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Studies of the ability of backfill to inhibit groundwater flow in a nuclear waste repository are reviewed. They involve permeability measurements, which are fundamental in determining whether the waste may be considered to remain isolated in the repository. Additional data on zeolite compositions have been obtained using new instrumentation and techniques for mineral separation. Tests using natural humic and fulvic acids taken from surface waters and added to groundwaters from wells in the Columbia River basalt show a strong correlation of americium complexation with acid concentrations in the groundwaters, but a weak correlation in the case of neptunium. A new effort to study the use of a TRUEX solvent extraction process for the Plutonium Finishing Plant waste stream is under way. The process is to remove plutonium and americium and then separate them. Destructive analyses of irradiated fuel rods continue. Work on several of the anticipated 16 or 17 rods has been accomplished.

SUMMARY

Alteration of Backfill Materials under Repository Conditions

A review is presented of work conducted for the U.S. Nuclear Regulatory Commission under Contract FIN A-2239. The experiments conducted in this project centered on measuring the permeability of backfill, because backfill may be relied upon to inhibit the flow of water in the vicinity of disposed nuclear waste. Increases in permeability of backfill as a result of exposure to steam may determine that the U.S. Nuclear Regulatory Commission cannot consider the disposed waste to remain isolated.

Trace-Element Transport

New instrumentation and techniques for mineral separation have been tested and used during this quarter, including an isodynamic magnetic separator and combined sedimentation-centrifugation techniques for separation of very fine-grained minerals. Further data on Yellowstone zeolite compositions were obtained by energy-dispersive microprobe analysis. Uranium and thorium isotopic ratios are being measured in a group of samples from the Yellowstone Y7 drill core. Major element data for Yellowstone Y7 and Y8 drill cores are summarized. Data indicate that considerable mobility of Si, Ca, Na, and K occurred during hydrothermal alteration of the rock, but that proportions of Al, Fe, and Ti remained essentially constant. In addition, loss of Mg during hydrothermal alteration is indicated. Various professional activities (e.g., conferences and publications) related to this program are enumerated for this quarter.
Another part of this program is to determine whether concentrations of humic or fulvic acid within the range of those found in natural groundwaters (1-10 mg(C)/L) produce measurable differences in sorption of americium and neptunium onto basalt compared with sorption in groundwaters containing no dissolved organic acids. To do this, natural humic and fulvic acids extracted from surface waters were added to groundwaters collected from deep wells in the Columbia River basalt of northeastern Oregon to obtain test solutions containing 1, 3, 5, 7, and 10 mg/L dissolved organic carbon (DOC). These solutions were spiked with $^{241}$Am and $^{237}$Np and allowed to react with crushed basalt for seven days. Initial results showed a strong trend of increasing complexation of americium with both humic and fulvic acids with increasing DOC concentration in the range of 1-10 mg/L. By contrast, the results of experiments with neptunium showed a very weak and erratic trend of increasing complexation with increasing DOC concentration. An interpretation regarding DOC effects in natural groundwaters is presented.

**Solvent Extraction for TRU Separations**

A new effort to study the use of a TRUEX solvent extraction process for the Plutonium Finishing Plant (PFP) waste stream began in December. The purpose of this process is to remove plutonium and americium from the PFP waste stream and then to separate them by differential stripping of the loaded organic phase.

The TRUEX process solvent is composed of a neutral, bifunctional, phosphorus-based extractant, octyl(phenyl)-N,N-diisobutylcarbamoylmethyl-phosphine oxide dissolved in a mixture of tributyl phosphate and a diluent. In earlier studies, the diluent was a normal paraffinic hydrocarbon, Conoco C12-C14, with an average carbon number of 13. The diluent of choice for this study is carbon tetrachloride, the nonflammability of which is the main consideration in its selection.

Along with flowsheet design, including mass balances of all species, we will (1) measure the extent and rate of the hydrolytic and gamma-radiolytic degradation of the PFP TRUEX solvent and study means of cleaning up the degraded solvent and (2) demonstrate parts of the flowsheet with simulated PFP wastes in a series of annular centrifugal contactors.

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

As part of a program for developing the technology of breeding with the $^{232}$Th/$^{233}$U nuclear fuel cycle, the Bettis Atomic Power Laboratory (BAPL) plans to estimate the fissionable content of the end-of-life (EOL) core in a Light Water Breeder Reactor (LWBR) that had been operated for five years. A statistical sample, comprising 500 core fuel rods, is being selected for assay by BAPL using a nondestructive delayed-neutron device. A comparison of the beginning-of-life core with the EOL core will establish the extent of breeding.

The role of ANL is to carry out destructive chemical, physical, and radiometric analyses of LWBR fuel rods, which will provide BAPL with calibration and correction factors for a production irradiated-fuel assay gauge. In this program, 16 or 17 full-length LWBR rods will be destructively analyzed after they have been assayed by BAPL. The work involves precision shearing...
of the rods into segments, dissolution of each segment, and sampling and analysis of the solution for uranium isotopes and selected fission products. Mass spectrometric isotopic dilution and alpha and gamma spectroscopy are used for these analyses. Fission gas content is also determined with gas mass spectrometry. The dissolver solution is disposed of by conversion to a cement waste form and transportation to an approved site away from ANL.

The work is being conducted fully remotely with equipment installed in manipulator-equipped cells. Pilot-scale work (phase 1) and design, development, and qualification of full-scale equipment (phase 2) are now complete. The third and final phase, the EOL campaign itself, started in August 1984 with the arrival of the first three EOL rods, and about one-fourth of the estimated year-long campaign has now been completed. A fully integrated computer system is used for process control and data acquisition, reduction and management. Dismantling of the cells and disposal of all waste is expected to require a year after completion of the campaign.

Reported upon this quarter are (1) cask unloading and fuel storage; (2) the full-scale shear facility; (3) the dual dissolver system; (4) analytical operations; and (5) support operations, i.e., computer system and data management, radiation monitoring systems for cell ventilation air, fissile material inventory, scrap and waste disposal, and facility maintenance.
I. ALTERATION OF BACKFILL MATERIALS UNDER REPOSITORY CONDITIONS
(M. G. Seitz)

A. Introduction

Reported here is a summary of studies of the permeability of backfill, which were conducted at ANL for the U.S. Nuclear Regulatory Commission (NRC) under Contract FIN A-2239. Remaining to be completed in the project are hydrothermal experiments, which have been subcontracted to the University of Michigan, Department of Geological Sciences.

High-level nuclear waste may be disposed in excavations mined deep underground. For the disposal of the waste to be satisfactory, the NRC has specified that the waste be substantially contained within the waste packages for up to 1000 years, and that release thereafter be less than 1 part in 100,000 of the inventory of each radionuclide calculated to be present at 1000 years following permanent closure [USNRC].

This program addresses the issue of backfill degradation in proposed high-level nuclear waste repositories in response to the expected thermal, hydrothermal, and radiation environments. The most likely cause of containment failure and release of radionuclides is groundwater contacting waste canisters. Hence, hydrologic properties—most importantly, permeability—of materials surrounding the waste need to be known for times up to 1000 years and more. The beneficial property of bentonite to sorb radioelements is being addressed in another related NRC project [SOUDEK].

The current U.S. Department of Energy reference design indicates that drifts, shafts, and an annulus around the waste will be backfilled with some type of earth materials. For the planned repository in basalt, a packing material, called backfill, is proposed to consist of 25% bentonite and 75% crushed basalt [ALLEN, ROCKWELL]. In the repository, the backfill will be subjected to a range of severe environmental conditions, namely, temperatures up to 300°C [ALLEN, ROCKWELL], radiation dose rates up to $10^3$ GY/h ($10^5$ rad/h), and contact with water, initially as vapor and subsequently as liquid. Wet-dry cycling may occur locally as the repository is completed or throughout the repository due to regional changes in hydrology.

The primary purpose of the work is to examine the capability of backfill to inhibit water flow around canisters of nuclear waste. Backfill may degrade in a repository environment, becoming more permeable to water flow; for example, through a loss of its swelling ability or by fracturing following hydrothermal cementation of the grains. The second objective of this project is to evaluate the changes in chemistry of backfill and groundwater. These data are used to predict the long-term physical behavior of backfill and can be used to evaluate the influence of backfill on metals corrosion and waste-form leaching.

Evidence prior to that obtained in this project was that bentonite is modified by reaction with basalt and liquid groundwater at 300°C [ALLEN, BRADLEY, KRUMHANSL, PEACOR]. However, because the clay in the bentonite retains the montmorillonite structure, the backfill is presumed to retain its desirable swelling property [ALLEN, BRADLEY, KRUMHANSL] and, hence, its impermeability.
Work in this program is to examine the permeability of backfill materials that were subjected to hydrothermal conditions including both vapor and liquid water phases. The relationships between permeability, swelling ability, and structure of the clay are made so that the long-term performance of proposed backfill materials can be assessed. The extent to which backfill is cemented is examined using the results of hydrothermal tests in open and closed systems and observations of natural systems. The degradation of backfill by radiolysis at elevated temperatures in both stagnant and flowing groundwater is assessed to determine long-term performance. Sequential alteration in a moist, then wet, environment is examined to give a realistic idea of expected long-term behavior. Changes due to wet-dry cycling are examined to determine the effect of combining these two different modes of alteration. The results of this project will be integrated with results of other projects to assist in developing a methodology that NRC can use in assessing licensing applications for the disposal of high-level waste.

B. Materials and Methods

The bentonites used in this project consist primarily of montmorillonite with sodium as the predominant exchangeable cation. They also contain various proportions of plagioclase and quartz, with small amounts of potassium feldspar, illite or mica, calcite, gypsum, and apatite. The bentonites were from four sources. Two of the bentonites, Envirogel 200 and National Standard, were obtained commercially and had been pretreated by drying, crushing, and sieving. Two other clays, SWy-1 and montmorillonite 27, were obtained as source materials through the Clay Mineral Society and the American Petroleum Institute.

Rocks used in this work were from the Pomona flow of the Saddle Mountains basalt formation and the Umtanum flow of the Grande Ronde basalt formation within the Columbia River basalt group. The Pomona basalt consists of high-magnesium (~7.0 wt % MgO) tholeiite and occurs at a depth of 250 m at the reference location of the repository [ROCKWELL]. The Umtanum basalt was core recovered from the 938.2-m depth in well DC-6. The Umtanum flow, consisting of a low-magnesium (~3.5 wt % MgO) tholeiite, is in a proposed location for the waste repository.

Water used in the experiments was reagent water (Type 1 of the American Society for Testing and Materials DL193-77 [ASTM]) or it was reagent water mixed with chemicals to represent groundwater from the Hanford site. Two solutions were used in this program. The first solution was prepared to represent the composition of the groundwater from well DC-6 in the Grande Ronde formation of the Columbia Plateau, which was sampled primarily from 200 m below the Umtanum unit [GEPHART]. The solution contained 720 mg/L dissolved solids, with sodium the major cation and chloride and sulfate the major anions. The major elements were within the range of compositions of waters obtained from the Umtanum flow tops [ROCKWELL]. This solution was used in flow experiments with radiation and as the source of water vapor in experiments of vapor alteration. The second solution was similar in composition to the first one, but was simpler, not having boron, magnesium, or silicon added to it. This second solution was used in hydrothermal experiments.
The experiments centered on measuring the permeability of backfill, because of the possible reliance on backfill to inhibit the flow of water in the vicinity of the waste package. Measurements of permeability were made before, during, and after backfill was exposed to temperature and vapor conditions expected in a waste repository.

Apparatus for the permeability measurements consisted of a pump, a forced-convection oven, and indicators to record temperature, pressure, and flow of water through backfill. Pressure differences were kept below 0.3 MPa across 7.0-cm thick samples to avoid an irreversible decrease in permeability caused at higher gradients. Absolute pressure was kept sufficiently high (up to 5.1 MPa) with a back-pressure regulator so that water remained saturated at temperatures to 260°C during the measurements. Measurements of water flow both at the inlet and outlet of the backfill were made to confirm that the apparatus did not leak. Backfill was injected with dye after permeability measurements and inspected visually to establish where water flowed through the test specimens.

Pressure vessels were used to alter backfill in the presence of water vapor, radiation, or flowing water. The vessels were metal (Type 316 stainless steel, Inconel, and Hastelloy C-276) with swaged or gland fittings having small dead volumes, or they were silica tubes. In addition, Tem-Pres standard cold-seal pressure vessels were used in some tests.

The radiation field from a 60Co gamma source used in some tests was measured to be from $5 \times 10^4$ to $1.0 \times 10^5$ rad/h at various sample positions. The 60Co source was used to irradiate backfill in stagnant and flowing groundwater streams.

C. Results

1. Permeability Measurements

The results of permeability measurements showed that backfill mixtures exhibited Darcy behavior from ambient temperature to 250°C, with values of permeability reproducible from sample to sample.

Unaltered backfill mixtures have very low permeabilities. Values of $9 \times 10^{-19}$ m$^2$ at 25°C and $1.1 \times 10^{-18}$ m$^2$ at 150°C were determined for mixtures compacted to a dry bulk density of 1.60 g/cm$^3$. In other tests, the permeability was measured to be $4.0 \times 10^{-18}$ m$^2$ at 200°C and $5.2 \times 10^{-18}$ m$^2$ at 250°C (dry bulk density = 1.65 g/cm$^3$). Reversing the flow did not change the observed permeabilities. These measurements are shown in Fig. I-1.

Materials exposed to water vapor at high temperature have much higher permeabilities, as shown in the figure. Exposure to the water vapor introduced prior to saturating the backfill with liquid caused increases in permeability by factors up to $10^5$. After saturation with liquid, permeability was nearly independent of temperature and did not change with time. Thus, alteration by water vapor is irreversible within the time scale of the experiments.

The increase in permeability was found to be due to a large decrease in the swelling capacity of the clay that occurred during the tests. This
conclusion prompted a systematic determination of the effects of water vapor on bentonite at high temperatures. In the tests, various amounts of clay and deionized water or basaltic groundwater were reacted in small pressure vessels.

Results of this work were reported by Couture [COUTURE-1984 -1985A -1985B]. The results confirmed that bentonite lost ability to swell when exposed to water vapor at temperatures greater than 150°C. The reason for the change in swelling capacity of the clay is a change in uptake of water in interlayer spaces of the montmorillonite lattice.

The change in swelling capacity is not accompanied by a major change in mineralogy, as detectable by X-ray diffraction. Both the altered and unaltered clays consist mainly of a montmorillonite clay with an X-ray diffraction peak at 1.50 Å and a basal spacing of 17 Å, as observed when they were treated with ethylene glycol. The change in swelling can be detected by X-ray diffraction if wet samples are studied. By absorbing water in hydration layers, the lattice of unaltered montmorillonite expands from a basal spacing of 10 Å in the dry state to over 100 Å in liquid water [NORRISH]; whereas, after alteration at 250°C, the basal spacing expands to no more than 19 Å.

The results of the radiolysis experiments confirmed the production of nitric acid in water saturated with nitrogen. Analyses were extended to show that oxides of nitrogen can form in air in the absence of water and can react subsequently with water to produce nitric acid. In the reducing environment of basalt, radiolysis of nitrogen would also be expected to produce ammonia.
Both nitric acid and ammonia can react with bentonite to produce a modified product. This reaction could be with 20% or more of the exchange sites of bentonite in the first 100 years, as calculated from estimates of radiation fields. It is known that the H⁺ ion exchange form of montmorillonite is unstable, with divalent cations apparently being released from the lattice [BROWN], causing collapse of the highly swollen c axis. The extent to which ammonia might react with backfill and the consequences of this reaction are not known.

2. Implications for Licensing

The rapid change in montmorillonite properties seen in this project may have important implications for the reactions of clays and other silicates in nuclear waste repositories. Current plans for a basalt repository are that it be located about 600 to 900 m below the water table in fractured rock. Therefore, the repository is expected to fill first with steam and then with liquid water [COUTURE-1984, ROCKWELL]. Data show that only a few days exposure to steam causes extensive degradation of bentonite; however, the duration of exposure may be many years [ROCKWELL]. Thus, the permeability of the backfill would be greatly increased, and the ability to swell and fill fractures would be greatly decreased.

The results of this project strongly indicate that if bentonite is exposed to moisture in a repository at temperatures of 250°C or above, it will lose a considerable fraction of its swelling ability. For backfill mixtures containing 25% bentonite or less, the permeability will increase by five orders of magnitude or more. Calculations completed in this project suggest that increases in permeability of this magnitude may have a substantial bearing on the estimate of waste package lifetime and the subsequent release of radioactivity. To the extent that degradation of swelling ability may have been incomplete in the experiments, the permeability in a repository could be even higher than in these experiments. Inasmuch as reduction of swelling capacity has been observed at 150°C, it is also possible that, in time, increases in permeability may occur as a result of alteration at temperatures of 150°C or even lower. Consequently, in some repositories, degradation of bentonite-based backfill in tunnels and drifts by alteration with heated vapor must be considered.

In the long run, a possible decrease in volume due to mineralogical transformation of the clay and an increase in volume due to alteration of basalt will probably continue to change the permeability (but not necessarily to increase it). Ion exchange with radiolysis products may also have an effect on the properties of the clay that is yet to be determined.

3. Required Information for Licensing

The critical evaluation of plans for repository design need to be continued. The evaluation can now be done by combining results of various projects. For example, the changes in permeability observed in this project can be coupled with increasingly accurate descriptions of host-rock hydrology to determine the consequences of the changes to repository integrity. Modification of groundwater by radiolysis of backfill described in this project
can be input to calculations of waste canister corrosion. The evaluation will produce a methodology that the NRC can use to assess license applications for the disposal of high-level waste.

Needed is information to make possible more accurate projections to long time periods, and to generalize behavior of waste packages in repository conditions other than those already tested. The bases for extrapolating to long times and for evaluating proposed designs will come from understanding phenomena and principles of waste package alteration.

Waste packages that include backfill may be effective in limiting the flow of water if the peak temperature is under 200°C, or if bentonite constitutes much greater than 25% of the backfill. These possible configurations may be proposed in repository design and must be examined.

The following topics need to be developed for a better understanding of waste package performance in a repository environment:

1. alteration by moisture at elevated temperatures;
2. sequential degradation in a moist, then wet, hydrothermal environment;
3. changes in physical properties caused by radiation;
4. changes due to wet-dry cycling; and
5. integration of results with results of other projects for evaluation of repository performance.

The NRC may use this better understanding of these topics to assess applications for the disposal of high-level nuclear waste.

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GEPHART

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SOUDEK

USNRC
U.S. Nuclear Regulatory Commission, Rules and Regulations, Disposal of High-Level Radioactive Wastes in Geologic Repositories; Licensing Procedures, 10 CFR 60 (June 30, 1983).
II. TRACE-ELEMENT TRANSPORT
(N. C. Sturchio, M. G. Seitz, S. Boggs, Jr.,*, and D. Livermore†)

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

1. Progress in Laboratory Work

New techniques for mineral separation and analysis have been employed this quarter. A Frantz Isodynamic Magnetic Separator (Model LI) was acquired, set up and tested, and used successfully in a number of mineral separations.

Fine-grained clay separates were made from several matrix samples from the Y7 drill core (Yellowstone National Park), following the method of Schoen and Lee [SCHOEN]. One of these (Y7 199) has been analyzed by inductively coupled plasma atomic emission spectroscopy (ICP). Other clay separates obtained by this technique will be analyzed by ICP and X-ray diffraction (XRD), and determination of oxygen isotope ratios will be made.

New zeolite analyses from Yellowstone drill core samples were acquired by an energy-dispersive electron microprobe technique, following Hollister et al. [HOLLISTER] with modifications. The results are more accurate than previous wavelength-dispersive analyses, because loss of sodium is minimized by the much lower beam current used in the energy-dispersive analyses.

Fifteen Y7 samples are now being processed for U and Th isotopic analysis by alpha spectrometry. These data will supplement other U-Th data described earlier [STEINDLER], and will allow absolute constraints to be placed on the age of the thermal activity and the rates of transport of U and Th in Y7.

2. Summary of Major Element Geochemistry of Y7 and Y8 Drill Core Samples

The data set for major element composition of the Y7 and Y8 drill core samples from Yellowstone is nearly complete. We summarize the salient features of the behavior of Si, Al, Ca, Fe, K, Mg, Na, and Ti during hydrothermal alteration of these rocks. The samples have been thoroughly characterized by Keith et al. [KEITH].

Figure II-1 is a triangular plot showing the atomic proportions of Al, Fe, and Ti in the rocks and minerals analyzed. It shows that the proportions of Al, Fe, and Ti remain essentially constant in all rock samples, indicating that, regardless of the extent of alteration, there is no significant gain or loss of Al, Fe, or Ti on the scale of this analysis.

This indication also supports the assumption that all rock samples were initially homogeneous in composition. Also shown in the figure are the compositions of unaltered hydrated glass, zeolites, and clays from Y7 and Y8.

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Because the alteration products of glass consist primarily of zeolite and clay, the relative proportions of zeolite and clay can be estimated from this diagram using the lever rule: there are roughly six parts zeolite for every part clay replacing glass in a sample where glass has been completely replaced by zeolite and clay.

Figure II-2 is a triangular plot showing the atomic proportions of Ca, Na, and K in all rocks analyzed. It is apparent from this diagram that considerable mobility of Ca, Na, and K has occurred during hydrothermal alteration. The compositions of Y8 samples are significantly different than those of Y7 vitrophyre samples (which represent the original unaltered rock). The Y8 vitrophyre and matrix samples are more Na- and Ca-rich, and Y8 tuff samples are more Ca- or K-rich, than Y7 vitrophyre. The compositions of the zeolites, clinoptilolite and mordenite, from several Y7 and Y8 vitrophyre and matrix samples are also shown in this figure and indicate that the changes in whole rock composition are closely related to the zeolite compositions. For example, Y7 clinoptilolite has a composition very similar to that of the hydrated glass it replaces; therefore, even in the most altered samples of Y7 vitrophyre and matrix, there is not very much change in bulk composition. However, clinoptilolite in Y8 vitrophyre is generally more Na- and Ca-rich than the hydrated glass it replaces, and this is reflected in the whole rock compositions of Y8 vitrophyre and matrix samples. Mordenite from Y8 tuff is considerably richer in Ca and Na than is clinoptilolite in Y8 vitrophyre. Mordenite is the only zeolite in Y8 tuff [KEITH], and some Y8 tuff samples are more Ca-rich than Y7 and Y8 vitrophyre and matrix samples. However, several Y8 tuff samples are very rich in K, rather than Ca, because of their high amount of adularia. Because there is no corresponding increase in Al in these K-rich samples, the adularia must have formed at the expense of mordenite by a reaction (involving thermal water) such as:

\[
\text{Mordenite} + 4 \text{K}^+ + 6 \text{adularia} + 24 \text{H}_2\text{O} + 12 \text{SiO}_2 + 2 \text{Na}^+ + \text{Ca}^{2+}
\]

The extent of this reaction can be estimated for a sample by its relative position on the mordenite-adularia mixing line. Such mineral-water reactions probably serve as buffer-like controls of thermal water composition.
Silicon is very mobile in geothermal systems, as evidenced by the abundance of silica deposits underground and on the surface (in discharge areas) and by the high dissolved silica content of thermal waters. Although we have not analyzed whole rock samples of Y7 and Y8 drill cores for Si, its behavior can be inferred from glass, clay, and zeolite analyses in conjunction with petrographic observations, as well as by dilution effects observed in the whole rock concentrations of immobile elements. For example, the SiO$_2$/Al$_2$O$_3$ ratio of hydrated glass in Y7 and Y8 is about 6.3; whereas, that of clinoptilolite ranges from about 5.2-6.2, that of celadonite ranges from about 3.8-5.2, and that of adularia is about 3.3. Therefore, during replacement of glass by zeolite and clay, Si is lost. The maximum loss of Si occurs in Y8 tuff, where whole rock concentrations of immobile elements (e.g., Ti) are elevated by as much as 24% with respect to unaltered samples, implying that about 30% of the Si originally contained in glass was lost during hydrothermal alteration. In contrast, whole rock Ti concentration in one sample of Y8 tuff is decreased by nearly 50% with respect to unaltered samples; this sample is thoroughly silicified and has clearly experienced silica deposition from thermal water.

Finally, by inspection of Mg/Ti ratios, the behavior of Mg on the whole rock scale can be assessed. The Mg/Ti ratios of most Y7 matrix and all Y8 vitrophyre and matrix samples are significantly lower than those of Y7 vitrophyre samples, implying loss of Mg during hydrothermal alteration. Magnesium is probably lost from both glass and pyroxene. The Y8 tuff samples exhibit variable Mg behavior; of ten samples, six have no significant change, three have substantial decreases, and one has a substantial increase in Mg/Ti ratio.

3. Meetings and Publications

Some of the results obtained in this program since its inception were presented at scientific meetings and submitted for publication this quarter. The meetings are as follows:
(1) Natural Analogues to the Conditions Around a Final Repository for High-Level Waste (Workshop on Radionuclide Migration), Lake Geneva, Wisconsin (October 1-3, 1984).

(2) Scientific Basis for Nuclear Waste Management (Materials Research Society Annual Meeting), Boston, Massachusetts (November 26-30, 1984).


Manuscripts submitted for publication are as follows:

(1) "Investigations of the Empire Creek Stock, Montana, as a Possible Analogue to a Nuclear Waste Repository," submitted to Chem. Geol.


B. Complexing of Actinide Elements with Natural Organic Molecules in Groundwater
(S. Boggs, Jr.,* D. Livermore,† and M. G. Seitz)

1. Introduction

A series of batch experiments has been conducted to study the complexing of radionuclides with organic substances in natural groundwaters. Natural humic and fulvic acids extracted from surface waters were added to groundwaters collected from deep wells in the Columbia River basalt, northeastern Oregon, to obtain test solutions containing 1, 3, 5, 7, and 10 mg/L dissolved organic carbon (DOC). These solutions were spiked with $^{241}$Am and $^{237}$Np and allowed to react with crushed basalt for seven days. The purpose of the experiments was to determine whether concentrations of humic or fulvic acid within the range of those found in natural groundwaters [41-10 mg(C)/L] produce measurable differences in sorption of americium and neptunium onto basalt compared with sorption in groundwaters containing no dissolved organic acids. Decrease in radionuclide sorption owing to addition of humic or fulvic acid is taken as an indication of complexation of the radionuclides with the humic or fulvic acid.

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Initial results of experiments with americium and some results of experiments with neptunium have been reported previously [STEINDLER]. These preliminary results showed a strong trend of increasing complexation of americium with both humic and fulvic acids with increasing DOC concentration in the range of 1-10 mg/L. By contrast, the results of experiments with neptunium showed a very weak and erratic trend of increasing complexation with increasing DOC concentration. We give additional data here on experiments with neptunium and also describe the results of experiments made to determine the effect on the initial activity of test solutions caused by filtering the solutions after spiking with a radionuclide.

2. **Batch Experiments with Neptunium**

a. **Analytical Methods**

Methods for collecting, filtering, and analyzing the groundwaters for indigenous DOC, and the analytical procedures used in the batch partitioning experiments, have been described [STEINDLER]. Pertinent data on the groundwaters are given in Table II-1. Values of distribution ratio \((R_d)\) for neptunium were calculated from the relationship

\[
R_d = \frac{\text{activity/gram of rock}}{\text{activity/milliliter of solution}}
\]

where activity on the rock (basalt) is determined by subtracting the final activity in the solution from the initial activity.

b. **Results**

Initial results of experiments with five neptunium-spiked groundwaters were reported [STEINDLER]. These results showed neptunium distribution ratios that were extremely low compared with those obtained in experiments with americium. Distribution ratios for all nine groundwaters tested are given in Table II-2.

Two observations can be drawn from the data in Table II-2. First, the distribution ratios obtained in experiments with neptunium, natural groundwaters, and basalt are extremely low, even in the experiments where no fulvic or humic acid was added to the groundwater. Secondly, although Table II-2 suggests a weak trend of decreasing sorption (increased complexation) with addition of 1-10 mg(C)/L humic or fulvic acid for most samples tested, the trend is erratic. The conclusions that we draw from these observations and by comparison of the above data with data obtained in previously reported companion experiments with americium are: (1) compared with americium, neptunium is very poorly sorbed by fresh, crushed basalt, even in groundwaters that contain no added humic or fulvic acid and (2) addition of humic or fulvic acid to natural groundwaters in concentrations of 1-10 mg(C)/L does not produce a statistically significant change in neptunium distribution ratios, suggesting that sorption of neptunium is changed only very slightly by the presence of humic and fulvic acids in amounts that might be expected in natural groundwaters.
Table II-1. Groundwaters Used in 1984 Batch Partitioning Experiments.
All samples collected from wells drilled in Columbia River Basalt, Umatilla and Morrow Counties, NE Oregon.

<table>
<thead>
<tr>
<th>Well Name</th>
<th>Location</th>
<th>Date Collected</th>
<th>Depth, ft</th>
<th>pH at 22°C</th>
<th>DOC, mg(C)/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grieb</td>
<td>1N/26E 5BAA</td>
<td>5/09/84</td>
<td>1500</td>
<td>8.00</td>
<td>0.58</td>
</tr>
<tr>
<td>Port of Morrow</td>
<td>4N/25E 1OBDC</td>
<td>5/11/84</td>
<td>685</td>
<td>8.58</td>
<td>0.85</td>
</tr>
<tr>
<td>Turner</td>
<td>1N/26E 26CCC</td>
<td>5/25/83</td>
<td>960</td>
<td>8.40</td>
<td>1.04</td>
</tr>
<tr>
<td>Davis 419</td>
<td>3N/34E 4BCC</td>
<td>5/24/83</td>
<td>1680</td>
<td>8.35</td>
<td>0.96</td>
</tr>
<tr>
<td>Petrik</td>
<td>3N/30E 30CAB</td>
<td>5/10/84</td>
<td>1086</td>
<td>7.70</td>
<td>0.59</td>
</tr>
<tr>
<td>Stanfield</td>
<td>4N/29E 32BBC</td>
<td>5/19/83</td>
<td>1161</td>
<td>8.25</td>
<td>0.94</td>
</tr>
<tr>
<td>Vey</td>
<td>1N/27E 24DDD</td>
<td>5/09/84</td>
<td>777</td>
<td>8.38</td>
<td>0.68</td>
</tr>
<tr>
<td>Branstetter</td>
<td>3N/30E 1ADC</td>
<td>5/10/84</td>
<td>925</td>
<td>7.42</td>
<td>4.10</td>
</tr>
<tr>
<td>Kinzua</td>
<td>2S/26E 21CAC1</td>
<td>5/11/84</td>
<td>850</td>
<td>8.02</td>
<td>2.51</td>
</tr>
</tbody>
</table>

*Laboratory measurement.

In analyzing the data from this series of experiments with neptunium and the previously reported results of similar experiments with americium, we have not yet been able to assess the effects of indigenous dissolved organic substances on the results. As shown in Table II-1, the indigenous DOC in these groundwaters ranges from 0.58 to 4.10 mg(C)/L. The cation and anion content of the nine groundwaters used in the experiments is now being analyzed.

3. Change in Activity of Test Solutions as a Result of Filtration

The procedure for counting the radioactivity remaining in batch partitioning experiment test solutions after reacting with basalt requires that the solutions be filtered before counting on the scintillator. There is a possibility that some activity may sorb onto the filters during this process, thereby reducing the activity in the final filtered solutions used for counting. Sorption of activity onto the filters would thus have the effect of increasing the magnitude of the calculated distribution ratio, which in turn would indicate a lower degree of complexation than actually exists.

To test the magnitude of radionuclide sorption onto the filters used in the experiments, two groundwaters spiked with americium and two spiked with neptunium were selected for testing. Water samples containing no added humic/fulvic acid and containing 10 mg(C)/L added fulvic or humic acid were tested.
Table II-2. Results of Batch Partitioning Experiments with $^{237}$Np in Natural Groundwaters from Nine Wells with Added Concentrations of Humic and Fulvic Acids\(^a\)

<table>
<thead>
<tr>
<th>Concentration of Added Acid, mg/L</th>
<th>Distribution Ratio ($R_d$), $^b$ mL/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Turner</td>
</tr>
<tr>
<td>0</td>
<td>1.6</td>
</tr>
<tr>
<td>1</td>
<td>1.2</td>
</tr>
<tr>
<td>3</td>
<td>1.7</td>
</tr>
<tr>
<td>5</td>
<td>1.2</td>
</tr>
<tr>
<td>7</td>
<td>0.6</td>
</tr>
<tr>
<td>10</td>
<td>0.8</td>
</tr>
</tbody>
</table>

|       | Turner | Kinzua | Branstetter | Petrik | Vey | Morrow | Grieb | Stanfield | Davis |
| 0     | 3.3    | 2.3    | 2.9         | 3.2    | 2.5 | 1.3    | 2.9   | 4.7       | 3.0   |
| 1     | 4.6    | 1.5    | 2.7         | 2.8    | 2.4 | 1.9    | 3.3   | 2.5       | 2.5   |
| 3     | 4.6    | 1.3    | 2.6         | 2.3    | 1.7 | 2.0    | 2.6   | 2.6       | 2.0   |
| 5     | 4.7    | 1.4    | 2.7         | 2.6    | 2.0 | 2.0    | 2.7   | 2.0       | 2.2   |
| 7     | 1.8    | 2.0    | 2.6         | 1.9    | 1.6 | 2.3    | 2.5   | 2.4       | 2.3   |
| 10    | 2.4    | 0.7    | 2.5         | 2.3    | 2.3 | 2.2    | 2.4   | 2.3       | 2.1   |

\(^a\)Distribution ratio was measured in experiments using crushed Pomona basalt (60-80 mesh) reacted with groundwaters for seven days at 22°C. Initial pH of groundwaters is shown in Table II-1; pH was not adjusted after addition of either acid.

\(^b\)Arithmetic mean of distribution ratios calculated from triplicate runs.
Because these waters had previously been filtered through a 0.45-μm filter, all organic carbon particles larger than 0.45 μm had already been removed from them. The experiment involved three steps: (1) removal of a 1-mL aliquot of each radionuclide-spiked test solution before filtering, (2) removal of an additional 1-mL aliquot of the solution after it had been filtered through a 0.45-μm Nuclepore filter, and (3) scintillation counting of each aliquot to see if the activity in the solution changed as a result of the filtration process.

The results of the experiments are given in Table II-3. These results show quite clearly that the filtering process does remove some activity from solution. In the case of americium, about 20% of the activity remained on the filters in Vey groundwater containing no added humic or fulvic acid. In Vey water containing 10 mg(C)/L fulvic or humic acid, retention was reduced to about 14 and 8%, respectively. Experiments with neptunium showed a lower percentage of retention. Nonetheless, about 11% of the neptunium activity remained on the filters in an experiment with Stanfield water containing no added humic or fulvic acid. Retention was reduced to about 2% in Stanfield water containing 10 mg(C)/L fulvic acid and to about 1% in Stanfield water containing 10 mg(C)/L humic acid.

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Groundwater</th>
<th>Organic Acid Added, mg/L</th>
<th>Activity in Solution, cpm/mL</th>
<th>Net Change after Filtering</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Humic</td>
<td>Fulvic</td>
<td>Unfiltered</td>
</tr>
<tr>
<td>Americium</td>
<td>Vey</td>
<td>-- none --</td>
<td></td>
<td>3604</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Neptunium</td>
<td>Stanfield</td>
<td>-- none --</td>
<td></td>
<td>2363</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
</tbody>
</table>

It is evident from these results that filtration of the radionuclide-bearing groundwaters through a 0.45-μm filter caused a measurable decrease in activity of the filtrate and, furthermore, that the amount of activity retained by the filters decreased when humic or fulvic acid was present in the water. There appear to be at least two explanations for the observed results. (1) Americium and neptunium are sorbed directly onto the filters as the spiked solutions pass through the filters. The presence of dissolved humic or fulvic
acid reduces sorption, presumably owing to the formation of soluble organo-
radionuclide complexes. This possibility is supported by the fact that nept-
tunium retention by the filters is lower than americium retention, which is
consistent with the generally lower tendency of neptunium to sorb to solid
surfaces. (2) Some americium and neptunium may form colloids in the ground-
waters rather than going into true solution. If these colloids exceed 0.45 μm
in size, they would be filtered out and retained as the solutions pass through
the filters. The presence of humic or fulvic acid would presumably decrease
the tendency toward colloid formation by tying up more of the radionuclides in
soluble complexes.

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III. SOLVENT EXTRACTION FOR TRU SEPARATIONS
(G. F. Vandegrift and R. A. Leonard)

A. Introduction

A new effort, funded by Rockwell Hanford Operations, was begun in December to study the use of a TRUEX solvent extraction process for the Plutonium Finishing Plant (PFP) waste stream.* The purpose of this process is to remove plutonium and americium from the PFP waste stream and then to separate them by differential stripping of the loaded organic phase. Distribution ratios measured by E. P. Horwitz and other members of the Separations Group of the ANL Chemistry Division show that the process will be very effective.

The TRUEX process solvent is composed of a neutral, bifunctional, phosphorus-based extractant, octyl(phenyl)-N,N-diisobutylcarbamoylmethyl-phosphine oxide (O\text{D}[iB]\text{CMPO}) dissolved in a mixture of tributyl phosphate (TBP) and a diluent. In earlier studies [VANDEGRIFT-1984A], the diluent was a normal paraffinic hydrocarbon (NPH), Conoco C\text{12}-C\text{14}, with an average carbon number of 13. The diluent of choice for this study is carbon tetrachloride; its nonflammability is the main consideration in choosing it over an NPH diluent [VANDEGRIFT-1984B].

Along with flowsheet design, including mass balances of all species, we will be (1) measuring the extent and rate of the hydrolytic and gamma-radiolytic degradation of the PFP TRUEX solvent (0.25M O\text{D}[iB]\text{CMPO} - 0.75M TBP-CCl\text{4}) and studying means to cleanup the degraded solvent and (2) demonstrating parts of the flowsheet with simulated PFP wastes in a series of annular centrifugal contactors.

B. Progress

Twelve new stages (3 banks of 4 stages each) of a 4-cm annular centrifugal contactor have been fabricated and are now set up in a vacuum frame (vacframe) hood for hydraulic testing of each rotor. The testing system and, later, the operating system are being set up so that the liquids will contact only stainless steel, fluorocarbon resins, high density polyethylene resins, and polypropylene resins. In addition, the operating system will be closed so that evaporative losses of carbon tetrachloride will be limited to those that occur past the splash plate at each contactor stage. Thus, it should be possible to estimate solvent (carbon tetrachloride) losses in the centrifugal contactor under typical operating conditions. A glove box is being prepared for the tests with americium and, perhaps, plutonium.

In Table III-1 are three compositions of PFP wastes that are representative of those actually generated in the plant [SCHULZ]. The first (reference) waste, PFP-REF, is typical of standard day-to-day operation and will be used for subsequent studies. The second and third compositions occur only under special conditions. The PFP-U waste occurs only when plutonium-uranium scrap is processed in the Plutonium Recovery Facility and uranium is rejected to the

---

*This program is a collaborative effort of the ANL Chemistry and Chemical Technology Divisions.
Table III-1. PFP Waste Compositions

<table>
<thead>
<tr>
<th>Constituent</th>
<th>PFP-REF</th>
<th>PFP-U</th>
<th>PFP-DBP</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₃</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>0.43</td>
<td>0.43</td>
<td>0.43</td>
</tr>
<tr>
<td>F⁻</td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.06</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.06</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>0.003</td>
<td>0.003</td>
<td>0.003</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.003</td>
<td>0.003</td>
<td>0.003</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>6 x 10⁻⁴</td>
<td>6 x 10⁻⁴</td>
<td>6 x 10⁻⁴</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>5 x 10⁻⁴</td>
<td>5 x 10⁻⁴</td>
<td>5 x 10⁻⁴</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>4 x 10⁻⁴</td>
<td>4 x 10⁻⁴</td>
<td>4 x 10⁻⁴</td>
</tr>
<tr>
<td>Cr³⁺</td>
<td>4 x 10⁻⁴</td>
<td>4 x 10⁻⁴</td>
<td>4 x 10⁻⁴</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>3 x 10⁻⁴</td>
<td>3 x 10⁻⁴</td>
<td>3 x 10⁻⁴</td>
</tr>
<tr>
<td>Be²⁺</td>
<td>7 x 10⁻⁵</td>
<td>7 x 10⁻⁵</td>
<td>7 x 10⁻⁵</td>
</tr>
<tr>
<td>Pu⁴⁺</td>
<td>3 x 10⁻⁵</td>
<td>3 x 10⁻⁵</td>
<td>3 x 10⁻⁵</td>
</tr>
<tr>
<td>Am³⁺</td>
<td>6 x 10⁻⁶</td>
<td>6 x 10⁻⁶</td>
<td>6 x 10⁻⁶</td>
</tr>
<tr>
<td>UO₂²⁺</td>
<td>3 x 10⁻⁶</td>
<td>5 x 10⁻³</td>
<td>3 x 10⁻⁶</td>
</tr>
<tr>
<td>HDBP</td>
<td>0</td>
<td>0</td>
<td>6 x 10⁻⁴</td>
</tr>
</tbody>
</table>

aData from Rockwell Hanford Operations [SCHULZ].
aqueous raffinate; it differs from PFP-REF waste only in its concentration of uranium being $5 \times 10^{-3} \text{M}$ rather than $3 \times 10^{-6} \text{M}$. The PFP-DBP waste is generated when the spent carbonate wash of 20% TBP-CCl$_4$ solvent is combined with other aqueous wastes; this waste will contain large amounts of dibutyl phosphoric acid (HDBP).

Twenty liters of synthetic PFP waste solution (which has the composition of PFP-REF as shown in Table III-1 except that it contains no uranium, americium, or plutonium) was prepared according to the list of ingredients described in Table III-2. Actinide elements will be added later from concentrated stock solutions. Five hundred milliliters of this solution was provided to E. P. Horwitz, ANL Chemistry Division, for flowsheet development studies.

Experiments are being planned and equipment is being procured for studying the hydrolytic and gamma-radiolytic degradation of the TRUEX solvent.
Table III-2. Preparation of Simulated Nonradioactive PFP Waste Solution

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Form</th>
<th>Formula Weight, g</th>
<th>Concentration</th>
<th>[NO₃⁻] Added, M</th>
<th>Other Constituent Added, M</th>
<th>Amount Added, mg/L</th>
<th>Measured Results, a mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₃</td>
<td>Concentrated Solution</td>
<td>15.6 M</td>
<td>1.5 x 10⁰ (1.41 added)</td>
<td>1.808 g/L</td>
<td>H⁺(1.41)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Be</td>
<td>Be</td>
<td>9.01</td>
<td>7 x 10⁻⁵</td>
<td>0.0126</td>
<td>-</td>
<td>H⁺(1.4x10⁻⁴)</td>
<td>6.45 x 10⁻¹</td>
</tr>
<tr>
<td>Na</td>
<td>Na₂SO₄</td>
<td>142.0</td>
<td>1.34 x 10⁻²</td>
<td>19.03</td>
<td>SO₄²⁻(6.7x10⁻³)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Na</td>
<td>NaNO₃</td>
<td>85.0</td>
<td>2.66 x 10⁻²</td>
<td>45.22</td>
<td>0.0266</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mg</td>
<td>Mg(NO₃)₂·6H₂O</td>
<td>256.41</td>
<td>6 x 10⁻²</td>
<td>307.69</td>
<td>0.12</td>
<td>-</td>
<td>1.46 x 10³</td>
</tr>
<tr>
<td>Al</td>
<td>Al(NO₃)₃·9H₂O</td>
<td>375.13</td>
<td>4.3 x 10⁻¹</td>
<td>3226</td>
<td>1.29</td>
<td>-</td>
<td>1.16 x 10⁶</td>
</tr>
<tr>
<td>K</td>
<td>KO₃₃</td>
<td>101.1</td>
<td>3 x 10⁻³</td>
<td>6.07</td>
<td>0.003</td>
<td>-</td>
<td>1.14 x 10²</td>
</tr>
<tr>
<td>Ca</td>
<td>Ca(NO₃)₂·2H₂O</td>
<td>236.16</td>
<td>6 x 10⁻³</td>
<td>283.39</td>
<td>0.12</td>
<td>-</td>
<td>2.40 x 10³</td>
</tr>
<tr>
<td>Cr</td>
<td>Cr(NO₃)₃·9H₂O</td>
<td>400.18</td>
<td>4 x 10⁻⁴</td>
<td>3.20</td>
<td>0.0012</td>
<td>-</td>
<td>2.08 x 10¹</td>
</tr>
<tr>
<td>Mn</td>
<td>MnSO₄·H₂O</td>
<td>169.02</td>
<td>3 x 10⁻³</td>
<td>10.14</td>
<td>-</td>
<td>SO₄²⁻(3x10⁻³)</td>
<td>1.65 x 10²</td>
</tr>
<tr>
<td>Fe</td>
<td>Fe(NO₃)₃·H₂O</td>
<td>404.0</td>
<td>3 x 10⁻²</td>
<td>242.46</td>
<td>0.09</td>
<td>-</td>
<td>1.69 x 10³</td>
</tr>
<tr>
<td>Ni</td>
<td>Ni(NO₃)₂·6H₂O</td>
<td>290.82</td>
<td>4 x 10⁻⁶</td>
<td>2.33</td>
<td>0.0008</td>
<td>-</td>
<td>2.35 x 10¹</td>
</tr>
<tr>
<td>Cu</td>
<td>CuSO₄·5H₂O</td>
<td>249.68</td>
<td>3 x 10⁻⁴</td>
<td>1.50</td>
<td>-</td>
<td>SO₄²⁻(6x10⁻⁴)</td>
<td>1.90 x 10¹</td>
</tr>
<tr>
<td>Zn</td>
<td>Zn(NO₃)₂·6H₂O</td>
<td>297.5</td>
<td>6 x 10⁻⁴</td>
<td>3.57</td>
<td>0.0012</td>
<td>-</td>
<td>3.92 x 10¹</td>
</tr>
<tr>
<td>Pb</td>
<td>Pb(NO₃)₂</td>
<td>331.23</td>
<td>5 x 10⁻⁴</td>
<td>3.31</td>
<td>0.001</td>
<td>-</td>
<td>1.04 x 10²</td>
</tr>
<tr>
<td>F⁻</td>
<td>Conc. HF soln</td>
<td>28.3 M</td>
<td>9 x 10⁻²</td>
<td>63.6 g/mL</td>
<td>-</td>
<td>H⁺(0.09)</td>
<td>-</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Listed above as the metal-ion salts</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CuSO₄·5H₂O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Listed above as the metal-ion salts</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MnSO₄·H₂O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Listed above as the metal-ion salts</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

a Inductively coupled plasma/atomic emission spectroscopic analyses were performed with an error of 3 to 10%.
b Estimated error is greater than 10%.
REFERENCES

SCHULZ

VANDEGRIFT-1984A

VANDEGRIFT-1984B
IV. LIGHT WATER BREEDER REACTOR PROOF-OF-BREEDING (LWBR-POB) ANALYTICAL SUPPORT PROJECT

(N. M. Levitz, R. A. Benson, F. L. Callis,* T. F. Cannon, G. L. Chapman,†
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J. E. Kincinas, J. M. Leddin,† R. A. Leonard, F. J. Martino,
H. A. Myers, R. E. Nelson, J. Osudar,** D. O. Pushis,
D. J. Raue, L. N. Ruppert, C. G. Wach, and P. Walker)

This project is part of a national effort, sponsored by the DOE Division of Naval Reactors, to develop the technology for breeding in a Light Water Breeder Reactor (LWBR), using the 232Th/233U cycle. Argonne's role is to provide physical, chemical, and radiometric data on full-length irradiated fuel rods from the LWBR, which operated at Shippingport, PA, from September 1977 to October 1982. These data are largely derived by destructive analyses and will be used by the Bettis Atomic Power Laboratory (BAPL) to calibrate and corroborate results from its production irradiated-fuel assay gauge (PIFAG). The PIFAG is a delayed-neutron device for nondestructively assaying the fissionable uranium content of fuel rods from the end-of-life (EOL) LWBR core and will allow determination of the extent of breeding. In the ANL program, 16 or 17 EOL fuel rods are to be destructively analyzed after they have been assayed by the PIFAG; the bulk of the work is being done remotely in manipulator-equipped shielded cells.

The project at ANL has three phases. In phase 1, completed in 1980, pilot-scale equipment was developed and used to process several sections of irradiated experimental fuel rods. Results of this work demonstrated ANL's operational concepts and also allowed BAPL to calibrate and validate a developmental model of the PIFAG; subsequently, the final design of the PIFAG was implemented by BAPL.

In phase 2, recently completed, full-scale shear and dissolver systems were developed. The equipment was designed, procured, and installed in manipulator-equipped shielded cells. A computer system, assembled using commercial hardware and ANL-designed software (named POBSYS), provides automatic data acquisition, reduction, and management plus equipment control and monitoring. Analytical equipment, including dedicated mass spectrometer and alpha/gamma spectrometer systems, was acquired for processing solution samples. A waste treatment facility was designed and installed to dispose of the dissolver solution as a cement waste.

Phase 3 is the EOL campaign itself, which started in August 1984 and is scheduled to continue for about one year. Its purpose is to provide BAPL with data to "fine-tune" the PIFAG during BAPL's EOL campaign. The ANL campaign will be followed by equipment dismantling and disposal and cell cleanout by the end of FY 1986 or early FY 1987.

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†Chemical Technology Division Computer Section.
‡Co-op student from Lewis University, Romeoville, IL.
**Science Applications, Inc., Schaumburg, IL.
This report period is the first full period devoted to the EOL campaign. Current operations involve the processing of power-flattening-blanket (PFB) rods, which are 1.34 cm (0.527 in.) in diameter and about 3 m (10 ft) long. The ongoing work is reported according to the normal sequence of activities: cask unloading and fuel storage, shearing, dissolution, analysis, and support (computer system and data management, radiation monitoring systems for cell ventilation air, fissile material inventory, scrap and waste disposal, and facility maintenance).

Although all fuel rods bear serial numbers, they each receive a single-letter designation, when received at ANL, for convenience in the use of the automated data handling and management system and in reporting.

A. Cask Unloading and Fuel Storage

The third and fourth shipments of EOL fuel rods were received during this reporting period. The third shipment, received in November, consisted of a reflector rod in its secondary container (R-40), both housed within another container (IN-40). The fourth shipment, received in December, consisted of three standard blanket rods, each in a secondary container (designated LLR by BAPL) and all in a WAPD-40 cask.

During unloading of the WAPD-40 cask, an unusual situation was encountered when its rear shield plug was removed. In prior shipments, no detectable radiation had been noted at this end (actually the bottom) of the cask because of the use of a 25-cm (10-in.) -long stainless steel spacer shield plug; however, this time a radiation level of 180 mR/h emanated from the open end. Inspection of the opening with a mirror showed that no spacer plug was present. A check was then made to establish whether the cask was in proper orientation, or whether the ends had been reversed. (The cask top is normally the front end, with the plenum ends of the rods forward.) The inspection showed that the spacer was absent. Unloading was resumed, and was completed without incident or unreasonable exposure to personnel. A written report of this abnormal rod-loading procedure was sent to BAPL. The three loaded LLR containers were moved individually to the storage cell.

B. Full-Scale Shear Facility (FSSF)

Effort during this quarter involved processing the last four (of six) PFB fuel rods. Processing, after initial photo documentation, consisted of several preliminary steps, i.e., tang cutting, weight and length measurements, and fission gas sampling, prior to actual shearing of the rod into specified segments; cutting plans were provided by BAPL. Following the shearing of each rod, steps were taken to minimize cross contamination with the next rod. The shear die and sample collection station were decontaminated, and the shear blade either was rotated to expose a new cutting edge or a new blade was installed; one blade is used for shearing two entire rods of the same type.

Physical examination of these rods disclosed a ring-like appearance in the Zircaloy cladding along the entire length of the fuel-bearing section at positions equivalent to pellet-pellet interfaces; therefore, some diametrical
measurements were taken of Rod D (it being representative of the batch), in addition to the other preliminary operations noted above. These measurements were made at nine different locations, starting from the top end of the rod. Two readings were taken at each location, 90° apart. Diameters in the plenum section of the rod ranged from 0.5270 to 0.5279 in. The greatest ovalness was measured at the 10- and 10.5-in. positions where the difference between readings was 0.7 mil. Measurements taken at the 20- and 30-in. positions were slightly smaller than those at the plenum section and ranged from 0.5262 to 0.5266 in. For reference, the nominal rod diameter is given as 0.527 in.

The ring-line phenomenon was next profiled to determine the depth of the rings, which are apparent only in reflected light. The measurements were taken by mounting a dial indicator in the center of a 3-in.-long V-block and passing the block over the ringed portion of the rod. The rings proved to be real depressions in the rod, ranging in depth from 1.0 to 1.5 mils; discussions with BAPL indicated that this cladding sag is not unexpected.

Photographs of the top 60 in. of Rod E were taken, at about a 2X magnification, and made into a montage, 13 ft long. The montage was sent to BAPL for evaluation. The Zircaloy cladding had a relatively blemish-free plenum area and a spotted surface in the fuel area, as did the other rods.

A summary of the shearing results is presented in Table IV-1. Recovery was above the 99.75 wt % recovery requirement in all cases. Segment boundary cuts for all fuel-bearing segments were within prescribed limits, i.e., within 1 to 2 mils of the required location. Boundary cuts for the final all-metal stub-end segments deviate considerably more, up to 25 mils, because these segments are not clamped during shearing; they are simply pushed forward into the shear by a push rod that, in turn, is clamped in the carriage jaws. Such deviation at this point in the shearing operation is tolerable.

Shearing of all the rods was characterized by modest slippage (~2 mils) of the rod in the carriage jaws for some but not all the segments, and by occasional kickback of the spring-loaded carriage jaws. Each of these actions is monitored automatically by the computer system, using sensitive displacement sensors [linear variable displacement transformers (LVDTs)] mounted on the carriage; one of the LVDTs is associated with the rod-end locator (REL). To correct for total slippage displacement, the rod is reclamped in the carriage jaws as needed, so that the prescribed cut plan is followed.

Exceptions to full-normal operations were few, but are noted to indicate the variety of situations that were encountered, yet were fully recovered from in that no pertinent information or material was lost. Thus, no impact on final results was incurred.

(1) The first try at puncturing the plenum of Rod E to get a fission gas sample had to be aborted when a leak developed at the special saddle valve; however, it was determined that the plenum itself had not been punctured, so no gas was lost. A second try was successful.

(2) A bladder in the hydraulic system accumulator (a pressure-loading device) failed while processing Rod F, but shearing was continued
Table IV-1. Shearing Results for Power-Flattening-Blanket Fuel Rods

<table>
<thead>
<tr>
<th>Rod Designation&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Shearing Time, h</th>
<th>No. of Cuts</th>
<th>Rod Recovery, wt %</th>
<th>No. of Fuel-Bearing Segments&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANL</td>
<td>BAPL</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>2502102</td>
<td>8</td>
<td>454</td>
<td>99.886</td>
</tr>
<tr>
<td>E</td>
<td>2102187</td>
<td>8</td>
<td>456</td>
<td>99.882</td>
</tr>
<tr>
<td>F</td>
<td>2400408</td>
<td>9</td>
<td>459</td>
<td>99.936&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>G</td>
<td>2300711</td>
<td>8</td>
<td>453</td>
<td>99.864</td>
</tr>
</tbody>
</table>

<sup>a</sup>Nominal length, 3 m (10 ft); nominal weight, 3.6 kg (8 lb).

<sup>b</sup>Excludes all-metal plenum and stub end segments.

<sup>c</sup>Includes recovery of the stub end of the rod during preshearing operations for the next rod; this piece was ~1 cm (3/8 in.) long and weighed 6.104 g (about 0.2 oz).

by repressurizing the accumulator (with a built-in hydraulic pump) after each segment was sheared. Normally, the bladder is filled with nitrogen to a pressure of 1200 psig, but is cycled between 1200 and 3000 psig by the pressure exerted on it by the hydraulic fluid.

(3) During a normal carriage retraction step, associated with installation of a push rod to facilitate shearing of the last 20 in. of the rod (Rod F in this case), the carriage jaws were apparently not fully free of the rod. The rod was snagged by the jaws and pulled out of the shear housing. Fortunately, no fuel was lost from the open cut end of the rod, as indicated by visual surveys, surveys with a radiation meter, and a typically high weight recovery (99.936 wt %).

Following shearing of Rod G, the shear die and sample collection station were successfully decontaminated to cell background levels. The shear die has been placed in storage, because no further shearing of PFB rods is planned. A new shear die was installed for Rod H (BAPL Serial No. 3211456), which is a reflector-type rod. Transfer of Rod H from the storage cell into the shear cell was deferred until next quarter, when work on Rod H will begin.

C. Dual Dissolver System (DDS)

During this quarter, canned segments from Rods D, E, F, and G were received at the DDS cell for processing. For each rod, the low-uranium-bearing segments were processed in dissolver system 1 (DS1), and segments having a higher uranium content were processed in dissolver system 2 (DS2).
Processing of the segments from Rods D, E, and F was completed and processing of Rod G was initiated at DS2; work on three of its eight fuel segments was completed prior to the end of the quarter. Use of the DS1 work station for remaining low-uranium Rod G segments was delayed while needed equipment repair was performed.

1. Segment Processing

In general, processing of the canned PFB segments and blank runs in each dissolver, to check residual uranium levels, upon completion of work on all segments from an entire rod progressed at a good pace in spite of a number of minor operations-related nuisances. Although none of the problems resulted in a loss of critical data, they merit reporting from an operational experience standpoint.

a. Solution Transfer

Transfer of solution from dissolution of high-burnup segments (-02 to -05 for rods B and C) between the dissolver and the blend tank became inordinately time-consuming (3 to 4 h for a several-liter batch of solution) as a result of undissolved solid buildup in the in-line filter; more specifically, these are solids collected on a screen in a narrow portion of the filter inlet. The design of the system could not be readily altered as it was important to retain these solids, particularly if it was undissolved fuel, in a region where backwashing into the dissolver would be effective, i.e., where a high backflush flow rate would be achieved. A partial solution was found in the use of a 30-s back purge of the line with air, temporarily halting solution flow. This apparently dislodged the deposited solids. With repetitive use of air, as needed, the transfer time was cut about in half for the high-burnup segments. In contrast, lower-burnup segments required only 20 to 45 min. Exceptions are plenum segments, which result in relatively large solid residues, and require as much as 3 h to effect transfer of the primary dissolver solution.

b. Uranium Dissolution in the Primary Dissolution Period

Earlier analytical results for the three most highly irradiated segments (-03, -04, -05) of PFB Rods B and C (which contained an estimated 11.5 g of uranium per segment) showed uranium dissolution in the primary dissolution cycle to be about 90 wt %; these segments (except for C-04) had been dissolved in 3.0 L of Thorex (the primary dissolution reagent consisting of 13.5M HNO₃ and 0.06M HF). Upon increasing the Thorex volume to 3.5 L for segment C-04, uranium recovery from the primary dissolution increased to 99.9 wt %. Preliminary analytical results obtained for the corresponding three segments of Rod D, also dissolved in 3.5 L of Thorex, indicate uranium recoveries from the primary dissolver solution to be >98 wt %. The remaining PFB fuel rods to be processed also had relatively high-burnup segments but reduced uranium levels (e.g., 7.0 g of uranium per segment for Rod E), so the procedure reverted to the use of the original 3.0-L Thorex volume; anticipated good dissolution was achieved while a bit less liquid waste was produced. Maximizing of uranium dissolution in the primary dissolution period is desirable and, overall, should ease the problem of uranium cleanup and minimize the chance of cross contamination between segments and rods.
c. **Dissolver Flange Leakage**

During the processing of Rod D, the occurrence of four separate instances of dissolver pressure loss as a result of leakage at the top flange where a Teflon gasket is used led to modification of the standard bolting procedure. The air pressure to the impact wrench used to tighten the flange bolts was raised from 40 to 50 psig. In addition, the operator is now prompted, by a message displayed at the operating terminal, to retighten the flange (to reseat the gasket) during warmup when the dissolver skin temperature reaches 150°C. (During dissolution, nominal skin temperature is \( \sim 450^\circ\text{C} \).) This final tightening should help take up any slack created by relaxation of the Teflon-lined gasket as it warms up. This technique was used successfully while checking for leakage during the dissolution of D-06. No other vessel leaks have been experienced since this new procedure has been incorporated into the operating procedure.

d. **Failure of the Dissolver Pressure Control Valves**

Acute problems with the individual pressure control valves on both DS1 and DS2 were experienced this quarter. At DS1, one hour into the 4-h primary dissolution of F-06, pressure readings (a drop in dissolver pressure and a corresponding increase in hold-tank pressure) showed direct evidence of some leakage through the control valve. A temporary fix was achieved by increasing the control valve dome pressure from the normal 125 to about 133 psig and occasionally repressuring the dissolver with air to the normal pressure of 120 psig. This technique allowed both the primary dissolution and the 3-h secondary dissolution to be completed. The valve was replaced with a new one, and the old valve will be decontaminated and examined as time permits.

At DS2, during the last hour of the primary dissolution of F-03, the pressure control valve failed and allowed rapid venting of the overhead gas (including fission products) to the hold tank, in contrast to the slower release of gas referred to above. The rapid depressurization may have resulted in carryover of dissolver solution to the off-gas system. After this incident, the gas in the off-gas tank was sampled. Draining of the hold tank showed no liquid present. The control valve was removed for decontamination and examination, and the bulk solution was allowed to remain in the dissolver. There was caked material on the Teflon diaphragm, which apparently disrupted valve operation, i.e., prevented full seating of the diaphragm. After cleanup, reassembly, and bench testing of the control valve, the valve was reinstalled.

To ensure the recovery of any dissolver solution that may have entered the vent line and demister when the pressure control valve failed, the line was backflushed with dilute acid and the solution was returned to the dissolver. (The demister is piped so that it self-drains to the dissolver; thus, it did not require flushing.) Radiation readings along the entire length of the line before and after the flush, and at the demister and hold tank, were near background, indicating little if any dissolver solution had been lost.
The primary dissolution was restarted ~40 hours after the loss of pressure occurred. The dissolution of this segment was continued to completion, although a slight but tolerable leak at the pressure control valve did exist during the completion of the primary dissolution and throughout the secondary dissolution. During these dissolution periods following the malfunction, the dissolver vessel was easily maintained at normal operating pressure (120 psig) by means of intermittent, manual additions of air; the computer was bypassed during these additions, but use was made of the computerized process and instrumentation graphics available at the operation station video terminal to monitor the operations.

2. Equipment Maintenance

A good deal of effort was spent repairing or replacing DDS equipment during the last part of the quarter. This was not unexpected considering the continuous use of each dissolver system. All systems were in effective working order by the end of the quarter.

A facility, including required tools and apparatus, was set up in the manipulator-equipped storage area of the DDS cell to permit remote in-cell disassembly, acid washing, reassembly, and leak testing of dissolver system in-line filter assemblies. The need for such a facility became evident when previously used filter assemblies showed contamination levels as high as 1000 mR/h on the surface of housing parts, which is too high for safe removal and direct handling to facilitate decontamination. Various reagents were tried in an attempt to decontaminate filter parts out-of-cell, but were not successful. Although requiring patience and a steady hand, the remote disassembly and reconstruction of the filter assemblies can be done readily in-cell. To date, all 20 filter assemblies have been successfully cycled through the in-cell operation at least once. The in-cell procedure will be used for the duration of the EOL campaign.

A few programmatic bugs in OPRDDS, partly associated with installation of a new PDP-11/73 processor,* were uncovered and fixed. Some OPRDDS text modification was made to improve text description and instruction.

D. Analyses

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

1. Analytical Operations

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

This section deals with the various types of analytical operations carried out by the Analytical Chemistry Laboratory (ACL) in support of FSSF and DDS operations; the results of this work constitute the major part of the summary reports discussed in Section IV.D.2. During this quarter, analytical measurements on Rods C, D, E, and F were essentially completed, and those for Rod G were begun. Samples of dissolver solutions and dissolver off-gas samples from individual fuel rod segments were analyzed to determine total uranium,

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uranium isotopic composition, fission product monitors, and fission gases. Measurements were also made to determine uranium levels in the blank dissolutions carried out with each dissolver after all segments from a given rod had been processed, and to determine uranium levels in blend tank (BT) rinse solutions generated during decontamination of BTs prior to their reuse in dissolver operations; strict requirements for each of these levels have been set. A number of special samples, taken to follow up unusual events that occurred during dissolution of segments from Rod C, were also processed. These special samples consisted of a solution generated during rinsing and leaching the filter assembly from segment C-03, and several tissue samples obtained during a wipedown of the dissolver flanges after a vapor leak occurred during dissolution of segment C-04. Uranium assays by the mass spectrometric isotope dilution (MSID) method, using NBS 993 spike material, were performed on each of these special samples.

In general, each of the measurements was performed in routine fashion according to established ANL procedures. The analytical operations proceeded smoothly and at a brisk pace. A minor problem developed early in the quarter during counting of a few of the solution aliquots prepared for measuring the fission product monitor \(^{95}\text{Zr}\) by gamma spectrometry: the gamma peak used to determine \(^{144}\text{Ce}\) (now used as a yield monitor in the \(^{95}\text{Zr}\) determination) overflowed the multichannel analyzer before sufficient counts accumulated in the \(^{95}\text{Zr}\) peaks to give the desired counting statistics. Thus, the use of a single spectrum for measuring both nuclides was precluded, and it became necessary to take one spectrum with a short count time to measure \(^{144}\text{Ce}\) and a second one with a long count to measure \(^{95}\text{Zr}\). This requirement stems from the relatively low activity level of \(^{95}\text{Zr}\) in these samples that, in turn, is due to the short half-life of this nuclide (64.02 days). (The fuel has now been cooled for more than two years.) To accommodate this situation, the computer programs that control the automated gamma spectrometer were changed to allow the acquisition and processing of the two requisite spectra on a single sample in the automated operating mode.

On several occasions during the quarter, minor electronics problems arose in the project-dedicated VG54R thermal-ionization mass spectrometer. However, through efficient in-house diagnosis and replacement of failed integrated-circuit chips from the spare parts inventory of the mass spectrometry laboratory, downtime was limited to only a few hours in each case.

Besides providing support in the form of analytical measurements, the ACL also serves the POB project by supplying prepared reagents of specified composition. During this quarter, a 50-L batch of each of the three dissolver reagents (Thorex, Thorex-Al, and dilute nitric acid rinse solution) was prepared and analyzed. The Thorex reagent and Thorex-Al are analyzed to measure acidity and fluoride, cesium, cerium, and uranium impurities; the 0.5N nitric acid rinse is analyzed for acidity and uranium impurities. Density of each of the solutions is also measured.

2. Results and Error Analysis

(D. G. Graczyk)*

The analytical nature of the LWBR-POB project and the stringent tolerances required for measurements on the EOL fuel rods demand that strict

*Analytical Chemistry Laboratory, ANL.
control be maintained over every facet of operations, data taking, and reporting. During the development of equipment and procedures for the destructive assay of LWBR fuel rods, a comprehensive error analysis was carried out for the project by the ACL to provide a reliable evaluation and demonstration of ANL measurement capabilities. Insight into the sources of error associated with each measurement, as provided by this error analysis, guides the statistical analysis of data and aids the generation of reports. In addition, by comparing statistics derived from specific measurements made during the EOL operations with those obtained from pre-EOL test results, it can be determined whether the performance of individual systems within the project remains at the high level achieved under the test conditions. As a consequence of the ACL role in project quality assurance, responsibility for compiling, reviewing, and reporting data and results generated by the project has fallen in large share to the ACL as part of its error analysis support function. During this report period, work in this area was primarily directed toward compiling, reviewing, reducing, and reporting data from the ongoing processing of EOL fuel rods. Reports were completed this quarter for Rods B, C, D, E, and F. Data handling was carried out with the aid of report-generation software developed specifically for the POB project. Each report comprises some 15 to 20 pages of detailed tables and graphs on shear results, ACL chemical and radiometric results with complete error estimates, and discussion of special situations requiring extraordinary analytical work. A sample of results showing uranium isotopic distribution for Rod E is given in Fig. IV-1.

Weight Percent Abundances of Uranium Isotopes In Segments from Rod E (Ser.No.3102187 )

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>E-01</td>
<td>0.0116</td>
<td>99.2317</td>
<td>0.7098</td>
<td>0.0134</td>
<td>0.0003</td>
<td>0.0332</td>
</tr>
<tr>
<td></td>
<td>+/- 0.0004</td>
<td>+/- 0.0237</td>
<td>+/- 0.0004</td>
<td>+/- 0.0189</td>
<td>+/- 0.0001</td>
<td>+/- 0.0189</td>
</tr>
<tr>
<td>E-02</td>
<td>0.0245</td>
<td>94.6110</td>
<td>4.6147</td>
<td>0.4520</td>
<td>0.0454</td>
<td>0.2524</td>
</tr>
<tr>
<td></td>
<td>+/- 0.0008</td>
<td>+/- 0.0076</td>
<td>+/- 0.0006</td>
<td>+/- 0.0057</td>
<td>+/- 0.0001</td>
<td>+/- 0.0056</td>
</tr>
<tr>
<td>E-03</td>
<td>0.0926</td>
<td>90.1469</td>
<td>8.2662</td>
<td>1.1787</td>
<td>0.0981</td>
<td>0.2284</td>
</tr>
<tr>
<td></td>
<td>+/- 0.0029</td>
<td>+/- 0.0076</td>
<td>+/- 0.0009</td>
<td>+/- 0.0056</td>
<td>+/- 0.0001</td>
<td>+/- 0.0055</td>
</tr>
<tr>
<td>E-04</td>
<td>0.1448</td>
<td>87.6684</td>
<td>10.1189</td>
<td>1.6747</td>
<td>0.1511</td>
<td>0.2122</td>
</tr>
<tr>
<td></td>
<td>+/- 0.0045</td>
<td>+/- 0.0082</td>
<td>+/- 0.0012</td>
<td>+/- 0.0057</td>
<td>+/- 0.0001</td>
<td>+/- 0.0058</td>
</tr>
<tr>
<td>E-05</td>
<td>0.2088</td>
<td>90.8655</td>
<td>7.4699</td>
<td>1.1076</td>
<td>0.0997</td>
<td>0.0035</td>
</tr>
<tr>
<td></td>
<td>+/- 0.0064</td>
<td>+/- 0.0079</td>
<td>+/- 0.0008</td>
<td>+/- 0.0042</td>
<td>+/- 0.0001</td>
<td>+/- 0.0041</td>
</tr>
<tr>
<td>E-06</td>
<td>0.1451</td>
<td>93.1347</td>
<td>5.9873</td>
<td>0.6944</td>
<td>0.0339</td>
<td>0.0037</td>
</tr>
<tr>
<td></td>
<td>+/- 0.0045</td>
<td>+/- 0.0085</td>
<td>+/- 0.0007</td>
<td>+/- 0.0056</td>
<td>+/- 0.0001</td>
<td>+/- 0.0055</td>
</tr>
<tr>
<td>E-07</td>
<td>0.0452</td>
<td>97.5695</td>
<td>2.2549</td>
<td>0.1177</td>
<td>0.0027</td>
<td>0.0099</td>
</tr>
<tr>
<td></td>
<td>+/- 0.0014</td>
<td>+/- 0.0101</td>
<td>+/- 0.0004</td>
<td>+/- 0.0072</td>
<td>+/- 0.0001</td>
<td>+/- 0.0072</td>
</tr>
</tbody>
</table>

Notes: Uncertainties are one-sigma limits; random and systematic error contributions are included.

Fig. IV-1. A Computer-Generated Report of Uranium Isotopic Distribution
Analytical performance of the ANL systems continued at a high level this quarter. Destructive analysis of Rods C, D, and E was completed and reports were transmitted to BAPL; workup of data on Rod F was nearly complete as the quarter ended. The results in all cases met or exceeded requirements. Discussion of special situations that arose in the FSSF and DDS operations requiring special analytical treatment is presented below, for specific rod segments. None of these cases impacted final results, but are of interest to show the broad variety of situations that could be recovered from using special analytical techniques.

a. Rod C

During the processing of Rod C, situations requiring special calculations included (1) the presence of nitrogen and oxygen in the gas samples taken during puncture of the rod plenum, probably as a result of in-leakage of air; (2) the need to replace a filter that became plugged during transfer of dissolver solution to the BT after the second dissolution cycle for segment C-03; and (3) the development of a vapor leak at the sealing gasket of DS2 during the primary dissolution cycle for segment C-04. Fission-gas results for the plenum were calculated based on a composition for the gas that excluded the air components. The assay results for segments C-03 and C-04 were corrected for losses of solution from the dissolver system during replacement of the plugged filter and during the vapor leak, respectively. The magnitudes of these corrections were estimated from analytical results obtained for special samples taken specifically for this purpose at the time of each incident. Neither of the incidents was found to significantly affect the quality of the destructive assay results because appropriate actions were taken to deal with them as they happened.

b. Rod E

The analytical performance of the ANL systems for Rod E was similar to that for previously processed rods with the exception that a larger than usual disparity between rod weights measured before and after puncturing the plenum (0.5 g compared to an expected <0.3 g) was observed. Because no physical cause of a real weight gain by the rod during puncture could be identified, ANL attributed this disparity to the occurrence of an outlier among the rod weight measurements. With the exclusion of this deviant rod weight, the results of the physical, chemical, and radiometric measurements on Rod E met or exceeded requirements for precision and accuracy in every case.

The quantities of uranium (0.00080 g as $^{233}$U) and thorium (1.0068 g as thoria) recovered from dissolver operations on the plenum segment (E-00) of Rod E, although quite small, were sufficiently large to warrant special review. Of fundamental interest was the identification of the source of this fuel material, i.e., whether it was (1) a chip of fuel that came off the end of the Rod E fuel stack or (2) fuel carried over into Rod E from the shearing of Rod D, which was previously processed in the FSSF. Differentiating between these sources is important because chipping of the fuel-stack end during shearing of a rod is an expected and therefore acceptable occurrence, whereas fuel carryover (cross-contamination) between rods represents a deficiency in the ANL systems and is highly undesirable. The uranium found in the Rod E plenum was postulated to be a mixture of uranium from Rod D, uranium from segment E-01 (the segment next to the plenum), and natural uranium from ambient sources such as reagents or traces of dissolver solution spiked
with NBS SRM 950a; then, using the measured or known isotopic compositions of each of these materials in a regression analysis based on standard isotope dilution formulas, ANL was able to demonstrate that the bulk of the fuel found in the Rod E plenum had indeed come from the Rod E fuel stack. As a result, any uncertainty that might have arisen concerning fuel carryover in the shearing operations was allayed.

E. Support
(G. L. Chapman,* J. C. Hoh, R. W. Kessie,* J. M. Leddin,†
R. A. Leonard, R. E. Nelson, J. Osudar†)

1. Computer System and Data Management
(J. Osudar,† G. L. Chapman,* R. W. Kessie,* and J. M. Leddin†)

An integrated computer system has been developed for use by the LWBR-POB Analytical Support Project. This system provides automatic data acquisition, various monitoring functions, and several degrees of automated control for the equipment, instrumentation, and procedures by which ANL processes and analyzes fuel rods. In addition, the computer system is used for compiling data, calculating results, and generating reports. Development of the computer system was initiated in 1980 with the specification of the main elements of the hardware systems and scoping of the major software requirements. Ancillary hardware items have been added as needs were identified during system development. Although the overall design of the software systems has remained constant, refinement of these systems has continued during their development, particularly after experience in their use has been gained. A detailed description of computer hardware and software systems was presented previously [STEINDLER].

a. Hardware

Installation of a new, higher-speed microprocessor, a PDP-11/73, was completed. It was put into use in time for the processing of Rod D segments in the DDS. Its effect was immediately obvious, as the time required to display successive OPRDDS steps and the associated graphics was noticeably reduced. More importantly, the new computer also permitted simultaneous use of both dissolver systems and the full-scale shear, which previously had overloaded the original PDP-11/23-PLUS** system.

b. Software

(1) Recent Progress

Implementation of project software required effort in seven major areas, as follows: (1) report-generation programs, (2) modifications and enhancements to the DDS procedures and programs, (3) modifications and enhancements to the FSSF procedures and programs, (4) modifications and enhancements to the overall software system (POBSYS), (5) analytical programs, (6) data transfer and backups, and (7) documentation.

*Chemical Technology Division Computer Section.
†Co-op student from Lewis University, Romeoville, IL.
‡Science Applications, Inc., Schaumburg, IL.
**Digital Equipment Corp., Maynard, MA.
(a) **Report-Generation Programs**

Programs were written to reformat project data for use with spreadsheet programs on the VAX 11/780 computer.* Minor adjustments were made to several report-generation programs, as requested by BAPL.

(b) **Dissolver Procedures**

Minor changes to procedure step descriptions and code were made as a result of EOL operating experience.

(c) **Shear Procedures**

The automated cut cycle code was modified to provide enhanced blade position data storage. Data from all cuts can be recorded and subsequently plotted. Also, a new naming system for blade position data files was implemented, to aid in managing the increased amount of data.

(d) **POBSYS Modification**

Several POBSYS programs that were limited in size by the PDP-11/23-PLUS CPU were expanded after the PDP-11/73 CPU and RSX-11M-PLUS* operating system were installed.

(e) **Analytical System**

New system software was installed on the analytical PDP-11/23 minicomputer (GAMMA).

(f) **Data Transfer and Data Storage**

A system to transfer data generated during the EOL campaign from the PDP-11/73 to the VAX 11/780 has been implemented.

(g) **Documentation**

Program logic flowcharts have been drawn up for major components of POBSYS, and a detailed document describing the software system is being written.

(2) **Summary**

Hardware and software systems for the LWBR-POB EOL campaign have been in use throughout the quarter, and have functioned well. The POBSYS system has been used to process several entire rods, and report-generation programs have been used to produce complete reports for processed rods.

2. **Radiation Monitoring Systems for Cell Ventilation Air**
   (R. A. Leonard and J. C. Hoh)

A multipurpose, automated, stack monitor system measures the discharge of radioactive effluents in the high- and low-flow (HF and LF)

*Digital Equipment Corp., Maynard, MA.*
ventilation air streams from each of the four shielded cells as irradiated fuel is processed in the LWBR-POB project. The monitoring system was designed and assembled by ANL Electronics Division personnel. The overall task was coordinated by the ANL Occupational Health and Safety Division.

The system was installed prior to the validation rod (VR) run in December 1983 and was operated during the VR run to check out its radiation monitoring capabilities. Based on this run and subsequent calibration tests using known amounts of $^{85}$Kr as determined by the ACL, the operation of the automated stack monitoring system, which is controlled by a GIMIX* computer, was good. In the previous quarter, the system was used to measure the $^{85}$Kr gas release for the first EOL rod, Rod B. In this quarter, further analysis was done on the data from Rod B, and the work was extended to the next five rods, C, D, E, F, and G. In addition, calibration factors were obtained for the backup stack monitoring system, which uses Geiger-Muller (G-M) tubes, through use of the GIMIX computerized system. Although emphasis is on monitoring $^{85}$Kr release, the computer system also can detect particulate solids, $^{129}$I$_2$, and thoron ($^{220}$Rn).

a. Release of $^{85}$Kr during Fuel Rod Plenum Puncturing and Shearing

The $^{85}$Kr gas release during fuel rod plenum puncturing and shearing is measured by both the computerized and G-M systems. When the plenum is punctured, the gas is contained in a closed space of known volume, and a sample is taken for ACL analysis. The remaining gas is released directly to the HF stack in the shear cell where the $^{85}$Kr concentration is measured by both radiation monitoring systems; the HF stack handles the bulk of the air flow and the LF stack mainly handles the air drawn from around the shearing head. Results obtained for the $^{85}$Kr content of the fuel rod plenums and $^{85}$Kr released during segment shearing for the first six EOL fuel rods are shown in Table IV-2. These results were obtained using the computerized system for the shear cell and a calibration factor (determined by earlier comparison with ACL results) of 0.0205 μCi·min/(m$^3$·c), where c is the excess counts above background.

The ACL data are also shown in the table for the gas recovered when the rod plenum is punctured. The difference between the two plenum values for each rod reflects computerized system error that is typically ±20% for readings above 5 mCi; the error increases for readings below 5 mCi.

When a fuel rod is sheared, $^{35}$Kr is released with each stroke of the shear as the fuel is pulverized; individual segments require 6 to 75 cuts each, and shearing an entire rod requires about 450 cuts. This release is primarily to the LF stack and is measured by both the computerized and G-M systems. This is, in fact, the only way the release can be measured, because the system does not incorporate a hold tank, as does the DDS system. A small fraction of the $^{85}$Kr escapes to the HF stack as a result of the split in ventilation flow and is measured by the G-M system only; the computerized system can monitor the two independent HF and LF exhaust systems for the shear cell, but only one at a time. The amount of $^{85}$Kr shown is the combined total for the LF and HF stacks; the split between the two stacks averaged 90% and 10%, respectively.

*GIMIX, Inc., Chicago, IL.
<table>
<thead>
<tr>
<th>Segment</th>
<th>Rod B</th>
<th>Rod C</th>
<th>Rod D</th>
<th>Rod E</th>
<th>Rod F</th>
<th>Rod G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Puncturing Plenum</td>
<td>14.7</td>
<td>6.7</td>
<td>2.0</td>
<td>2.0</td>
<td>2.6</td>
<td>11.9</td>
</tr>
<tr>
<td>Plenum (ACL)</td>
<td>13.9</td>
<td>7.1</td>
<td>0.9</td>
<td>1.7</td>
<td>1.5</td>
<td>9.9</td>
</tr>
<tr>
<td>Shearing 01</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Shearing 02</td>
<td>4.6</td>
<td>3.4</td>
<td>1.5</td>
<td>1.3</td>
<td>0.6</td>
<td>6.0</td>
</tr>
<tr>
<td>Shearing 03</td>
<td>11.3</td>
<td>11.9</td>
<td>5.1</td>
<td>5.4</td>
<td>3.0</td>
<td>15.5</td>
</tr>
<tr>
<td>Shearing 04</td>
<td>14.7</td>
<td>14.8</td>
<td>8.2</td>
<td>7.8</td>
<td>4.8</td>
<td>20.5</td>
</tr>
<tr>
<td>Shearing 05</td>
<td>13.9</td>
<td>12.9</td>
<td>5.9</td>
<td>5.1</td>
<td>5.7</td>
<td>19.1</td>
</tr>
<tr>
<td>Shearing 06</td>
<td>7.6</td>
<td>4.2</td>
<td>1.4</td>
<td>2.0</td>
<td>0.6</td>
<td>0.9</td>
</tr>
<tr>
<td>Shearing 07</td>
<td>0.6</td>
<td>0.7</td>
<td>0.3</td>
<td>0.4</td>
<td>0.0</td>
<td>1.2</td>
</tr>
<tr>
<td>Shearing 08</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0</td>
<td>-</td>
</tr>
<tr>
<td>Subtotal (shearing)</td>
<td>52.7</td>
<td>47.9</td>
<td>22.4</td>
<td>22.0</td>
<td>14.7</td>
<td>63.2</td>
</tr>
<tr>
<td>Total</td>
<td>67.4</td>
<td>54.6</td>
<td>24.4</td>
<td>24.0</td>
<td>17.3</td>
<td>75.1</td>
</tr>
</tbody>
</table>

*Also referred to as segment 00.

b. Independent check on $^{85}$Kr, as determined by ACL.

Errors in the $^{85}$Kr values obtained during rod shearing are probably similar to those indicated above for the plenum measurements. The segments near the rod ends were loaded with thoria-only pellets and show less $^{85}$Kr content than those near the center, which contained binary (ThO$_2$-UO$_2$) pellets. In general, the relative amount of $^{85}$Kr released from each segment corresponds to the uranium content in the segment; thus, the $^{85}$Kr values are considered quite reasonable. In general, the $^{85}$Kr found in a plenum and that released during shearing are about 0.1% and 1%, respectively, of that found in an entire rod.

b. Calibration Factors

In the process of calculating the $^{85}$Kr gas releases shown in Table IV-2, calibration factors for the two G-M tubes in the shear cell stacks are calculated along with the split in flow of the $^{85}$Kr-containing gas between the HF and LF exhaust gas systems during the shearing of the fuel rod. The
calibration factors are obtained by comparison of the data with results from the computerized system, which itself was calibrated by comparison with ACL results. Results of these calculations for Rods B through G are shown in Table IV-3 (the G-M tube factors are inversely related to those of the computerized system). Each calibration factor for the LF stack is lower than that for the HF stack, with one exception (Rod F). The average variance in the other five cases is about 20% as a result of the smaller diameter of the LF stack (6-in.) than that of the HF stack (8-in.). For no apparent reason, the LF stack calibration factor is higher than expected for Rod F. Inasmuch as computer data are available where LF stack data are needed, this variance has no impact on the $^{85}$Kr releases for Rod F, as reported in Table IV-2.

<table>
<thead>
<tr>
<th>Stack</th>
<th>Rod B</th>
<th>Rod C</th>
<th>Rod D</th>
<th>Rod E</th>
<th>Rod F</th>
<th>Rod G</th>
</tr>
</thead>
<tbody>
<tr>
<td>G-M Tube Calibration Factor, $a$ c.m$^3$/($\mu$Ci-min)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LF$^b$</td>
<td>49,000</td>
<td>40,600</td>
<td>40,700</td>
<td>41,300</td>
<td>66,300</td>
<td>43,100</td>
</tr>
<tr>
<td>HFC$^c$</td>
<td>55,000</td>
<td>55,000</td>
<td>45,600</td>
<td>52,300</td>
<td>52,300</td>
<td>50,800</td>
</tr>
</tbody>
</table>

| Fraction of $^{85}$Kr in the HF Stack during Rod Shearing | 0.11 | 0.05 | 0.11 | 0.01 | 0.20 | 0.01 |

$^a$Based on the computerized system calibration factor of 0.0205 $\mu$Ci-min/(m$^3$.c).

$^b$Computer monitors LF stack during rod shearing.

$^c$Computer monitors HF stack during plenum puncturing.

**c. Release of $^{85}$Kr during Fuel Rod Segment Dissolution**

Because ACL has a reliable procedure for analyzing the off-gas from the dissolvers, a detailed analysis of the $^{85}$Kr releases associated with the dissolutions in the DDS cell will not normally be carried out. However, to reconstruct the $^{85}$Kr released while dissolving segment C-04 (a leaky dissolver flange gasket had caused a problem), the stack monitor $^{85}$Kr data from Rods B and C were analyzed in some detail. The results, given as the variation of computer calibration factor for $^{85}$Kr with Rods A, B, and C, are given in Table IV-4. From these data, it is clear that the computer calibration factor for $^{85}$Kr has been fairly stable during the past year. However, because the time of the C-04 gas release was partially within a measurement period in which readings were taken at intervals long with respect to the release time of the gas, thereby reducing data reliability, the $^{85}$Kr release was calculated indirectly, as outlined in Section IV.E.2.a.
Table IV-4. Ratios of ACL to Computer Data and Computer Calibration Factors for $^{85}$Kr in the Exhaust Gas System of the DDS Cell

<table>
<thead>
<tr>
<th>Rod Segment</th>
<th>Rod A</th>
<th>Rod B</th>
<th>Rod C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ratio of $^{85}$Kr Value from ACL to That from the Computerized System$^a$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>02</td>
<td>b</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td>03</td>
<td>1.21</td>
<td>1.26</td>
<td></td>
</tr>
<tr>
<td>04</td>
<td>1.24</td>
<td></td>
<td>c</td>
</tr>
<tr>
<td>05</td>
<td>1.13</td>
<td>1.08</td>
<td></td>
</tr>
<tr>
<td>06</td>
<td>1.25</td>
<td>1.20</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>1.0$^d$</td>
<td>1.21</td>
<td>1.16</td>
</tr>
</tbody>
</table>

Computer Calibration Factor, $\mu$Ci-min/(m$^3$-c)

<table>
<thead>
<tr>
<th></th>
<th>0.0214</th>
<th>0.0259</th>
<th>0.0248</th>
</tr>
</thead>
</table>

$^a$The computerized system used a calibration factor of 0.0214 $\mu$Ci-min/(m$^3$-c), which was determined using ACL values for gas from the Rod A plenum puncture.

$^b$No computer data because the HF stack was erroneously being monitored.

$^c$Some gas lost due to a leak at the dissolver flange gasket.

$^d$Basis for calibration factor.

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

A procedure has been developed to track the fissile material (FM) (mainly $^{233}$U, but also containing a small amount of $^{235}$U) in POB operations during the EOL campaign. Part of the procedure involves the use of log sheets kept in an FM inventory notebook. The remainder of the procedure uses a series of interconnected electronic spreadsheets using DICICALC.* All results are combined in the spreadsheet, SUMMARY, to give an overall picture of the FM inventory. Other spreadsheets contain data specific to a system, e.g., fuel

*WHY Systems, Inc., Redmond, WA.
rod data (INITIAL, UPDATE), waste tank data (WT1, WT2),* sample data (SAMPLES), and waste data (WASTE). All parts of this procedure are now in place and fully operational.

The INITIAL and UPDATE spreadsheets work together to give the best value for the FM in each segment of each rod. The INITIAL spreadsheet contains an estimate of FM provided by BAPL. These initial values are used in the UPDATE spreadsheet until the ACL values are available. Two programs, RUPDATE and RSAMPLES, have been written that search the ACL computer files and obtain pertinent ACL data in a form that can be read directly into the spreadsheets, UPDATE and SAMPLES. Other spreadsheets reference the UPDATE spreadsheet to get the best value for the mass of FM in each rod and rod segment.

The SAMPLES spreadsheet keeps track of the FM in samples sent to ACL and to archives, as well as in spikes added to blend tanks and to samples during analysis by ACL. These sample data are used to calculate the fraction of FM in the various liquid portions associated with a given rod or rod segment.

The waste tank spreadsheets, WT1 and WT2, combine liquid volume information from the log sheets with the mass of FM from UPDATE and the FM fraction from SAMPLES to calculate both the total FM and the concentration of FM in each waste tank. Using the spreadsheet system, it was possible to determine the volume in the waste tank at the time the first solution was removed to the waste treatment cell to be mixed with cement, without use of the liquid level indicator. This is an important capability because, based on our experience with the liquid level indicators in this cell, the waste tank indicators in the DDS cell need recalibration. A solution sample was provided to ACL where its density, uranium concentration (grams of uranium per gram of solution), and ratio of uranium isotopes were measured; with the spreadsheet, the amount of FM in the waste tank was calculated. Combining these quantities, the solution volume in the tank can be calculated with less than 1% error. Subtracting this volume (82.7 L) from the estimated volume of liquid added to WT-2 since December 1983 (105.2 L), we determined that 22.5 L of solution had been lost through evaporation and radiolytic decomposition in nine months, a loss of 2.5 L/mo. The amount of FM withdrawn to make the cement in Cell K-1 is calculated in the appropriate waste tank spreadsheet and used in the WASTE spreadsheet. The WASTE spreadsheet keeps track of the FM as it is combined with cement and shipped.

The SUMMARY spreadsheet receives information from the nonelectronic pre-waste-tank log sheets and calls in data from the other six spreadsheets. It shows and sums the FM at each location. The total FM for all locations is compared with the total FM to be accounted for. Any FM not accounted for is noted on the spreadsheet.

*To differentiate between the spreadsheet programs for waste tank data and the waste tanks themselves, the initializations for the former are closed up (e.g., WT1) and those for the latter are hyphenated (e.g., WT-1).
The spreadsheets are normally updated after each rod is dissolved, or as otherwise appropriate. All but WASTE and SUMMARY were updated just before operations were shut down at the end of the quarter. The calculations prior to shutdown showed that there was less solution in WT-1 than had been expected. Operations are being reviewed to determine whether solution from WT-1 was inadvertently pumped into WT-2. Unfortunately, the present waste tank liquid level probes do not indicate a significant change until 20 L has been accumulated in the tank. In this case, the amount of solution in WT-1 was less than 20 L. So, even if the liquid had been pumped from WT-1 into WT-2, the transfer would not have been detected by the gauge on WT-1; however, the WT-2 gauge would have shown the transfer, but it was not monitored. The overall calibration of these probes with actual waste solution needs to be established; in the interim, weight data on solution additions serve as reference information and as a possible basis for constructing a calibration curve.

For special-materials records, we must identify the mass of thorium that is put in each can of cemented waste. The FM spreadsheets can be modified to get these thorium values, and work on a modified set of spreadsheets has been started.

4. Scrap and Waste Disposal
(R. E. Nelson)

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

Final testing of all in-cell equipment and procedures was completed in preparation for actual waste processing.

a. Waste Processing

During the quarter, seven 2.6-L batches of dissolver solution were successfully processed into cemented waste. Most of the batches were prepared from the accumulated solution stored in one of the two 370-L waste tanks in the DDS cell, WT-2. An exception was a batch that was stored in WT-1 containing dissolver solution from the highest burnup segments of Rods B, C, and D. In this instance, during mixing, the cement set up prematurely, seized the mixing blade, and stopped the mixing motor. This occurred about two hours into the normal three-hour mixing period. All efforts to lower the can away from the mixing blade failed. The premature setting of the cement is believed associated with greater self-heating of this higher-activity solution.

The stuck blade and cemented primary can have been removed from the mixing station, and a new blade will be installed as soon as possible. The task remains to remove the mixing blade from the cemented waste so the batch can be processed for shipment to the waste storage facility.
A subsequent batch of cement was successfully prepared using ~500 mL of the high-activity solution mixed with 2100 mL of less radioactive solution (from WT-2), an additional 25 mL of 100 XR agent (a set retardant), and an additional 100 mL of water.

b. **Radwaste Cask Loading and Radiation Survey**

Trial loading of a radwaste cask was conducted to verify that the cask was adequate for reducing the radiation level below the required limit of 200 mR/h at the surface of the drum in which the cask is housed. The selected cask was one of 50 casks received last quarter. All the casks passed inspection from a lead weight standpoint, but radiographs of selected casks revealed voids in the lead region. (The cask selected for the test appeared to have the largest voids.) Diameters of the voids are given by the radiographer (Pittsburgh Testing Laboratory); however, no information on their depth or thickness was given. The question of void size and depth has been referred to the ANL Procurement Department for review.

For the loading test, one secondary waste can containing two primary cans, each with a load of cemented waste, was loaded into the radwaste cask, and a comprehensive radiation survey was made to determine the radiation levels at the surface of the cask. The highest reading was 90 mR/h, detected at the center of the cask cover, well below the 200-mR/h limit. The survey readings also indicated relative and adequate uniformity of lead shielding. No outer (55-gal) drum was used in the test; thus, we should have no radiation-level problems with the complete package.

c. **Miscellaneous**

Procurement of 50 additional radwaste casks from the same vendor that fabricated the original 50 casks is in progress. Delivery is expected about July 1985. Dunnage is being installed inside the steel bins that will house 55-gal waste drums during transport to the waste storage facility. Twelve bins will be so equipped to handle the waste drums; the bins will be reused throughout the campaign. Color coding and identification painting of the drums is necessary and will be started shortly.

5. **Facility Maintenance**

(J. C. Hoh)

Master/slave manipulator breakdowns continued to occur, but the types of breakdowns were varied and did not point to any particular operation or component as the cause. Most breakdowns can be attributed to fatigue, because the equipment is in use on a three-shift basis, five days a week.

Two boots (plastic sleeves for the in-cell portions of the manipulators) were remotely replaced in the dissolver cell again this quarter. Both replacements required manipulator removal. The boots are intended to enhance manipulator life by keeping sliding surfaces clean.
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