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Progress Report
3

Research and Development Related to Nevada Nuclear Waste Storage Investigations

April 1—June 30, 1979

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Compiled by
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RESEARCH AND DEVELOPMENT RELATED TO NEVADA NUCLEAR WASTE STORAGE INVESTIGATIONS

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ABSTRACT

Geochemical laboratory support for Subtask 3.2.2, Tuff Media Investigations; geologic support for Subtask 2.5., Tectonics, Seismicity, and Volcanism; and administrative support for Subtask 5.2, Quality Control is presented. Mineralogic-petrologic examination of material from Yucca Mountain hole UE25A#1 is nearing completion. Sorption measurements on tuff from holes J-13 and UE25A#1 are continuing with both natural and synthetic ground waters and under aerobic and anoxic conditions. Column work is continuing. A standardized batch procedure for Am and Pu has been adopted. A preliminary probability analysis has been performed for volcanic hazards of the Crater Flats basalts.

I. INVESTIGATIONS OF THE SORPTIVE PROPERTIES OF TUFF

Batch desorption measurements of cesium, strontium, barium, cerium, and europium with samples from hole UE25A#1 under aerobic conditions and with water from well J-13 have been completed. After 21- and 42-d contact times, the aqueous and solid phases were separated, the pH values of the solutions were recorded, and aliquots of the aqueous and solid phases were taken for counting.

The correlation between R_d values and particle sizes for desorption measurements is generally similar to that observed in the sorption measurements. For example, the R_d values for strontium, cesium, and barium on cores YM-38, YM-48, and YM-49 decreased as the sieve fraction size decreased, while the values for

the rest of the samples tended to increase or remain approximately constant with decreasing size. Cerium and europium seem to behave differently. It was thought that fractionation of minerals in the sieving process might explain these results. However, preliminary X-ray diffraction analyses indicate no difference in X-ray patterns or intensities. Thus, unless the difference in sorption behavior is due to a relatively minor component which is not resolved by X-ray diffraction, it is unlikely that mineral fractionation can explain these results. A more likely explanation may come from the fact that the smaller fraction (<106 μm) has been ground to particles smaller than natural grain sizes, exposing different surfaces, and perhaps destroying others.

Sorption-desorption ratios are high for some samples which were previously thought to be low in zeolites, leading to the conclusion that alteration to zeolites or clays may not be a necessary condition for high sorption ratios of tuff. However, additional analyses have indicated that preliminary descriptions were probably incomplete and zeolites may be present in these samples. Mineralogical characterization of the YM tuff cores is continuing.

A series of batch sorption experiments with Yucca Mountain cores YM-22, YM-38, and YM-54 are being started under anoxic conditions (<0.2 ppm oxygen) in anaerobic boxes to investigate possible changes due to a non-oxidizing atmosphere. Well J-13 water and nuclides of strontium, cesium, barium, cerium, and europium are being used so that the results may be compared with those under aerobic conditions.

Effects of changes in the composition of ground water are being investigated with batch experiments with Jackass Flats tuffs using two simple synthetic ground waters and nuclides of strontium, cesium, barium, cerium, and europium. The experiments are being run in air for 4- and 8-week contact times. One of the artifical waters is of low ionic strength, and the other is relatively high. The four-week experiments indicate that the composition of the water appears to be a major factor in the observed sorption ratios. For example sorption ratios for cesium and europium increase dramatically with ionic strength for the devitrifed tuff JA-32. For cesium, strontium, and barium with the concentrated simple water, the results are similar to those with the J-13 water obtained earlier.

Sorption measurements with "Barco Bond" and "Eco Bond" epoxys were made because it was thought that if an epoxy that is non-sorptive and stable could be found, it might be useful as a "container" for whole-core columns. Although the R_d values are generally small, results do indicate that, particularly for cesium

and europium, these epoxys may cause problems if used in sorption measurements on a core.

Technetium sorption ratios on three Yucca Mountain cores, YM-22, YM-48, and YM-49, have been measured under aerobic conditions with four concentrations of technetium. After 41-d sorption and 65-d desorption contact times, the aqueous and solid phases were separated, the pH values of the solutions were recorded, and aliquots of the aqueous and solid phases were taken for counting. In all cases the sorption ratios are close to zero and no concentration effect is observed.

Sorption ratios of U(VI) on Jackass Flats tuffs at 70°C have been measured and are several times greater than those at room temperature but still less than 20 ml/g. Desorption ratios are on the average 2.3 times the sorption ratios.

The results to date for the batch measurements of the sorption of Pu and Am on Jackass Flats tuffs are summarized in Table I. Sorption ratios were averaged

TABLE I

AVERAGE SORPTION RATIOS (ml/g) FOR Am AND Pu

			Dried Feed		pH Adjusted Feed	
Element	Core	Temp. (°C)	Sorption	Desorption	Sorption	Desorption
Am	JA-18	22	180	1 100	435	
		70	230	3 400		
	JA-32	22	130	2 200	1 100	1 500
		70	110			
	JA-37	22	670	17 000	8 800	4 600
		70	970	34 000		
Pu	JA-18	22	140	350		
	JA-32	22	110	1 200		750
	JA-37	22	280	3 300		1 100

over available data (four experiments), contact times from one to eight weeks, 106-150 and 355-500 μm particle sizes, and $\approx 10^{-6}$ and $\approx 10^{-13}$ M Pu concentrations. Radiochemical analyses for ^{239}Pu and desorption measurements for the most recent experiments are still in progress. The quoted R_d values were calculated from direct counts of the solids and aliquots of the aqueous phases after they were centrifuged but before they were filtered.

Several general conclusions can be made for the Pu and Am results: The sorptive properties vary with the mineralogy; R_d values are highest for the

zeolitized tuff (JA-37). At least qualitatively a decrease in particle size is accompanied by a small increase in sorption ratio. The R_d values tend to increase with increasing temperature, at least for Am. The results for Core JA-37 for feed solutions prepared by adding acid tracer solution to the ground water and readjusting the pH to its original value suggest nearly a factor of ten higher R_d value for $\approx 1 \times 10^{-6}$ M ^{239}Pu than for $\approx 2 \times 10^{-13}$ M ^{237}Pu. This may be due to a tendency for the more concentrated solution to form centrifugable Pu species. The method of preparing the traced feed solutions appeared to influence the observed sorption ratios; the "pH adjusted" method giving higer R_d values than the method of drying and redissolving the tracers. In the most recent experiment, five different feed solutions of ^{241}Am and two of ^{237}Pu were prepared by the "ph adjusted" method with no observable differences in their behavior. The results of the earlier measurements using a single such feed solution were, therefore, assumed to be valid. For "dried" feed solution the R_d values for desorption were greater than for sorption; as yet, no definitive conclusion can be made for the "pH adjusted" feed solutions with respect to sorption/desorption measurements.

With respect to the effects of procedural variables for Am and Pm, the following general statements can be made: Container sorption for "controls," which are prepared exactly as the samples except they contain no crushed rock, is much greater than for samples containing crushed rock. Container sorption for tuff samples is probably negligible; using results from "controls" to correct for container sorption with samples is probably inappropriate. After contact there was a significant amount of centrifugable species in the "controls" and, therefore, presumably in the samples where it would be combined with the crushed rock. Each of three centrifugings (1h, 1h, 2h) removed additional activity from Am solutions and, therefore, would appear to be necessary. (Such measurements were not made for the Pu solutions, but presumably the results would be the same.)

The most recent procedure for centrifuging and transferring after contact gave Pu solutions from which no additional Pu was removed by filtering. This was not true for Am, where a factor of two or more of the activity was sometimes removed by filtering the centrifuged solutions, the results varying with the contact temperature used. This Pu result suggests that Pu does not significantly sorb on polycarbonate filter membranes, at least in the time required for filtering. The activity present in a Pu solution after it has been centrifuged three

times is, therefore, probably the "true" value for calculating sorption ratios. For Am, centrifuging the solution after contact would appear to establish a lower limit to the sorption ratio since crushed rock particles and particulates remaining with the solution would tend to lower the calculated R_d. The mechanism by which additional Am activity is removed from the centrifuged "solutions" by filtering is not understood; it could be removal of particulates which is desirable, or sorption on the membrane, which is undersirable. Taking the conservative approach, we have therefore decided to report Pu and Am sorption ratios based on the solutions after centrifuging but without filtering.

Seven crushed rock columns of NTS tuff were described in the last quarterly report. Four of these columns are still being eluted with rock pre-treated waters. A third column of YM-54 tuff (free column volume = 0.297 mℓ) was recently prepared because preliminary data from the first two YM-54 columns indicated that the R_d for Cs was lower than the value obtained from batch experiments. The concentration of Cs in the batch measurements was $\approx 10^{-3}$ times that of the Cs spike added to the first two YM-54 columns. The new YM-54 column is being run with a "continuous feed" of ^{137}Cs, in a concentration comparable to that of our batch experiments, $\approx 10^{-9}$ M.

The only columns for which data collection and analysis are complete are those of the JA-32 tuff. Three columns of different size and flow rate were run for comparison. Flow rates from 0.082 ml/h to 18 mℓ/h gave sorption ratios for Sr from 35.2 to 55.2 mℓ/g. Thus, even an extreme variation in flow rate made little difference. The flow rates of subsequent columns have ranged from 0.08 to 0.03 mℓ/h. The average R_d obtained from the three JA-32 columns is 43 ± 11 mℓ/g, which is comparable to the average batch R_d of 52 ± 9 mℓ/g.

II. MINERALOGICAL-PETROLOGICAL STUDIES

Petrological characterization of tuff from Yucca Mountain exploratory drill hole UE25a#1 is on schedule. Petrographic description and modal analyses were completed; electron microprobe chemical analysis and bulk powder X-ray diffraction analysis of phases present were completed during the quarter.

X-ray analysis indicates that cristobablite, quartz, and feldspar are the principle phases in the Tiva Canyon member of the Paintbrush Tuff and in the welded horizons of the Topopah Springs member of the Paintbrush Tuff and of the Prow Pass and Bullfrog members of the Crater Flat Tuff. Heulandite/clinoptilolite and mordenite are the principle zeolite phases ocurring in the nonwelded zones of

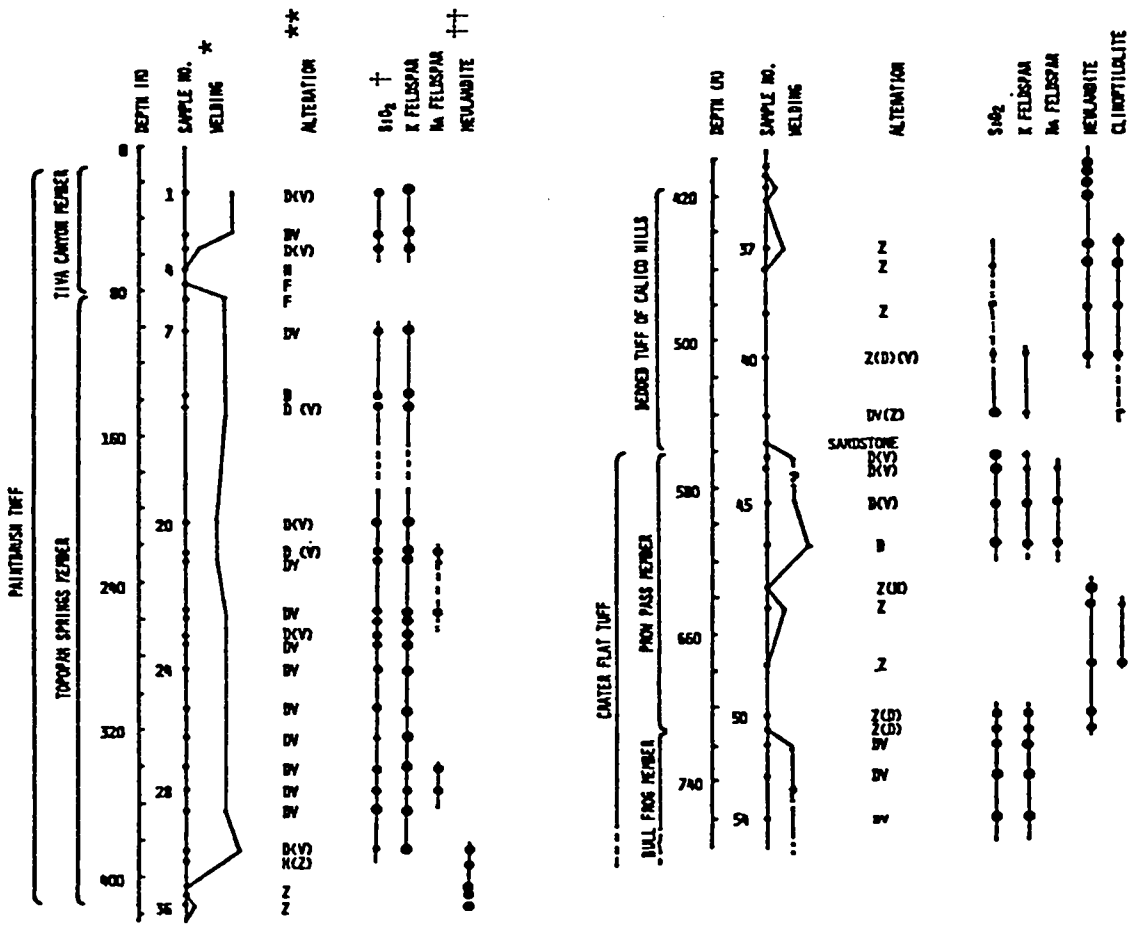

Fig. 1

Alteration Phases in Samples from the Yucca Mountain Drill Hole UE25A#1

* Samples may be nonwelded (eg., YM-4); partially welded (eg., YM-37); moderately welded (eg., YM-20); densely welded (eg., YM-24); to vitrophyric (eg., YM-30). ? indicates texture obscured by alteration.

** D: devitrification; V: vapor phase crystallization; H: hydration; Z: zeolitization; ( ) minor alteration.

† Cristobalite or quartz. Large circles: >60%; medium circles: 30-60%; small circles: <30%.

†† Zeolites are classified on the basis of chemical composition. Minor amounts of mordenite have been identified by X-ray diffraction.

the Topopah Springs member, the Prow Pass member, and the Tuffaceous Beds of Calico Hills. Many of these horizons are almost completely zeolitized.

The degree of welding; lithic and crystal enrichments; and mode, composition, and occurrence of alteration phases are summarized in Fig. 1.

III. VOLCANIC HAZARD STUDIES

Surface geologic field mapping of the basalts of Crater Flat have been completed. Fourteen volcanic centers have been recognized in the Crater Flat area. These centers include:

1. Four centers comprising the Little Cone - Red Cone - Black Cone northeast-trending arc
2. Lathrop Wells center
3. Six centers associated with deeply eroded dike-cone sequences of the north-south trending cone setting
4. Three buried centers inferred from aeromagnetic patterns.

The typical basalt center is represented by Red Cone. Red Cone volcanic activity commenced with construction of several small cinder cones (Strombolian eruptive activity) located southeast and south of Red Cone. Activity shifted to Red Cone with construction of the largest cinder cone of the Center (approximate diameter of 0.6 km) accompanied by extrusion of viscous aa lava flows from the southeast side of Red Cone. These lavas flowed a maximum distance of 1.3 km from the Red Cone vent and surrounded the early cinder cones. Continued Strombolian activity at Red Cone built the cinder cone to a height of approximately 105 m. Final activity at the center comprised aerial eruption of viscous magma blobs which plastered and infilled the summit vent of Red Cone.

Preliminary probability calculations have been performed for the basalts of Crater Flat assuming conservative rates of volcanism with no structural control of vent locations (random). The probability of volcanism is assumed to be a special case of conditional probability (P) where:

$$P = R \times A$$

where R is the rate of volcanism and A, the area consideration.

The rates of volcanism are divided into two cases (Table II):

1. Center Count
2. Vent Count.

Based upon magnetic polarity data, the 14 cone centers or 40 vents are all

considered to be younger than 2.5 Myr. The data clearly show the activity peak (Table II) to lie in the interval 2.5 Myr to 0.7 Myr; however, this interpretation has a high degree of uncertainty. Therefore, the rate of volcanism is calculated assuming a uniform distribution through the last 2.5 Myr.

TABLE II

PROPERTIES OF VOLCANIC CENTERS

Center	Number of Events	Magnetic Polarity	K-Ar Age (Myr)
1. Little Cones	2	Reverse	1.2
2. Red Cone	9	Reverse	---
3. Black Cone	3	Reverse	1.4
4. Coyote Cone	1	Reverse	---
5. North Big Bomb Cone	2	Reverse	---
6. South Big Bomb Cone	3	Reverse to Normal (?)	---
7. West Dike Center	3	Reverse	---
8. North Dike Center	2	Reverse	---
9. South Dike Center	2	Reverse	---
10. Yucca Mountain Center	1 (?)	Reverse	---
11. Lathrop Wells Center	3	Normal	0.23
12. West Buried Cone	?	Reverse (?)	---
13. East Bured Cone	?	Normal (?)	---
14. Lathrop Wells Buried Cone	?	Reverse (?)	---
TOTAL	31		

Ave. vents/center = 2.82 ± 2

Total Adjusted = 40 cones

$$R\ (\text{cone count}) = \frac{14}{3.5 \times 10^{6}\ \text{years}}$$

$$= 5.6 \times 10^{-6}\ \text{cones per year}$$

$$R\ (\text{vent count}) = \frac{40}{2.5 \times 10^{6}\ \text{years}}$$

$$= 1.6 \times 10^{-5}\ \text{vents per year}$$

Various disruption zone assumptions can be made for the area considerations associated with basaltic volcanism which are described by Crowe[1]. For the Yucca Mountain case, deep burial geometry is assumed (>500 m) and an area consideration defined by a circle drawn around the Yucca Mountain site of interest with a radius of 25 km (area = 1,963 km^2). Assuming an at depth area of disruption of 2.1 km^2 for a basaltic feeder dike yields:

$$A\ (\text{cone count}) = \frac{(2.1\ km^2)\ (2.82\ \text{vents per cone})}{2.0 \times 10^{3}\ km^2}$$

$$= 3.0 \times 10^{-3}$$

$$A\ (\text{vent count}) = \frac{2.1\ km^2}{2.0 \times 10^{3}\ km^2}$$

$$= 1.0 \times 10^{-3}.$$

Therefore the probability of volcanism for the two cases becomes:

$$P\ (\text{cone count}) = (5.6 \times 10^{-6}/\text{year})\ (3.0 \times 10^{-3})$$

$$= 1.7 \times 10^{-8}/\text{year}$$

$$P\ (\text{vent count}) = (1.6 \times 10^{-5}/\text{year})\ (1.0 \times 10^{-3})$$

$$= 1.6 \times 10^{-8}/\text{year}$$

These probabilities correspond to the case of the occurrence of future volcanism that intersects and disrupts a repository. The figures are highly speculative and represent an unrealistic case of volcanism (random) that ignores the obvious structural control of volcanism in the Great Basin. Much more refined calculations are in progress, and therefore, the above probability values should not be quoted without the accompanying assumptions required for the calculations.

IV. QUALITY ASSURANCE

Implementation of the quality assurance program was continued. Surveillance was performed and documented for all areas. Two quality assurance documents were developed, issued, and implemented this quarter: TWS-CNC-11-DP-5, RO, "Sorption-Desorption Ratio Determinations of Geologic Materials By a Batch Method," and TWS-G6-33/79-4, RO, "Tuff Experiments and Petrology Studies By G-6."

All project procedures are presently under revision to incorporate a new identification system. Two audits of LASL operations were held this quarter: An internal quality assurance audit was held on April 24, 1979 and NV and Sandia Overview auditors audited the LASL operation on May 1, 2, and 3, 1979. Project procedures are being revised to incorporate audit comments.

LASL QA participated in the NV and Sandia Overview audit of the the USGS on May 28, 29, and 30.

LASL QA met with USGS personnel on June 25, 1979 at LASL to discuss the final draft of their QA Program Plan. Unit Task Procedures which were due to be completed on June 15 were discussed in this meeting.

V. PUBLICATIONS AND TALKS

1. B. R. Erdal, R. D. Aguilar, B. P. Bayhurst, P. Q. Oliver, and K. Wolfsberg, "Sorption-Desorption Studies on Argillite," Los Alamos Scientific Laboratory report LA-7455-MS (1979).

2. K. Wolfsberg, B. P. Bayhurst, W. R. Daniels, B. R. Erdal, F. O. Lawrence, and A. E. Norris, "Sorption-Desorption Studies on Tuff," Los Alamos Scientific Laboratory report LA-7480-MS (1979).

3. J. L. Thompson and K. Wolfsberg, "Applicability of Microautoradiography to Sorption Studies," Los Alamos Scientific Laboratory report LA-7609-MS (1979).

4. J. R. Smyth, K. Wolfsberg, and J. L. Thompson, "Microautoradiographic Studies of U and Am Sorption on Minerals," presented at the Joint Symposium on Radioactive Waste Disposal, Honolulu, Hawaii, April 1-6, 1979; abstract LA-UR-78-2439 (1978).

5. K. Wolfsberg, B. P. Bayhurst, B. M. Crowe, W. R. Daniels, B. R. Erdal, D. C. Hoffman, F. O. Lawrence, and J. R. Smyth, "Sorptive Properties in Tuffs," presented at the Joint ACS/CSJ Symposium on Radioactive Waste Disposal, Honolulu, Hawaii, Arpil 1-6, 1979; abstract: LASL report LA-UR-78-2440 (1978).

6. W. R. Daniels, F. O. Lawrence, P. Q. Oliver, and S. Maestas, "Sorption of Pu and Am on Tuff, Granite, and Argillite," presented at the Joint ACS/CSJ Symposium on Radioactive Waste Disposal, Honolulu, Hawaii, April 1-6, 1979. abstract: LA-UR-78-2400.

7. K. Wolfsberg and E. N. Vine, "Nuclide Sorption - Tuff," presented at Technical Review of Media Studies, NNWSI, NV, April 25, 1979.

8. B. R. Erdal, "Nuclide Sorption Studies on Argillite and Granite," presented at the Technical Review of Media Studies NNWSI, April 25, 1979.

9. W. R. Daniels, "Chemistry of Americium and Plutonium " presented at the Technical Review of Media Studies, NNWSI, April 25, 1979.

10. W. R. Daniels, "Laboratory Flow Experiments in Granite and Tuff," presented at the Technical Review of Media Studies, NNWSI, April 25, 1979.

11. J. Smyth, "Mineralogy of Tuff in Western Jackass Flats and Yucca Mountain," presented at the Technical Review of Media Studies, NNWSI, April 25, 1979.

12. M. L. Sykes, "Petrology and Secondary Alteration of Tuff Units at Yucca Mountain," presented at the Technical Review of Media Studies, NNWSI, April 25, 1979.

REFERENCE

1. B. M. Crowe, "Disruptive Event Analysis: Volcanism and Igneous Instrusion," Battelle Pacifie Northwest Laboratories report (in press).

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