. It occurs during vapor contact, but not necessarily during liquid contact (leach tests).
- Dissolution is the process by which the glass matrix and modifiers become solvated in solution. Whereas hydration and devitrification can occur in water vapor because they depend only on a thin film of water on the glass surface to maintain the reaction process, dissolution is generally thought to require enough water to actually remove and isolate the glass constituents from the surface. The dissolution of glass is strongly dependent on the concentration of elements in solution and the formation of alteration products on the glass surface. The surface-area-to-volume (SA/V) relationship strongly affects dissolution. Vapor phase reactions involve an SA/V of $\sim 10^6$ times greater than "normal" leach tests.

(2) Relationships Among the Alteration Processes

Acceleration of glass degradation should refer to an increased rate in all processes, because they are interrelated. It is not sufficient simply to increase the rate of release from the glass, because the release is likely to be dependent on alteration-product formation; nor is it sufficient to increase the rate of alteration-product formation without allowing for some release, because such formation is dependent on solution concentration. The initial elemental release is not dependent on alteration-product formation, because there are no alteration products. Later, however, release into solution will be controlled by such products. Only if no alteration-product formation occurred (large flow rate with no saturation) and the corrosion rate of the glass was large, would alteration-product formation be unimportant.

(3) Steps in the Test Process

The sequence of conditions during the testing can be described as follows. To simplify, assume one drop (0.075 mL) of water remains on the top of the glass. The next drop then causes some water to flow over the sides of the glass. After this happens, assume one drop clings to the bottom of the glass; therefore, both the top and bottom are in constant contact with water. The drop is replenished periodically, so flow over the

sides will consist of somewhat saturated water, and the sides will likely be covered with a very thin film of water. As the sides are washed, accumulated elements will be picked up and transported to the bottom.

The top surface of the glass will have an SA/V of $\sim 27/\text{cm}$ and, based on expected conditions, the first drop should reach saturation after ~ 2.2 days (excluding the contribution by J-13 water). A new drop would be 50% diluted, thus, after the initial drop it should take ~ 1.1 days to saturate the drop. During the remaining 2.4 days before a new drop is added, alteration-product formation presumably takes place along with devitrification and hydration. With the addition of a new drop it is not obvious what will occur; i.e., whether all alteration products that formed would be washed away or whether some would remain behind and be concentrated the next time saturation was reached.

(4) Acceleration of the Test Process

If temperature is increased, the hydration, devitrification, and alteration-product formation rates are increased, and for most elements the solubility is increased. Thus, by operating at increased temperature and pressure, some type of acceleration would be possible. By increasing pressure, i.e., maintaining saturation as temperature is increased, a new drop would not vaporize, but would react as in the 90°C case. Such testing should be possible with the present apparatus. The atmosphere could be recharged with the addition of each new drop.

Increasing SA/V by decreasing volume and keeping the drop rate constant increases release (probably because of higher pH at higher SA/V) as shown by MCC leach testing. In Phase 2 testing this would allow saturation to be reached sooner and would presumably allow for more alteration-product formation; the release would be from a saturated solution controlled by alteration-product formation. Still unknown would be the resaturation rate of the solution after the altered surface formed and whether the rate would reach a steady-state value.

Also unknown would be the limit of the volume reduction. It could be reached when the added water reacts with the surface and does not drip off, strictly vapor phase hydration. Although the same alteration products would form at a slower rate during intermittent saturation, the time until the solution becomes saturated would be shortened, accelerating the process. The actual elemental release is not accelerated because the amount of solution has been severely reduced, but if only saturated solution were being released and its composition did not vary, then all that would be necessary would be to project total release by multiplication. The composition of the saturated solution vs. time (degree of alteration) could be determined by changing the volume and keeping the drop rate the same. Alternatively, the drop rate could be reduced while keeping the drop size constant; however, evaporative complications might come into play.

Increasing the drop rate to decrease SA/V might be considered. (The drop size could not be increased due to the limited amount of water that can remain on the surface; if the drop is too big some will run over the side before it will react.) As the drop rate is increased less time

is available at saturation, but if it is increased too much then saturation will never be reached (the hydration layer is thicker and diffusion slows down the release). An increased drop rate will result in more elements being released from the glass (by dissolution), a thicker hydration layer (sodium is removed from the glass in solution), but no alteration. The solution concentration would probably vary continuously depending on the diffusion rate, and steady state (corrosion = diffusion) may never be reached.

3. 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 demonstrate how realistic T1 actually is.

Tuff cores (5" x 2-1/2" right circular cylinders) have been taken from a large piece of tuff and have been machined to a smooth finish. One core was 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 inside the apparatus was saturated to a predetermined level and the entire system was placed on end in an oven at 90°C. The inlet to the tuff allowed vapor to contact the top tuff surface, and was connected to a water reservoir held at 90°C. The outlet allowed total vapor contact with the bottom of the core, and was connected to a collection vessel. Initially, the collection vessel was at 90°C. Under these conditions, only gravity was the force to cause water flow through the tuff. After 17 days only ~0.05 mL of water had been collected, so the collection vessel was placed at room temperature. Under these conditions, >1 mL of water was collected over a four-week period. Most of it was collected during the third week of testing. After this the rate decreased to 0.05 mL/wk. When the system was disassembled after six weeks, the rock core had lost ~2 g of water. Apparently, the water was removed from the rock core but not replenished at the inlet.

Tests are now in progress in which the inlet water is supplied from a vessel of boiling water and the collection vessel is at room temperature.

4. Quality Assurance Plan

In cooperation with M. Agresta of the ANL Quality Assurance Division, a draft quality assurance test plan has been prepared. Modifications are being made to the plan so that it will meet DOE/ANL/LLNL requirements.

B. Basaltic Glass Analog Study

1. Introduction

One of the most critical needs the U.S. Nuclear Regulatory Commission (NRC) has in evaluating the technology of disposal of radioactive waste is to be assured that short-term laboratory experiments can be extrapolated confidently to repository-relevant time periods. The criteria of "reasonable assurance" has been applied to the disposal of high level waste. In its application, "reasonable assurance" requires that "... the Commission must

be satisfied that the performance assessment is sufficiently conservative and its limitations are sufficiently well understood that the actual performance of the geologic repository will be within predicted limits" (48 FR 28201). Data pertinent to the behavior of materials used in waste disposal are obtained from many sources, most of which are laboratory experiments. A common practice used to extrapolate data is to establish a data base using standard test methods and then to apply elaborate modeling procedures. However, the predictive capacity of this method is difficult to verify. Hence, the quality of reasonable assurance required by the NRC is sufficiently elusive to warrant a significant effort aimed at the connection between short-term laboratory results and long-term field applications. Part of such an effort should focus on the behavior of the waste form. This work will compare laboratory treatments and naturally occurring processes in the reaction of glasses. We anticipate that the results will provide the NRC with a sound basis for evaluating the extrapolation required to assign confidence to the models and their outputs.

The method that will be used to provide confidence in extrapolation models will be to compare the results obtained by artificially aging a natural volcanic glass with a description of the same glass whose geologic history and reactions have been well documented. A similarity between the laboratory and geologic reactions would indicate the important aging variables had been identified and incorporated into the experiments, and would provide some of the credibility that long-term predictions need.

If a comparison of the accelerated aging of natural glass and nuclear waste glass (NWG), combined with geochemical modeling and verification, indicates that a similarity in reaction processes exists for the two glasses, then the NRC will have a list of variables that must be addressed when making long-term extrapolations of NWG aging under potential repository conditions.

The specific objectives of the initial portion of this program are to:

- (1) provide a natural glass, similar in composition to proposed NWGs, that has been well characterized as to its geologic history, reaction kinetics, and reaction products and
- (2) perform accelerated laboratory testing on the selected, well-characterized unreacted natural glass to obtain reaction kinetics and identify reaction products.

Upon completion of (1) and (2), the results will be compared. Satisfactory agreement will, at a minimum, depend on the inclusion and control of all important variables in the test procedures. Continued effort will be to model the geochemical processes and to provide a relationship between NWG and natural glass performance.

2. Work to be Performed

Effort in this program is divided between ANL and the University of New Mexico. Work at the university will be directed toward obtaining detailed information on a natural basaltic glass that can be used as an NWG analog in

accelerated testing. Of paramount importance are three tasks: (1) provide ANL with samples for testing, (2) describe the geologic conditions to which the samples have been subjected, and (3) identify alteration products and reaction kinetics.

a. Natural-Glass Analog Studies

It is important that ANL begin laboratory testing before a complete description of the natural glass samples has been completed. Therefore, care must be exercised in choosing the initial glasses to be studied. The sample should be that which potentially will provide the most useful information. The ideal sample will be one for which the natural aging conditions can be duplicated in the laboratory and are relevant to a nuclear waste repository, and for which the alteration layer (products and kinetics of formation) can be characterized. The choice will be made by surveying existing samples of basaltic glass and matching the available sample descriptions with anticipated repository conditions. Samples will include nonreacted glass, and glass that has been exposed to fresh water, groundwater, and seawater under various conditions. These conditions are likely to include alteration by steam and hydrothermal and lower temperature environments. Likely candidates include Hawaiian samples, chosen because of relatively young age and the possibility that the samples have come into contact with seawater at elevated temperatures. Icelandic samples are also likely candidates because of a well-documented history and reaction with steam.

A complete description of the geologic conditions to which the natural samples have been exposed is required if those conditions are to be duplicated in the laboratory.

In documenting the aging conditions, the following variables will be noted:

- (1) the temperature history of reaction;
- (2) the phase of reactant (vapor or solution);
- (3) the initial groundwater composition and change in composition (including solid particulates in solution, pH, Eh, complexing agents);
- (4) the initial surface available for reaction, including degree of fracturing; and
- (5) the composition of all samples, including initial water content.

This documentation will be performed by a thorough onsite review of the factors listed above, and will include limited geologic mapping, a review of available groundwater chemistry data (e.g., reports and records of the Water Resources Division of the U.S. Geological Survey), and evaluation of the role of absorption or cation exchange in controlling solution compositions.

The primary effort has been to collect a suite of basaltic glass samples for the study of alteration effects and to provide material to ANL for experiments. Samples have been obtained from the collections of M. Jercinovic (University of New Mexico), Carl Allen (Rockwell Hanford Operations), and William Melson (U.S. National Museum, Smithsonian Institution). These samples, with appropriate references, are listed in Table III-3. Additional samples that will be obtained are listed in Table III-4. References to both tables are given in Table III-5. The final collection will represent basaltic glasses from the widest possible range of geologic environments: subaerial, subglacial, oceanic-emergent, and oceanic-abyssal. Preliminary efforts have been made (literature search and contact with pertinent researchers) to plan field work to collect samples in well-characterized geologic environments in New Mexico, Hawaii, and Iceland. Two preliminary samples of oceanic-abyssal basaltic glass have been provided to ANL for preliminary examination (USNM 111240 and USNM 113716). Chemical analyses of these samples are listed in Table III-6.

Table III-3. Current List of Basaltic Glass Samples at the University of New Mexico

Location	Sample	Source ^a	Reference ^b
<u>Subaerial Eruptives:</u>			
Hawaii			
Koko Crater (Oahu)	KK1	CA	1, 2, 3
Koko Head (Oahu)	KH1	CA	1, 2, 3
Hanauma Bay (Oahu)	HB2	CA	1, 2, 3
Diamond Head (Oahu)	DH1	CA	2, 3
Puukiai (1977 flow)	PK1	CA	
Mauna Ulu (1974 flow)	MU1	CA	
Mauna Ulu (1979 flow)	MU2	CA	
Mauna Iki	MI1	CA	
Iceland			
Krafla (7 Sep 77 eruption)	115380-3	USNM	
Hekla (NW vent 1970 eruption)	112041	USNM	
Hekla (SE vent 1970 eruption)	112055	USNM	
Galapagos Islands	113180	USNM	
Mariana Islands			
Pagan Island	109243-15	USNM	
California			
Warner basalt	113026	USNM	
<u>Subglacial Eruptives:</u>			
British Columbia (North-Central)			
Ash Mountain	A5A	MJ	4
Ash Mountain	A5B	MJ	4

(contd)

Table III-3. (contd)

Location	Sample	Source ^a	Reference ^b
<u>Subglacial Eruptives (contd):</u>			
British Columbia (North-Central)			
Ash Mountain	A9	MJ	4
Ash Mountain	A11A	MJ	4
Ash Mountain	A11B	MJ	4
Ash Mountain	A12	MJ	4
Ash Mountain	A19	MJ	4
Ash Mountain	A20A	MJ	4
Ash Mountain	A20B	MJ	4
Southern Tuya	AL14	MJ	4
Southern Tuya	AL15	MJ	4
Southern Tuya	AL17	MJ	4
Southern Tuya	AL18	MJ	4
Tuya Butte	TB1	MJ	4
Tuya Butte	TB2	MJ	4
Tuya Butte	TB5	MJ	4
Tuya Butte	TBW	MJ	4
<u>Oceanic - Dredge Samples:</u>			
Icelandic Shelf			
63.64°N 23.41°W, 67 m	113429-39	USNM	5
63.54°N 23.67°W, 112 m	113430-42	USNM	5
63.290°N 24.23°W, 99 m	113432-24	USNM	5
Reykjanes Ridge			
61.99°N 26.49°W 658-585 m	113521-27	USNM	5
61.99°N 26.59°W 658-585 m	113521-69	USNM	5
59.75°N 29.87°W 1116-1037 m	113531-6	USNM	5
52.67°N 34.94°W 3240 m	113427-24	USNM	5
52.67°N 34.94°W 3420 m	113427-25	USNM	5
Other Mid Atlantic Ridge			
45°31'N 29°34'W 136 km West of MRV	113487-3	USNM	5
23°01'58"N 45°02'03"W 2889-2475 m	113715	USNM	5
Kane Fracture Zone 9°36'N 40°39'W, 3340 m	111308	USNM	5, 6
Vema Fracture Zone 0.93°N 29.37°W 2304-1463 m	110728-468	USNM	5, 7

(contd)

Table III-3. (contd)

Location	Sample	Source ^a	Reference ^b
<u>Oceanic - Dredge Samples (contd):</u>			
Other Mid Atlantic Ridge			
0.91°N 30.28°W 2815-2470 m	110727-25	USNM	5, 7
21.87°S 11.84°W 3584-2999 m	115272-19	USNM	5, 6
Indian Ocean			
24°59'15"S 70°01'07"E 3522-3512 m	113716-1	USNM	5, 8
3°47.0'N 63°52.0'E 2200 m Carlsberg Ridge	115293-2	USNM	5
Southwest Pacific			
7°42'N 142°10'E 1800 m Sorol Trough	113774	USNM	5
Galapagos Area			
Galapagos Ridge 3°43.5'S 102°52.8'W 3650-3450 m	113152-17	USNM	5
2.18°S 101.96°W	113772-1	USNM	5
2.18°S 101.96°W	113434-3	USNM	5
2.42°N 95.41°W 2268 m	113434-15	USNM	5
2.44°N 95.62°W 2469 m	113156-5	USNM	5, 6
2.44°N 95.33°W 3136 m	113152-511	USNM	5
2.60°N 95.33°W 3136 m	113154-540	USNM	5
3.20°N 83.04°W 2600 m	113157-21	USNM	5
9.16°N 105.24°W 3625-3214 m	113249-705	USNM	5
	114045-3A	USNM	5
Gorda Ridge			
44.42°N 129.92°W 3084 m	111238-1	USNM	5, 6
44.42°N 129.92°W 3084 m	111239-175	USNM	5
44.67°N 130.33°W 2220-2195 m	111240-225	USNM	5, 8

^aSources: CA - C. Allen, Rockwell Hanford Operations.
 USNM - U.S. National Museum, Smithsonian Institution.
 MJ - M. Jercinovic, University of New Mexico.

^bReferences listed in Table III-5.

Table III-4. Anticipated Basaltic Glass Samples

Location	Reference ^a
<u>Subaerial Eruptives:</u>	
New Mexico	
Canjilon Hill	9
Isleta Volcano	9
Cochiti Diatreme	9
Pacific Northwest	
Depoe Bay, Cape Foulweather, and Pack Sack Lookout deposits	10
Columbia River basalt	11
Hawaii	
<u>Subglacial Eruptives:</u>	
Iceland: Various subglacial eruptives	12
<u>Oceanic-Emergent Eruptives:</u>	
Surtsey	13
Azores	14
<u>Oceanic-Abyssal Rocks:</u>	
Bermuda Rise area	
DSDP sites 417 and 418	15

^aReferences listed in Table III-5.

Table III-5. References for Tables III-3 and III-4

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(contd)

Table III-5. (contd)

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 15. Initial reports of the Deep Sea Drilling Project.
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Table III-6. Chemical Analyses of Two Samples of Oceanic-Abyssal Basaltic Glass^a

Constituent	Composition, wt %	
	USNM 111240	USNM 113716
SiO ₂	50.81 (23.75) ^b	51.52
Al ₂ O ₃	14.06 (7.44)	15.39
Fe ₂ O ₃	2.23 (1.56)	1.12
FeO	9.83 (7.64)	8.12
MgO	6.71 (4.05)	8.21
CaO	11.12 (7.95)	11.31
Na ₂ O	2.62 (1.94)	2.48
K ₂ O	0.19 (0.16)	0.09
TiO ₂	1.85 (1.11)	1.30
P ₂ O ₅	0.20 (0.09)	0.12
MnO ₂	0.22 (0.17)	0.17
Cr ₂ O ₃		
H _x O	0.02	0.18
Total	99.86	100.07

^aFrom reference 8, Table III-5.^bParenthetical entries are elemental compositions.

In addition to the basaltic glass samples, rhyolitic glasses (high silica content) have been added to the collection. These include samples from eastern Australia with estimated ages of 10^7 to 10^8 years and samples from the western U.S. that are 500, 5000, and 670,000 years of age. The samples of rhyolitic glass are of particular interest because of their great age and the experimental work that has already been completed on them (leaching and hydration rate studies).

b. Characterization Studies

A correspondence between natural and laboratory-aged samples will depend on the type and extent of alteration that is observed. The type of alteration will be described by identifying the alteration products that form on the glass surface. The detailed characterization may include the use of electron microprobe analysis (EMPA), scanning electron microscopy (SEM), X-ray diffraction (XRD), and standard petrographic techniques (transmitted and reflected light). Facilities for these techniques are available in the Department of Geology at the University of New Mexico. The major thrust of

this work will be to describe the compositional, mineralogical, and morphological changes that have occurred under natural alteration. Additional studies of surface layers may be completed using surface science techniques available at ANL. These include:

- (1) Secondary ion mass spectroscopy (SIMS),
- (2) Auger electron spectroscopy (AES),
- (3) Electron spin for chemical analysis (ESCA), and
- (4) X-ray photoelectron spectroscopy (XPS).

The extent of alteration will be derived by relating the depth to which the alteration process has penetrated the glass to the time and details of the alteration process. The layer thickness will be determined using SEM and EPMA.

Argonne will provide analytical capabilities, as required, to aid in the investigation of the altered layer, and will conduct accelerated testing of selected natural glass.

Continued effort has been directed toward the acquisition of samples of basaltic glasses from a wide range of geologic environments and the characterization of alteration products on basaltic glasses in the present collection at the University of New Mexico. The primary means of characterization includes petrographic examination (Table III-7), scanning electron microscopy (Table III-8) and electron microprobe analysis (Table III-9). The results from three principal localities are summarized below.

Table III-7. Samples from which Thin Sections Have Been Prepared and Examined Petrographically

British Columbia	Hawaii	Deep Sea Dredge Samples
A5A	MU1	USNM 113427-25
A5B	MU2	USNM 113715
A9	HB2	USNM 110728-468
Al1A		USNM 113716-1
Al1B		USNM 111240-225
Al2		
A19		
A20A		
A20B		
AL14		
AL15		
AL17		
AL18		
TB1		
TB2		
TB5		
TBW		

Table III-8. Samples Examined by Scanning Electron Microscopy

British Columbia	Deep Sea Dredge Samples
A5A	USNM 111240-225
A5B	USNM 113716-1
A11A	USNM 111239-175
A11B	
A12	
AL14	
AL15	
AL18	
TL1	
TB2	
TB5	
TBW	

Table III-9. Samples from British Columbia Examined by Electron Microprobe Analysis

A5A	AL14
A5B	AL15
A9	AL17
A11A	AL18
A11B	TB1
A12	TB2
A20A	TB5
A20B	TBW

(1) British Columbia

Samples range from slightly altered plinian ash (A11A, A11B, AL15, AL18) to highly altered surtseyan ash and hyaloclastite breccia (A12, AL14, TB2, TB5, TBW). Pillow basalt sideromelane rinds are virtually unaltered (A9, AL17). The most common and first-formed alteration product is palagonite, a vitreous, isotropic, pseudomorphic replacement product of sideromelane glass. The glasses from the British Columbia hyaloclastites are compositionally homogeneous, but the palagonites exhibit a compositional range. Tuya Butte palagonites are generally the lowest in aluminum and the highest in iron. Some Ash Mountain palagonites have completely retained aluminum during palagonitization. Palagonites with significant aluminum depletions (relative to parent glass) are usually associated with aluminosilicate authigenic cements (calcic zeolites and smectite).

(2) Hawaii

Samples MU1 and MU2 are glassy basalts from Mauna Ulu with little alteration. MU2 exhibits one sideromelane-dominated surface that is partially replaced by red-brown clay (about 20 μm thick). Sample HB2 is from a moderately closely altered deposit of sideromelane ash (most shards are <300 μm). Yellow isotropic palagonites form pseudomorphic replacement rinds on all glass surfaces. These glass surfaces exhibit dissolution pits. The average apparent rind thickness is about 15 to 20 μm . A zeolite (phillipsite?) and smectite cement are also observed.

(3) Deep Sea Dredge Samples

The pillow basalt rinds observed to date (USNM numbers 113716-1, 111240-225, 113427-25, and 113715) consist of thick (0.5 to 2 cm), clear, brown sideromelane glass. Phenocrysts are generally rare (olivine and/or plagioclase). Sample USNM 113427-25 has some generally isotropic, red-brown palagonite in some fractures. This alteration layer is 30 to 40 μm in apparent thickness. Sample USNM 113715 is highly fractured with somewhat birefringent, bright yellow, replacement-authigenic rinds in many fractures. The rind is usually <25 μm in apparent thickness and the glass surface is pitted. The outermost few micrometers of the alteration rind in USNM 113715 are distinctly birefringent. Sample USNM 110728-48 is highly altered sideromelane hyaloclastite. Some clear, brown, unaltered sideromelane can be seen. Yellow-brown rinds of banded, birefringent smectite are seen on all glass shards. The sample is cemented by green-brown formless birefringent cement. There are no remaining voids. Old shard boundaries are difficult to recognize.

In addition to the examination of samples, we have begun preparations for field work in Hawaii and Iceland. In Hawaii, the work will concentrate on the Honolulu Group volcanics that crop out at Hanauma Bay, Koko Crater, and Diamond Head in the form of basaltic hyaloclastites. Both seawater and meteoric water may be responsible for the alteration. The principal contact in Hawaii will be Richard Moore at the Hawaii Volcano Observatory. In Iceland, the initial target areas will include the major geothermal fields of southwest Iceland (e.g., Svartsengi, Eldborg, and Hveragerdi) as well as deposits of hyaloclastite and pillow basalt near Reykjanes (where possible seawater interactions have occurred) and at Esja (where deposits as old as 3 million years are exposed). We anticipate a field season in late July 1984; the principal contact will be Sveinn Jakobsson at the Icelandic Museum of Natural History.

c. Mechanistic Studies

During the aging of glass by reaction with water, three general types of alteration can be identified. These are (1) hydration, (2) devitrification, and (3) dissolution. These processes are described in Section III.A.2.b.(1). Each of these general reactions can occur to some degree in either liquid water or water vapor; they are controlled by rate limiting processes such as diffusion, alteration-product formation, solution saturation, etc. To understand the aging of glass, it is useful to identify how the reaction driving forces interact to produce the final reaction product.

This task, done in the laboratory, will strive to react glass samples, identify the reactions that occur, and incorporate, when possible, physical processes to explain how the reaction occurred. The thickness and composition of the hydration layer will be used as a measure of the reaction progress, and the kinetics of formation may give an indication of those processes involved in the reaction. The devitrified layer will be characterized according to its composition, and kinetics of the formation of this layer will be studied. The effects of dissolution will be monitored; the "dissolution" that occurs under water-vapor conditions will be considered as a method to accelerate the reaction.

Reactions in both water vapor and solution will occur in nature and will supply complementary information regarding reaction processes. The reaction conditions in vapor and solution differ, but the test analyses for both are similar. The purpose of the testing will be to develop a method of producing aged glass consistent with aging characteristics observed for natural glass. Thus, strict control of reaction variables will be exercised. Vapor phase tests will be run at selected temperatures to establish a reaction rate/temperature relationship and to identify reaction products. Process-controlling information concerning hydration, devitrification, and dissolution will be obtained using surface cross-section and profiling techniques (SEM, EMPA, and SIMS). The University of New Mexico may provide assistance in alteration-product identification.

Hydrothermal dissolution testing, using MCC-1 and MCC-2 procedures, will be initiated with the goal of studying dissolution and alteration-product formation. Attention will be given to the role of colloids in the reaction process. The kinetics of the process will be studied. The solution composition will be determined using inductively coupled plasma spectroscopy (ICP), and the relationship between the degree of saturation reached during testing and alteration-product formation will be noted. A mass balance of the components originally in the glass and groundwater will be made between the altered glass and leachate. The results of the laboratory testing will be continually compared to conditions found in natural samples, and the procedures will be modified, if possible, so that short-term accelerated testing will simulate natural aging as closely as possible.

Hydration tests and MCC-1 and MCC-2 tests are in progress. These tests use a synthetic glass based on a Hawaiian composition studied previously [EWING], chosen to be of different composition than the glasses supplied by the University of New Mexico because preliminary testing on sample USNM 113716 indicated that little alteration occurred under fairly strenuous conditions (7 days at 240°C). It is likely that the low rate of reaction was due to the low sodium content of these glasses (Na_2O ~2.5 wt %). The glass chosen for study has a higher sodium content (Na_2O ~5.5 wt %), but is still representative of a natural Hawaiian basalt.

The glass was made by mixing oxides of the glass constituents in a power mill, melting the oxides in a platinum crucible at 1500°C for two hours, quenching the melt in water, grinding and remelting the glass, and pouring the glass into a Pt 5% Au mold for sectioning. The glass composition was determined using quantitative energy dispersive spectroscopy (EDS) with sample USNM 11240 as a standard. The glass composition is given in Table III-10.

Table III-10. Composition of Synthetic Basaltic Glass^a

Element	Weight %	% Error	Oxide, wt %
Na	3.36	0.64	4.53
Mg	7.39	0.45	12.26
Al	5.75	0.20	10.86
Si	24.60	0.33	52.63
K	0.54	0.06	0.65
Ca	3.18	0.10	4.45
Ti	1.08	0.10	1.80
Mn	0.09	0.08	0.11
Fe	9.10	0.28	13.01
O ^b	45.21	-	-
Total	100.30	-	100.30

^aAnalysis by EDS, average of two determinations.

^bOxygen determined by stoichiometry.

The sequence of hydration tests is shown in Table III-11. Initial tests were done at 200 and 240°C to provide an indication of the degree of reaction that occurs. Some vessels included just the basaltic glass and some included both the basaltic glass and SRL 2% Ca glass. The SRL glass was included because its reaction rate has been determined previously and it serves as a standard.

The reacted samples are being studied with SEM and EDS; some results are discussed below. Sample H-3(200), which reacted at 200°C for 161 hours (6.71 days), has an appearance very similar to defense type glass SRL 131 or 211. The surface is covered with analcime and many smaller radially formed minerals. This mineral has been identified by XRD as gyrolite, $\text{Ca}_4(\text{Si}_4\text{O}_{15})(\text{OH})_2 \cdot 3\text{H}_2\text{O}$. A micrograph of this surface is shown in Fig. III-1.

A glass sample reacted for 4 days at 240°C [H-1(240)] had the same general appearance as that described above. However, the analcime was much smaller than the gyrolite and formed as a small center surrounded by a larger flat circular region (Fig. III-2). Figures III-3 through III-5 display higher magnification micrographs of the minerals formed on the basaltic glass surface.

MCC-1 and MCC-2 tests are being performed in deionized water at 90 and 190°C. A description of these tests is given in Table III-12. Although they do not use explicitly natural conditions, these tests will provide useful information on the hydrothermal reaction of basaltic glass.

d. Relation of the Natural-Glass Analog to Performance of Nuclear Waste Glass (NWG)

The thrust of the first three tasks--natural-glass analog, characterization, and mechanistic studies--has been to simulate in the laboratory those reactions observed to have occurred in nature. By choosing

Table III-11. Format for Hydration Tests

Sample Description	Test No.	Sample No.	Vessel No.	Temp, °C	Test Length, days	In		Out		Mass of Water, g		pH of Water Out
						Date	Time	Date	Time	In	Out	
Synthetic	S/H-1(200)	T-1	1	200	1	12 Dec 83	1620	13 Dec 83	1610	0.2644	0.2521	5
Basaltic	S/H-2(200)	T-2	2	200	2	12 Dec 83	1610	14 Dec 83	1620	0.2569	0.2425	5
Glass (H)	S/H-3(200)	T-3	3	200	6.7	12 Dec 83	1620	19 Dec 83	0910	0.2639	0.2230	9
	S/H-4(200)	T-4	4	200	3	14 Dec 83	1620	15 Dec 83	1615	0.2504	0.1908	5
SRL 2% Glass (S)	S/H-4(200)	T-5	"T1"	200	3	12 Dec 83	1620	15 Dec 83	1615	0.2645	0.2059	9
	Blank	T-13	5	200	6.7	12 Dec 83	1620	19 Dec 83	0910	0.2638	0.2350	5
	H-5(200)	T-7	1	200	4.8	22 Dec 83	1430	27 Dec 83	0820	0.2659	-	-
	S/H-6(200)	T-6	0	200	4.8	22 Dec 83	1430	27 Dec 83	0820	0.2656	-	-
	S/H-7(200)	T-8	2	200	5.8	22 Dec 83	1430	28 Dec 83	0820	0.2642	-	-
	S/H-8(200)	T-9	3	200	6.8	22 Dec 83	1430	29 Dec 83	0820	0.2660	-	-
	S/H-9(200)	T-10	6	200	6.8	22 Dec 83	1430	29 Dec 83	0820	0.2701	-	-
<u>Hydration Tests</u>												
Synthetic	H-1(240)	T-11	5	240	3.8	22 Dec 83	1430	26 Dec 83	0930	0.3555	0.3300	6
Basaltic	H-2(240)	T-13	6	240	4.8	22 Dec 83	1430	27 Dec 83	0820	0.3603	-	-
Glass (H)	H-3(240)	T-14	7	240	4.8	22 Dec 83	1430	27 Dec 83	0820	0.3527	-	-
	H-4(240)	T-15	8	240	4.8	22 Dec 83	1430	27 Dec 83	0820	0.3512	-	-
SRL 2% Glass (S)	H-5(240)	T-16	0	240	4	05 Jan 84	1345	09 Jan 84	1345	0.3518	0.3229	6
	H-6(240)	T-17	1	240	6	05 Jan 84	1345	11 Jan 84	1345	0.3556	0.3115	6
	H-7(240)	T-18	2	240	8	05 Jan 84	1345	13 Jan 84	1345	0.3689	-	-
	H-8(240)	T-14	3	240	-	05 Jan 84	1345	-	-	-	-	-
	H-9(240)	T-20	4	240	-	05 Jan 84	1345	-	-	0.3526	-	-
	H-10(240)	T-21	5	240	-	05 Jan 84	1345	-	-	0.3625	-	-
	H-11(240)	T-22	7	240	-	05 Jan 84	1345	-	-	0.3656	-	-
	H-12(240)	T-23	8	240	-	05 Jan 84	1345	-	-	0.3542	-	-

Fig. III-1. Micrograph of the Surface of a Synthetic Basaltic Glass Reacted for 161 Hours at 200°C (in saturated water vapor)

Fig. III-2. Analcime Formed on the Surface of Synthetic Basaltic Glass during Hydration in Saturated Steam for Four Days at 240°C

Fig. III-3. A High Magnification Micrograph
of Analcime

Fig. III-4. A High Magnification Micrograph
of Gyrolite

Fig. III-5. A High Magnification Micrograph of an Unidentified Alteration Product on the Glass Surface

the natural glass so that its major element composition closely mirrors that of an NWG, it should be possible to provide assurance of the overall behavior of NWG. However, because NWGs differ somewhat in composition from natural glasses and because they contain important actinide elements, it is necessary to (1) demonstrate that natural glasses and NWGs undergo the same general degradation process and (2) identify the course of actinide behavior during aging and release processes.

A fourth task, a comparison of the behavior of NWG and natural glass, will be undertaken by subjecting unreacted NWG to the same laboratory (i.e., accelerated) conditions as unreacted natural glass. Reaction rates and alteration products for the NWG will be determined. This will be done for both defense and commercial waste glass formulations. Glasses will be aged to simulate different repository conditions; the alteration phases containing the actinide elements and important radionuclides will be identified; and the release of elements into groundwater will be measured. Close attention will be given to relating those process controlling factors (diffusion, etc.) observed to occur in natural glasses to the reactions observed in NWGs.

e. Modeling of the Process--Identifying Important Variables

This task will combine the results from the previous four tasks to quantify the aging/release process into a useful predictive methodology. Using geochemical models presently available, the kinetic models determined in tasks 3 and 4 will be reconciled with the results from natural samples

Table III-12. Format for MCC-1 and MCC-2 Tests

Sample No.	Temp, °C	Test Length, days	In		Out		Mass of Sample, g		pH of Water		Mass, g				Leachant Type	Mass of Leachant, g		Surface Area, mm ²
			Date	Time	Date	Time	In	Out	In	Out	Empty Container	Grid	Container			In	Out	
													In	Out				
800	-	3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
801	-	7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
802	-	14	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
803	-	28	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
804	90	56	10 Jan 84	1415	-	-	0.1760	-	5.50	-	79.67	-	97.0334	-	DIW ^a	17.20	-	172.0
805	90	56	10 Jan 84	1415	-	-	0.1822	-	5.50	-	77.82	-	95.3335	-	DIW	17.37	-	173.7
806	90	91	10 Jan 84	1415	-	-	0.2035	-	5.50	-	104.38	-	122.4068	-	DIW	17.83	-	178.3
807	90	182	10 Jan 84	1415	-	-	0.1864	-	5.50	-	104.14	-	122.1073	-	DIW	17.80	-	178.1
808	90	182	10 Jan 84	1415	-	-	0.2089	-	5.50	-	104.33	-	121.9397	-	DIW	17.41	-	174.1
809	90	365	10 Jan 84	1415	-	-	0.1733	-	5.50	-	104.28	-	122.4377	-	DIW	17.99	-	179.9
810	90	365	10 Jan 84	1415	-	-	0.1789	-	5.50	-	104.13	-	121.5000	-	DIW	17.21	-	172.1
875	190	3	09 Jan 84	1640	12 Jan 84	1630	0.1588	0.1568	5.50	7.7	108.95	1.86	124.5215	124.4509	DIW	13.56	13.49	168.3
876	190	7	09 Jan 84	1640	-	-	0.1632	-	5.50	-	108.84	1.86	123.6911	-	DIW	12.84	-	160.4
877	-	14	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
878	190	28	09 Jan 84	1640	-	-	0.1816	-	5.50	-	97.46	1.85	113.1159	-	DIW	13.65	-	170.6

^aDeionized water.

obtained in tasks 1 and 2. The model will be used to predict the three general types of alteration, i.e., hydration, devitrification, and dissolution, and will be based on the alteration-controlling variables that have been identified. This task will provide an understanding of the dissolution of basaltic glasses in geologic environments and allow constraints to be placed on models used to predict the long-term release of radionuclides from NWG.

Already, one variable has been shown to affect the hydration rate: the degree of stress. A report describing the effect has been sent to the NRC and an article concerning it has been submitted to the journal, "Materials Letters."

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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 flowsheets 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). The two extractants are also referred to as CMP and CMPO, respectively. 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 done at Rockwell Hanford Operations (RHO) 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. To be nonTRU waste, the concentration of alpha activity must be less than 100 nCi/g of commercial waste; 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 each of two levels, 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 solvent-extraction laboratory tests of the 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 emission analysis, and an experiment performed to collect radionuclide data. The feed solution for the second test will contain radioisotopes of americium, plutonium, neptunium, and, perhaps, 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 on this project began this quarter by identifying the proper mathematical relationships to calculate material balance in the flowsheets; developing a methodology for using the new Questel Telesystemes substructure

*This effort began in mid-December 1983.

searching computer system to perform a literature survey on the two extractants under study and on their analogs; contacting potential suppliers of bulk quantities of these extractants; and making preparations for the laboratory part of the program, which is to begin in the spring of 1984.

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

(N. M. Levitz, R. A. Benson, E. L. Callis,* T. F. Cannon, G. L. Chapman,†
 P. G. Deeken, J. E. Fagan, D. G. Graczyk,* R. R. Heinrich,* J. C. Hoh,
 R. W. Kessie,† J. E. Kincinas, R. A. Leonard, F. J. Martino,
 R. E. Nelson, J. E. Parks, D. O. Pushis,† 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 March 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 fission product and uranium 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 equipment and procedures. Technical progress toward meeting these objectives is reported below, by major subtask.

A. Full-Scale Shear Facility (FSSF)

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

Effort in the FSSF was concentrated on preparing the facility for work with irradiated materials and the subsequent shearing of the full-length (~2.4-m) VR. Performance of the spare ball screw was evaluated, items necessary for dealing with irradiated fuel rods were installed, and all in-cell equipment was checked for proper operation. Minor changes were made to OPRFSS,†† the computerized procedure for operating the FSSF, to facilitate the processing of the VR.

Prior to closing and sealing of the FSSF alpha enclosure, which houses the shear itself along with some of the auxiliary equipment, the spare ~3-m long ball screw was installed in the shear assembly and characterized. (The ball screw implements feeding of the fuel rod into the shear.) The precision and accuracy of the thread on the ball screw were checked with a commercial laser-based measurement system. This work was facilitated by interfacing the laser system to the POB computer. Comparisons between displacements of the

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†Chemical Technology Division Computer Section.

‡On loan from ANL-EBR-II.

**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.

fuel-rod positioning system as measured with the commercial laser and corresponding measurements made with the POB shear feed system were used to assess ball screw performance. Analysis of the laser-test data showed the spare ball screw to be practically identical to the original screw; inaccuracies in the machining of the screw contribute only 0.032 mm to the standard deviation of measurements taken over a span of 2.286 m with the shear feed systems.

To test remote replacement of the ball screw assembly, the spare unit was removed after the performance tests, and the original unit was reinstalled using manipulators and the in-cell crane. The remote exchange of equipment was carried out successfully. A detailed procedure for replacing the ball screw was drafted based on this experience. The spare ball screw has now been cleaned, packaged, and stored in the cell.

Following the ball screw tests, the FSSF was prepared to receive and work with irradiated materials. Tools, shear dies, blades, etc., necessary for processing irradiated fuel rods, were transferred into the cell, and all equipment was checked for proper operation. Lead radiation shields were installed around remaining electronic components in the three in-cell balances that had been remoted (the bulk of the electronics removed to an out-of-cell chassis). An acrylic draft shield was installed around the 16-kg capacity fuel-rod weighing balance to eliminate balance-pan deflection due to air movement within the FSSF. BALQA, a quality assurance computer program designed by ANL, was successfully run on each balance to check for proper balance operation.

The OPRFSS program and associated FSSF software required some changing and upgrading. Modifications were made to the procedure for weighing sample cans such that cans and caps are now weighed together. The Segment Can Original Weighing Routine (SCOWR) was revised to use data available from the fuel rod information file (FRIF); the FRIF itself is prepared separately for individual rods prior to processing the rod. The Segment Can Replacement Weighing Routine (SCRWR) was written; this routine will handle the replacement of data necessitated by the replacement of damaged cans and caps. Several minor changes were made to the OPRFSS slave routines in response to needs arising from FSSF testing.

Among the other final preparatory items, the fission gas sampling system was calibrated. This system consists of a vacuum pump and piping, sample bottles, and a fuel-rod puncturing device that allows sampling of fission gas from the fuel rod plenum for analysis. The system was calibrated so the "free" volume of a given fuel rod may be determined from gas pressure measurements. The cell alpha enclosure was subsequently closed and sealed.

The VR was received at ANL and transferred into the FSSF on 1 December 1983. Unloading of the rod required only several hours, and went smoothly; however, actual processing of the rod was delayed several days until the fission-gas monitoring system for the cell exhaust stack became operational.

The rod was processed in a total working time of 30 h. The processing sequence included cutting the tang, making multiple length measurements, weighing, sampling and releasing of the excess plenum fission gas, reweighing, and shearing. The rod weighed 590.5 g and was 2.37 m long and 6.47 mm in

diameter. It was sheared into ten segments, including the plenum segment, the all-metal stub end, and eight thorium-only or binary ($^{233}\text{UO}_2\text{-ThO}_2$) segments, according to the shear plan provided by BAPL; 741 cuts, at a nominal length of 3.81 mm per cut, were made to cut up the entire rod.

Total fuel rod recovery was 99.87%, which is excellent and exceeds program specifications. The intersegment brushing operation, designed to recover loose material in the shear-die tooling, thereby reducing cross contamination, gave a total weight recovery of only 10 mg (0.002%); no Zircaloy cladding slivers were evident on the brushes. Computer-generated data summary reports that included detailed information on both the rod and the individual segments were supplied to BAPL. Overall, processing of the VR in the FSSF was considered very successful, with only minor problems being encountered with either facility hardware or procedure software.

B. Dual Dissolver System (DDS)

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

Considerable progress was made during the past quarter in preparing the DDS and related Cell M-1 facilities for EOL operational readiness. Additional modifications to OPRDDS,[†] the DDS computerized operating procedure, were incorporated as desirable refinements were recognized. Subsequently, the qualification of the DDS, followed by the destructive processing of the VR, were successfully accomplished during this quarter.

1. Equipment Installations and Testing

Larger motors for mixing the waste solution storage tank contents were received, modified for in-cell mounting and electrical service, installed, and successfully tested. The original motors had proved to have inadequate torque to continuously mix a full (370-L) tank of water.

A continuous stream of house-supplied air was provided to the vapor space of both waste solution storage tanks to enhance the evaporation of stored solution and thereby reduce the amount of liquid waste that needs to be processed into cement waste.

After DDS qualification, maintenance of and changes to some equipment became apparent as a result of experience during the qualification tests. The items are described below.

a. Demister

A modified demister and associated piping, which permits continuous drainage of condensed acid vapors back to the dissolver vessel, was installed on both dissolver systems.

*On loan from ANL-EBR-II.

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

b. Line Fitting

Changeover to an O-ring seal fitting on the solution inlet to the blend tank (BT) was made, thereby eliminating the need for wrench manipulation. This simplified remote manipulations involving connection of the dissolver solution transfer line to the BT.

c. Temperature Controllers

Upgraded BT heater temperature controllers, which facilitate narrow temperature variation such as that desired during the NBS-950a spike dissolution, were installed at both BT operating stations.

d. Air System

The supply air system for the large bank of solenoid-operated process control valves was upgraded as a precaution against impact to operations due to an inadequate air supply; pressure must be maintained at >650 kPa gage (95 psig). The DDS solenoid valve bank was disconnected from the M-Wing house-air supply, which had been erratic in maintaining pressure, and was fitted with its own gas cylinder air supply. Intravalve air leaks were eliminated through replacement of faulty solenoid valve units, so air consumption would be kept to a minimum. The system was checked as leak tight at 690 kPa gage (100 psig).

e. Cooling System

The capacity of the DDS out-of-cell condenser cooling system was increased after the DDS qualification operations. The original cooling system had been designed for use with the prototype dissolver, but proved to be inadequate when both dissolver systems were operated simultaneously at conditions typical for EOL operation, i.e., surface temperatures at ~450°C. The upgraded system uses a larger heat exchanger in the primary and secondary cooling loops. A second coolant supply pump was added to the primary loop so that each dissolver vessel now has its own supply pump, with a third pump on the secondary loop. Preliminary tests, with the dissolvers operating simultaneously at full capacity, revealed an achievable coolant flow of ~10 L/min (~2.7 gpm) at each dissolver and a typical input-output coolant differential temperature of 10-12 C. The new cooling system is more than sufficient for the EOL campaign, even when supplied with reduced building chillwater flow.

2. Computerized Operating Procedure

Operation of the two dissolver (DS1 and DS2) is carried out using OPRDDS, which is one component of POBSYS.* Minor procedure revisions, made as a result of tests performed with the DDS, continued through the quarter

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

and involved the following operations: (1) solution filter assembly replacement, (2) solution transfer line installation, (3) primary and secondary dissolution reflux rinses, and (4) off-gas handling. Procedural steps were inserted after the primary dissolution so that gas samples could be obtained separately from the primary and secondary dissolutions; previously, a combined sample was taken after the entire dissolution was complete. Several changes were also made to OPRDDS to prevent simultaneous use of the reagent charging station, which is common to both dissolver systems; two dissolver control programs (OPRDDS and CONDSP*) were combined into one that keeps track of the current state of each dissolver and prevents actuation of conflicting process-control states.

3. DDS Operation

a. Prequalification and Qualification Tests

Prior to the qualification of the DDS, tests were performed to determine the cause for the relatively high uranium carryover (defined as >0.01% of the total uranium of any dissolved segment carried into the following segment dissolution) experienced during prequalification tests. The source of the problem was the in-vessel terminus of the drain line, which had narrow drain slots. During draining of the dissolver solution after the primary dissolution, a portion of the undissolved simulated fuel (ThO_2) particles and Zircaloy fines apparently exited the dissolver, the solids being trapped by the in-line filter. On backflushing the filter, tests showed a portion of these solids became entrapped by the slots in the drain line and did not actually reenter the dissolver, so the effectiveness of the secondary dissolution was reduced. The end result was a small but significant residue of fuel material in the dissolver, which was subsequently detected in the following blank dissolution run. The drain lines were subsequently modified by use of a uniquely designed bending tool that raised the end of the drain line away from the bottom of the vessel. This provided a full-open line, and further testing showed the problem was resolved.

Other changes made to reduce uranium carryover included: (1) machining of corners and flat surfaces within the solution filter assembly to facilitate backflushing of fuel particles to the dissolver vessel; (2) addition of refluxing of the dilute nitric acid rinse solution after both primary and secondary dissolutions; and (3) operation at a higher input heater setpoint, 450 C instead of 400 C, to enhance agitation with a higher boilup rate, thereby improving dissolver performance.

These changes significantly improved DDS performance. Completion of qualification testing of the DDS early this quarter yielded analytical results that showed both dissolver systems met or exceeded requirements established by BAPL for the EOL campaign. Specifically, uranium recovery and carryover in the blank runs for DS1 and DS2 were 100.2% and 0.0041%, and 100.2% and 0.0017%, respectively.

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

b. Processing of the Validation Rod (VR)

After successful shearing of the irradiated VR in the FSSF into a total of ten segments, eight canned thorium or binary ($^{233}\text{UO}_2\text{-ThO}_2$) fuel segments and the rod plenum segment were transferred to the DDS facility using the intercell, narrow-gauge, radio-controlled transport cart ("MULE"). The tenth segment, an all-metal stub end, was left in the FSSF to be disposed of as scrap.

Prior to the start of the segment dissolutions, pertinent information needed to process a given segment was specified, e.g., reagent volumes needed for each step and the particular NBS-950a spike, blend tank, and filter identifications. This information was fed into the computer system fuel rod information file (FRIF). Also, the VR was identified as fuel rod "A", and segments were identified accordingly, A-00 (plenum) through A-08.

In planning the VR segment dissolution sequence, which is also entered into the FRIF, segments having increasing uranium content were to be dissolved in DS2, starting with the plenum segment A-00 and the low-uranium fuel segments A-01 and A-02, followed by higher uranium content segments A-07 and A-08. Segments A-03, -04, -05, and -06, with nominally similar uranium contents, were to be dissolved (in that order) in DS1. However, because of a drain line problem with DS2, as discussed below, dissolution of segment A-08 was also carried out in DS1 following completion of dissolution of segment A-06.

The entire DDS segment dissolution procedure, i.e., primary and secondary dissolutions, appropriate intermediate rinse steps, and liquid and fission gas sampling, was used for all VR segments except the plenum segment, A-00. One liter of Thorex solution and only the lower heaters were used for the primary dissolution of all segments except segment A-01; because segment A-01 was the longest of the segments, 93.46 cm (36.794 in.) compared to other segments ranging from 12.70 to 36.72 cm (5.000 to 14.455 in.), 3.0 L of solution and both lower and upper heaters were needed.

To establish the presence (or absence) of fuel in the plenum (segment A-00), a modified dissolution procedure was used: the primary dissolution, reflux, and cold rinse steps, only. The resulting solutions were collected in the blend tank, mixed, and sampled. No spiking of the blend tank solution was done, and no off-gas samples were drawn, as fission gas analysis for this segment was not requested by BAPL.

The dissolution procedure, including solution and fission gas sampling, was carried out on the nine segments in about two weeks of around-the-clock operation. In general, segment processing went quite well. Segments A-00 through A-07 were dissolved, in succession, in DS1 and DS2, as prescribed by the FRIF. However, after a defective drain line was discovered in DS2 during the dissolution of segment A-07, the final scheduled VR segment dissolution, segment A-08, was switched to DS1.

The recovered VR Zircaloy cladding hulls were found to be shiny and free of fuel. The 65-70% dissolution of hulls was similar to that obtained in earlier work.

Dissolver solution remaining in each blend tank at the end of the run was pumped to one of the two shielded waste storage tanks (WT-1 and WT-2) in the M-1 cell. Each blend tank was subsequently rinsed with about 200 g of dilute HNO_3 , which was also transferred to WT-2. The total volume of solution in WT-2, as recorded by the tank level probe, is 32 L; the volume of solution, as estimated by blend tank weight data, is about 30.7 L; the difference is an indication of the sensitivity of the tank calibration. The slow-bleed dry air purge of the tank vapor space is in use to effect evaporation and volume reduction of the waste solution.

A number of nuisance-type mechanical or procedural problems arose during processing of the VR in the DDS. A few of the more note-worthy are listed below. Regardless of inconvenience and delay, the experience gained in recognizing, reacting to, and satisfactorily resolving such encounters, which are not thought to be atypical for this type of operation, was invaluable training for EOL readiness.

(1) During the initial weighing routines of segment A-01, while using the DS2 300-g sample balance (BAL-8), some irregularities in balance performance were detected by the BALQA program; therefore, by means of a simple command issued at the computer terminal, the 300-g balance (BAL-7) at the DS1 station was made available for weighing the remainder of segment A-01, and all other weighings for both dissolver systems.

(2) Difficulties in starting the DS1 off-gas system pump when the hold tank was at a nominally high pressure required splitting the off-gas collection; the off-gases from the primary dissolution and secondary dissolution were collected separately and then sampled separately, which gave lower system pressures. Pump operation was satisfactory after OPRDDS was easily modified to accommodate this change in procedure.

(3) While heating solution from segment A-01 in the DS2 blend tank, during the NBS spike (^{238}U) dissolution, the hot plate failed. To complete the spiking operation for this run (and later for the segments A-02 and A-07), the blend tank, with solution, was moved by in-cell crane to the DS1 hot plate without interfering with the ongoing DS1 dissolution, then subsequently returned to its original position for the weighing and sampling operation.

(4) During the post-dissolution transfer of segment A-08 off-gas from the dissolver (DS1) to the hold tank, the gas pump bellows failed, resulting in the loss of some of the off-gas from the primary dissolution to the cell; this gas contains the bulk of fission gas (Kr and Xe) from the segment. The pump was subsequently isolated, and the gas that had been collected was transferred to the DS2 hold tank for collection, mixing, and sampling. A simple remote procedure was successful in bypassing the failed bellows, allowing the one remaining pump stage (and bellows) to be used for completion of the segment secondary dissolution and work on later segments.

(5) The most significant problem encountered during processing of the VR, detected during the dissolution of segment A-07, occurred in DS2 during the dissolution of segment A-02. A crack developed in the vessel

drain line at a transition weld several centimeters from its inlet, for reasons as yet undetermined. The effect of this failure was that about 450 g (~350 mL) of primary dissolution solution remained in the vessel; this residue was sequentially diluted with the primary rinse solution, secondary dissolution reagent, and secondary rinse solution, but about 350 mL of final solution from segment A-02 remained in the dissolver when the procedure for the next segment was started; i.e., when segment A-07 was loaded into the vessel.

Although a weight material balance check is built into the OPRDDS operating program for each solution transfer, the check did not work correctly for this particular step following the failure, and the shortage was not noticed. Subsequent computerized material balance checks of all other solution transfers (e.g., rinses) worked correctly, because each portion of solution added to the residual 350 mL was drained to the level of the crack in the drain line. The dissolution of A-07 proceeded without incident.

When it was subsequently discovered that the DS2 vessel drain line had actually failed during the dissolution of segment A-02, and that residual solution remained in the DS2 vessel after completion of the dissolution of segment A-07, the final solution remaining in the DS2 vessel was carefully transferred to a clean blend tank through a temporary plastic drain line. The vessel was then rinsed with refluxed and cold dilute nitric acid, which was then added to the recovered dissolver solution. The combined dissolver solution and rinses were then mixed and sampled to complete the dissolver solution recovery procedure for segment A-07. Analytical results on the recovered DS2 solution indicate little impact on A-02 and A-07 data from this line failure; these results are further addressed in Section V.E. Replacement of this vessel with one of the three spare units is planned for the next quarter.

In spite of these difficulties, this minicampaign of processing the segments from an entire irradiated fuel rod is considered successful and to be a major accomplishment. Such problems are not atypical of a facility as complex as this one, except that these failures of commercial items were certainly premature, calling for some evaluation.

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

1. Design and Fabrication Status of Equipment

Design work for the two in-cell (Cell K-1) mixing stations is still in progress, but is expected to be completed by the end of January 1984. As the component drawings are completed they are being processed into work packages and submitted to ANL Central Shops for fabrication. The design of a drum ring closure device, which facilitates remote sealing of the outer (55-gal) waste containers, is also expected to be completed in January 1984.

Components for the waste cell (Cell K-1) can-out hatch have been received. Some minor improvements were made by POB personnel to make the components workable in assembly. The complete system will be assembled and tested early next quarter. All design and fabrication work on cell components is expected to be completed next quarter.

An adequate design for the restraint of the 55-gal waste drum within its enclosure (the M-3 bin) during shipment has been completed. The design drawings have been forwarded to R-H for review and approval. Approval of this restraint-package design will complete the requirements imposed by the storage site operator to store LWBR-POB waste at its facility.

POB personnel have completed the design, fabrication, and installation of a hooded ventilation system for the manual preparation of the cement/lime slurry. This hood will reduce the dust problem normally associated with such an operation.

2. Procurement

Two prototype waste casks (which nest in the 55-gal drums) have been fabricated by a vendor, including the pouring of the shielding lead. The units are to be radiographed, and the results should be available to us for review in early January 1984. If the radiograph results are positive, the casks will be delivered to ANL for further inspection and testing; a plan and schedule have been prepared for this work. Upon approval of the units, the vendor will be authorized to complete the remaining 48 units, per contract.

3. Exemption Request

A written request was submitted to DOE-CH for an exemption from future changes to R-H specifications for burial of DOT-17C (55-gal drum) containers in lieu of compliance with current specifications. The request was granted, and formal approval has been received.

4. Experiment

An experiment was successfully completed to check the strength of the bottom seams of a DOT-17C 55-gal drum to determine whether corrective

design changes would be needed. A drum was loaded with 680 kg (1500 lb) of lead, placed on a 1.9-cm (0.75-in.) thick x 56.5-cm (22.25-in.) diameter disk of steel (simulating the actual assembly), and driven over 2660 km (1650 mi) of ANL roads in an ANL 12-m (40-ft) van during its normal use, to simulate distance and conditions of travel to the R-H burial site. No packaging-related design changes appear to be required, based on visual inspection of the drum.

D. Computer System and Data Management

(J. E. Parks, R. A. Leonard, 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 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 and/or procurement 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. Overall design and coding of the major software systems were completed during 1980-1981. Development of the computerized operating procedures (OPRFSS and OPRDDS) for the FSSF and the DDS (now completed) was initiated late in 1981. 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 was gained. Detailed descriptions of the computer hardware and software systems were presented in the previous report [STEINDLER]. Progress during this quarter on the hardware and software systems is described in this section.

1. Hardware

a. Description

No changes to the hardware system design were made during the quarter. Progress in completing the system is described below.

b. Recent Progress

Computer system hardware continues to function without any significant problems. The following hardware items have been received for eventual installation into the PDP-11/23-PLUS** minicomputer: (1) the major portion of the expansion backplane assembly necessary for the installation of other on-hand components and (2) an additional 256K of memory, for

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**Digital Equipment Corp., Maynard, MA.

a total of one megabyte of main memory, which is the capacity necessary to carry out simultaneous operation of the FSSF and the DDS during EOL operations. The memory has been installed; installation of the expansion backplane has been delayed until a needed cable is received. Several on-hand components will be installed with the backplane, including a system clock, a DZV-11* four-line interface for work station printers, and a DMV-11* high-speed network interface for interbuilding data transfer to the VAX-11/780* system. The DMV-11 interface was returned to the vendor for an exchange under warranty, but was lost in shipment after leaving ANL; the shipment is being traced. All installed systems have functioned reliably during the quarter, and performance was considered adequate for processing the VR (see Secs. V.A and V.B).

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 project 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, (4) analytical systems, and (5) report-generation programs.

(1) Operating Systems Maintenance

Operating system software (RSX-11M V4.1),[†] previously installed on both project PDP-11/23 minicomputers, has functioned well. Minor adjustments were made to those components that handle automatic printout of data files.

(2) POBSYS Testing and Modifications

The POBSYS software provides three main functions: (1) stepwise, computerized operating procedures for the FSSF and the DDS, with variable-level automation at each step; (2) continuous monitoring of all sensors associated with the FSSF and the DDS; and (3) automatic acquisition, collection, and transfer of data from the FSSF and the DDS into files on the VAX-11/780 central processing unit (CPU).

Functional testing and improvement of POBSYS have continued during its use in development and testing of procedures for the FSSF and the DDS. Several modifications were made to POBSYS during the

*Digital Equipment Corp., Maynard, MA.

[†]An updated software package provided by Digital Equipment Corp., Maynard, MA.

quarter. These changes are not specific to either the FSSF or the DDS, and include the following items: (1) the printers at individual work stations were integrated into the software system so that all alarms, data values, control operations, and operator comments are printed in a readily available log; (2) the Project Planning Program (P³) was modified to produce fuel rod information files (FRIFs) that are consistent in format with other project data files; (3) commands were added to the system to display sensor, program, and logging status information on video terminals at individual work stations; (4) the program providing calibration and quality assurance checks on balance performance (BALQA) was modified to display, for operator direction, the appropriate calibration procedure for the type of balance (PK-300 or PK-60, balances of 300-g and 60-kg capacity, respectively) being calibrated; and (5) BALQA and the balance calibration check program (BALCC) were both modified to correlate the values of weight standards used with the individual balance being tested, and to prevent a tare-reading error at the conclusion of a test from requiring a rerun of the entire test procedure.

(3) Development of OPRFSS and OPRDDS

Minor modification and debugging continued on both computerized operating systems. The systems were available for the DDS qualification test and processing of the VR, and worked fairly well. However, further changes have been identified and will be implemented and tested during the next quarter.

(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

The only portions of the software systems that still require substantial effort are the computer programs that will (1) access the data files created during automated processing of the fuel rods, (2) calculate analytical results, and (3) create summary reports. Preparation of specifications for these report-generation programs is in progress. During this quarter, a number of programs for data handling and reporting were written. A "file compression" program was written, which reads the complete data records generated during the execution of a procedure and writes a "compressed file" containing only data relevant to report generation. The latter data are also ordered for efficient access by a search routine, which was written this quarter; the search routine retrieves data from a compressed file in implementing report generation. Programs were designed and written to produce the "Fuel Rod Shearing Data Summary" and "Dissolution Data Summary" reports, and have been tested and reviewed by the Operations Group. Revisions were made to programs that produce plots of shearing and dissolution process data, and a new program was written to plot the fuel rod (axial) temperature profile. The data for the temperature plot are actually taken for each cut position during shearing by a sensor that contacts the rod as it enters the shear housing (see Fig. V-1);

binary fuel and nonfuel regions are readily discerned in the plot. Report-generation programs for the alpha and gamma spectrometry systems were completed during the previous quarter [STEINDLER].

Fig. V-1. Temperature Profiles of the Validation Rod and the Cell During Shearing, 6 December 1983, 12:12:00 to 21:52:03

(6) Summary

Hardware and software systems for the LWBR-FOB EOL campaign are near completion. A small number of hardware items remain to be installed or connected; this is expected to be completed early in 1984. The number of software modifications and additions requested during testing of the system has decreased significantly during the quarter. The POBSYS system has been used to carry out the processing of the VR, with only minor computer-related problems encountered during these operations; these problems either have been or are being corrected. Coding of the programs to generate summary reports is complete, and specifications for the programs to produce analytical reports are being written in conjunction with the reporting of results from the VR processing. We expect that the entire system will be available for use for the EOL campaign, which is scheduled to begin about April 1984.

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

The analytical nature of the LWBR-POB project at ANL and the stringent tolerances required for measurements made on the EOL fuel rods demand that extensive characterization and testing of project equipment and operations be performed in a manner that serves to reliably evaluate and demonstrate ANL measurement capabilities. The Analytical Chemistry Laboratory (ACL) has played a key role in these efforts by taking responsibility for carrying out a comprehensive error analysis for the project. Insight into the sources of errors associated with each project measurement, as provided by this error analysis, facilitates the development of test plans, guides the statistical analysis of data and interpretation of test results, 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, a very large effort in this area was expended toward the compilation, evaluation, and reporting of results from qualification tests carried out on the FSSF, DDS, and analytical procedures according to test plans that were reviewed and accepted by BAPL last quarter. Treatment of data from processing of the VR was also begun.

A tabular summary of results and conclusions from the qualification tests was prepared and submitted for evaluation by BAPL and the DOE Division of Naval Reactors (DOE-NR) at the operational readiness review meeting held at ANL on 17 November 1983. Subsequent to the meeting, the information in the summary was thoroughly reviewed by BAPL staff. By the end of November, a revised document, which incorporated additional data and modified data interpretation on some results in a manner agreeable to BAPL and ANL, was issued as part of the minutes of the meeting. On the basis of the test results presented there, BAPL and DOE-NR concurred that ANL operations had been demonstrated as being ready and qualified to receive and begin processing rods from the LWBR EOL core.

Late in the quarter, efforts in this subtask area were focused on compiling, reviewing, and reporting analytical results from the destructive assay of the VR. Results from uranium analyses, fission gas measurements, and the first of several fission product monitor determinations, ^{137}Cs , were transmitted informally to BAPL as preliminary data became available. Formal transmittal of these data will be made in early January 1984.

In general, the reduction and interpretation of data from analyses related to individual segments followed normal established procedures. However, for two fuel-bearing segments (A-02 and A-07, which were processed successively in DS2), special strategies for data treatment had to be derived as a result of a failure in the dissolver drain line. This failure occurred during the primary dissolution of segment A-02 in DS2, and resulted in an incomplete transfer of solution from the dissolver vessel to the blend tank following that step and in all subsequent operations wherein liquid transfers from the dissolver vessel to the blend tank were made for segments A-02 and

*Analytical Chemistry Laboratory (ACL), ANL.

A-07. The cumulative effect of these incomplete transfers was to leave a consequential volume (~350 mL) of solution, much diluted but still containing a significant fraction (about 1%) of the dissolved fuel material from the A-02 segment, in the dissolver vessel. Because the problem with the drain line was not recognized immediately, this solution remained in the vessel at the start of the dissolution sequence for the next segment, i.e., segment A-07. The drain-line problem was identified prior to the charging and dissolution of the next segment (segment A-08), so processing of this segment was shifted to DS1. Meanwhile, the residual solution remaining in DS2 after processing segment A-07, along with additional small batches of dissolver rinse solutions, were collected and separately analyzed.

By means of detailed records of solution weights added to and removed from the dissolver vessel in each step of the dissolution of segments A-02 and A-07, it was possible to calculate estimates of the amount of fuel from segment A-02 that was carried into the dissolution of segment A-07 and of the amount of fuel from segment A-07 that was left in the dissolver after processing this latter segment. The assumptions inherent in these calculations and the reliability of the calculations were validated using the data obtained on the residual solution recovered from DS2 after dissolution of segment A-07 was completed. Measurements of both uranium and ^{137}Cs in this solution indicated that the estimates were accurate to within, at worst, a few tenths of a percent of the initial fuel in the segment. Once the carryover from segment A-02 into A-07 was quantified and the results from the A-07 dissolution were corrected for fuel left in the residual solution in the dissolver, uranium isotopic data for segment A-07 were corrected for contamination by segment A-02 using standard isotope dilution formulas. Because the amount of carryover from segment A-02 into segment A-07 was small, about 0.1% of the uranium in A-07, we believe that the results reported for both segments will show uncertainties within allowable error limits in spite of the problems with the dissolver. A quantitative estimate of these uncertainties will be generated as part of the error analysis for this fuel rod; this analysis is expected to be completed during January 1984, for both the uranium and ^{137}Cs data.

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. Under the auspices of the LWBR-POB project, the ACL has pursued a vigorous development program aimed at establishing facilities, instrumentation, and methodology sufficient to meet the stringent error requirements and rapid pace of projected EOL work. During the past quarter, this ACL development program was completed, and work in direct support of irradiated fuel rod destructive assays was begun. Effort in each of these areas is summarized below

1. ACL Development Activity

Facilities for workup of samples for subsequent analysis by alpha/gamma spectrometry or mass spectrometry have been set up in Cell K-3

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of the M-Wing shielded cell complex and in laboratory M-150, all in the Chemistry Division (Bldg. 200). A final check of the equipment, procedures, and computer programs associated with operations in these facilities, as well as training of analysts designated for assignment to them, had been completed in the fiscal year that ended on 30 September 1983. Work associated with the installation, optimization, and characterization of the fully automated thermal ionization mass spectrometer used to measure uranium isotope ratios for isotope abundance determinations and uranium assays had also been completed at that time. Early in the current reporting period, final calibration of the automated alpha/gamma spectrometer system used in determining the fission product monitors, ^{137}Cs , ^{144}Ce , and ^{95}Zr , for the LWBR fuel rod destructive assays was validated, and development of this system was judged complete.

Qualification testing of all the analytical systems and procedures was then carried out by processing simulated EOL samples having uniform, known properties. All analysts designated for service in the EOL campaign were required to participate in the qualification tests. Acceptable performance was demonstrated for all uranium and fission product monitor analyses where specific error requirements exist, thus completing both the final phase of the development work and the staffing and training of qualified analysts for the EOL campaign.

2. Analytical Services

Analytical measurements on the VR, the first full-length irradiated fuel rod to be processed as part of the EOL campaign at ANL, were very nearly completed during this report period. This rod was treated according to normal EOL operating procedures even though it was not derived from the LWBR core sample. Because the segments from this rod are smaller than those from any of the LWBR core rods expected later in the campaign, and because more than ten years have elapsed since its irradiation, larger uncertainties for some analyses were projected to accrue when procedures intended for LWBR core rods were applied. In particular, the fission product monitors, ^{144}Ce and ^{95}Zr , and fission gases were expected to be difficult to measure with the same levels of precision and accuracy predicted for later segments. This situation was recognized and accepted by BAPL. As a result, only minimal efforts were made to adjust procedures to accommodate this special case. The determinations of ^{144}Ce were monitored closely, and an effort was made to obtain the best results achievable within the constraints of available time and sample-preparation procedures. No attempt was made to determine ^{95}Zr (64-d half-life) levels in the rod segments. Fission gases were measured as well as was practical using normal EOL procedures.

Samples analyzed in support of the destructive assay of the VR included 24 gas samples (either dissolver off-gas or rod-plenum gases) for mass spectrometric fission gas determination, 65 samples for uranium assay or uranium isotopic analysis, and 32 samples for measurement of the fission product monitors, ^{137}Cs and ^{144}Ce . Of these, only one sample required reanalysis due to unsatisfactory performance of the analytical sample as initially prepared. The bulk of this work was completed within 12 working days of the receipt of the first solution samples from the DDS.

Because of the low levels of ^{144}Ce in the dissolver solutions, samples prepared for measurement of this nuclide were gamma-counted using 60,000-s counting periods; to provide for efficient use of the gamma system, these samples were loaded into the automatic sample changer and their spectra acquired over the ANL holiday hiatus in December. This 12-day unattended operation of the system executed without any problems. In fact, no equipment malfunctions occurred in any ACL facilities during the processing of this rod.

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. Cask Unloading

The first shipment of irradiated fuel was received from BAPL this quarter in the form of the VR. Handling and unloading of the shipping cask (a 14-ton WAPD-40) proceeded smoothly even though the inner container configuration was neither exactly as had been used during training runs nor like the model for the writing of the rod unloading procedure to be used for EOL fuel shipments. The as-received WAPD-40 cask housed five individual long rod shipping (LRS) containers, one of which held the VR while the other four served as dunnage. Although on-the-spot unloading modifications were required, the WAPD-40 cask was docked and unloaded, and return shipment was made within 30 h.

No radiation was detected at the opened ends of the cask because of the geometry of the load; a solid lead plug had been inserted behind the rod, which shielded the back of the cask; also, the binary section of the rod was located at the end opposite the front opening of the cask. When surveyed the rod showed a nominally low radiation level, about 450 R/h with the detector one inch away from the rod. Radiation dosage to personnel involved in unloading operations was zero, as measured by personal dosimeters.

2. Transfer Systems

Contamination-free transfer of materials through Cell M-1 (DDS) and Cell M-3 (FSSF) alpha barriers was accomplished during processing of the VR. A number of dissolver solution sample transfers by the in-cell can-out transfer system, from the dissolver cell (Cell M-1) to the analytical cell (Cell K-3), were also made without contaminating facility equipment or corridors.

A minor malfunction of the lid-removal crank occurred at the Cell M-1 can-out hatch during processing of the VR, but it did not render the hatch unusable. Steps are being taken to repair the malfunctioning hatch and to prevent this type of problem (mainly a stainless steel threading problem) from occurring again.

3. Plenum Gas Measurement and Sampling

Calibration of the instrumentation used for measurement of plenum gas pressure and sampling of the plenum gas was performed this quarter. Also, several test plenums were fabricated and their volumes calibrated so that a determination of the calibrated volume of the gas measurement system could be made. Three calibration runs were made, and all were within 1% agreement of the three-run average.

4. Other Work

Twenty more binary ($^{233}\text{UO}_2\text{-ThO}_2$) fuel pellets were unloaded from the original 160-pellet shipment from BAPL. These pellets were used to repeat qualification runs in the DS1 and DS2 dissolver units. To date, 44 binary pellets have been unloaded satisfactorily (without spread of contamination), all using the same unloading procedures.

All waste solution containing binary fuel ($^{233}\text{UO}_2\text{-ThO}_2$) from DDS qualification runs has been collected and packaged for disposal by ANL Reclamation - Waste Management Operations.

H. Radiation Monitoring Systems

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

1. Introduction

A multipurpose, automated, stack monitor system was installed during this 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 (R. Fergus, Group Leader). The overall task was coordinated by Frank Marchetti, ANL Occupational Health and Safety Division.

The system is capable of monitoring the effluent 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 monitoring station has a gas sampling line from the cell exhaust ventilation duct(s) (see below). Each station has one or more detection elements, as appropriate. Each element measures specific gas characteristic: particulate solids are trapped on a filter disk, which is subsequently checked (counted) for activity levels; ^{85}Kr is detected by a Pilot B scintillator;* radioactive iodine is detected by use of a charcoal cartridge with a NaI gamma detector; and ^{220}Rn (thoron) is detected by use of a simulated Lucas-type cell[†] and photomultiplier tube, which are located between the filter and charcoal cartridge. The associated data acquisition system is currently programmed to provide the value of average radioactivity level for a 1-min interval, on a minute-by-minute or hourly basis. The system also

*Harshaw Chemical Co., Hinsdale, IL.

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

provides the accumulated values for krypton, thoron, and particulate solids, as requested. With this system, background data are obtained as well as effluent levels for a given operation, e.g., ^{85}Kr release during the shearing of a fuel rod segment.

Operating in parallel with the new stack monitor are the originally installed in-line Geiger-Muller (G-M) tubes, which are connected to count-rate meters and strip-chart recorders. These units require considerable manual effort to evaluate the data. A comparison of the two systems is planned.

In addition to these units, four count-rate meters were installed at M-Wing ventilation air inlets to check for radiation in the event air containing radioactive effluent being discharged from the cells is recycled back into the building. These will be provided with alarms that actuate at the POB operating stations so that appropriate action (mainly shutdown) is taken and a safe environment can be maintained. The POB operations will be regulated on the basis of the information obtained from these units and also from the stack monitor output, to ensure that ANL site release limits (e.g., regarding ^{85}Kr) are not being exceeded.

For safety reasons, each of the four cells in use has two operating exhaust systems, low and high flow. The low-flow system has one fan and one stack; the high-flow system has two fans and two stacks. One stack in each exhaust system of each cell is connected by sampling lines to the new stack monitoring system. Each line is connected to its stack near the G-M tube positions so that a direct comparison of the two systems can be made. Nominal gas flow in the low-flow exhaust system is $9.2 \text{ m}^3/\text{min}$ (325 cfm), except for Cell K-3 which has a nominal gas flow of $3.5 \text{ m}^3/\text{min}$ (125 cfm). Nominal total gas flow for the two stacks in each high-flow exhaust system (equal flow in each stack) is $37 \text{ m}^3/\text{min}$ (1300 cfm) for Cells M-1 and M-3, $25 \text{ m}^3/\text{min}$ (900 cfm) for Cell K-1, and $20 \text{ m}^3/\text{min}$ (700 cfm) for Cell K-3. However, for Cell K-3, one of the fans in the high-flow exhaust system is normally off, so that normal gas flow is only $10 \text{ m}^3/\text{min}$ (350 cfm).

The units were all essentially functional when processing of the VR was started. They were used primarily to monitor ^{85}Kr release data from three operations: (1) release of gas obtained from sampling the fuel rod plenum section, (2) Kr-85 release from the individual shear cuts (overall, 741 cuts were made in shearing the rod), and (3) ^{85}Kr release from venting the off-gas hold tanks associated with the DDS.

2. Results of Monitoring ^{85}Kr Release

a. Shear Cell (M-3)

Good agreement was obtained between gas sample data provided by the ACL and those obtained from the in-line G-M tube system, for krypton contained in the gas that was collected when the fuel rod plenum was punctured. The ACL analysis showed that the gas contained $7.0 \pm 0.5 \text{ mCi}$ of ^{85}Kr . After this analysis, the gas was released from its calibrated sample bulb directly into Cell M-3 and was exhausted through the ventilation system. The G-M tube

system then gave a value of 7.2 mCi of ^{85}Kr . On yet another sample, the new stack monitor gave a value 2.68 times lower than that of the G-M tube system. The cause of this discrepancy is under review.

b. Dissolver Cell (M-1)

Relatively good agreement was achieved between data from the G-M tube system and ACL data, based on analysis (and subsequent release to the ventilation air stream) of off-gas samples from individual segment dissolutions for the first two gas samples that had a consequential krypton content. These two samples (from segments A-03 and A-04) showed ^{85}Kr contents of 131 and 237 mCi, respectively, by ACL analyses, and 125 and 221 mCi, respectively, from G-M tube readings; the level of agreement is considered acceptable.

Later results (for other segments) were higher for the G-M tube system than for the ACL analysis. However, these G-M tube data are confounded by incomplete information on the effect of count-rate meter scale on the reading of background levels. This problem will be investigated during the next quarter, and further testing using other krypton-containing gas samples from the POB operations will be conducted. This further testing will permit calibration of the new stack monitor system.

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