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Laboratory and Field Studies Related to the Radionuclide Migration Project

October 1, 1986–September 30, 1987

Compiled and edited by Joseph L. Thompson

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ABSTRACT

In this report we describe the research done by personnel of the Los Alamos National Laboratory in support of the Radionuclide Migration project during FY 1987. We are engaged in collecting data concerning the movement of radionuclides at three locations on the Nevada Test Site. We continue to monitor the elution of tritium and krypton from the RNM-2S well at the Cambric site and have described in detail the elution of ^{36}Cl from the same well. The data from this field study provide us with the opportunity to test the validity of several models of solute transport through geologic media. We have detected tritium and fission products in a water sample from the hole UE20n #1, which was drilled this year at the Cheshire site on Pahute Mesa. We are also continuing our efforts to learn how radionuclides have moved in test areas 3 and 4 near the Aleman site. Our laboratory work this year includes (1) a characterization of the size and density of two stable plutonium(IV) colloid suspensions prepared by different techniques and (2) a study of the transmission of colloidal-size polystyrene beads through crushed-rock columns.

I. INTRODUCTION

The Radionuclide Migration (RNM) program was established in 1973 to study the extent and mechanisms by which radionuclides produced by underground nuclear tests move through the geologic media of the Nevada Test Site (NTS). Participating organizations include Los Alamos National Laboratory (LANL), Lawrence Livermore National Laboratory, the US Geological Survey, the Desert Research Institute, the Nevada Operations Office of the US Department of Energy, and various support organizations at the NTS. The contributions of LANL to this program are generally in the areas of radionuclide detection, geochemistry, radionuclide/rock interactions and radionuclide transport. We currently are engaged in field studies in three areas of the NTS. Since 1974 we have been monitoring the movement of tritium and fission products through alluvium at the Cambric site in Area 5. We have studied radionuclide migration from the Cheshire site in Area 20, where the nuclear test was conducted in fractured rhyolite. Most recently, we have initiated studies of radionuclide transport in the vicinity of the Aleman test, which was fired in the layered tuff of Area 3. The levels of radioactivity at each of these sites are rather low and generally not hazardous from a health physics perspective, but a sufficient variety of radioactive species are present to enable us to study their behavior in an underground environment. These field studies allow us to corroborate predictions based on laboratory measurements and validate mathematical models that describe radionuclide migration. There are obvious areas of mutual interest in the RNM program and the Nevada Nuclear Waste Storage Investigations (NNWSI) project, and LANL personnel contribute to both programs. In this report we will review work we accomplished during FY 1987, including both field studies and laboratory work applicable to the RNM program. We have described past accomplishments in this program in a number of journal articles and annual reports.[1-10]

II. CAMBRIC STUDIES

Our first field experiment in the RNM program has been a long-term single-well pumping test in which the cavity of a nuclear explosion is treated as the slug-injection point and tritium and fission products serve as the tracers. We chose the 0.75-kt nuclear test called Cambric for this experiment because (1) the small yield did not affect the natural hydrology of the area to any great extent, (2) there was sufficient tritium and fission products to serve as tracers for water movement and to provide sorption data, and (3) the alluvium was relatively uniform so that modeling would be simplified. The two wells at the Cambric site are 91 m apart; the RNM-1 well extends through the cavity and is pumped yearly to monitor the concentrations of radionuclides in the cavity region, whereas the RNM-2S well is pumped continuously at a rate of 2.3 m^3/min. Effluent from the RNM-2S well is sampled monthly for tritium and ^{85}Kr. Large-volume samples (208 ℓ) are collected monthly also; we either boil these samples down to dryness and examine the residue for gamma-emitting fission products, or we store them for special analyses for such radionuclides as ^{36}Cl, ^{129}I, or ^{99}Tc. A more complete description of our sampling and counting protocols is given in Ref. 9. In the following sections, we present data acquired during the past year concerning tritium and fission product concentrations in RNM waters, and we relate this information to earlier data. We also discuss the application of a model to the elution of ^{36}Cl from the Cambric cavity.

A. Tritium Migration (S. Maestas and J. L. Thompson)

The tritium concentration in the effluent from RNM-2S continues to diminish at an ever slower rate. Numerical data for the past year are given in Table I; in Figs. 1 and 2 we display the complete data set. We are interested in defining the shape of the tritium elution tail because this region of the curve may be critical for determining the model parameters giving the best fit (see the discussion under ^{36}Cl migration). We calculate that at the end of September 1987 about 80% of the tritium initially present in the cavity has been pumped out through RNM-2S. The concentration of tritium remaining in RNM-1 is now quite low, as is shown in Table II.

B. Fission Product Migration (S. Maestas, F. O. Lawrence, J. Drake, D. W. Efurd, J. D. Gallagher, and J. L. Thompson)

As we have shown in Table III and Fig. 3, the ^{85}Kr in RNM-2S water is decreasing at approximately the same rate as the tritium. The ratio of ^{85}Kr/tritium may be changing

TABLE I. TRITIUM ANALYSES OF RNM-2S WATER SAMPLES

Identification Number	Date Collected	Volume Pumped (10^6 m^3)	Tritium[a] (10^{-4} μCi/mℓ) At Counting Time	At T_o 5/14/65
G 1463	10/17/86	11.667	8.68	28.9
G 1464	11/21/86	11.784	8.34	28.0
G 1465	12/22/86	11.887	8.23	27.8
G 1466	01/30/87	12.018	8.03	27.2
G 1467	02/20/87	12.088	8.02	27.3
G 1468	03/17/87	12.171	7.91	27.0
G 1469	04/16/87	12.270	7.61	26.1
G 1470	05/21/87	12.384	7.55	26.0
G 1471	06/24/87	12.498	7.26	25.2
G 1472	07/24/87	12.598	7.18	25.0
G 1473	08/20/87	12.683	7.07	24.7
G 1474	09/15/87	12.769	6.98	24.5

[a] Standard deviation of counting data <1%.

TABLE II. TRITIUM CONCENTRATION IN RNM-1 WATER (1987)

Identification Number	Volume Pumped (m^3)	Tritium Concentration (10^{-6} μCi/mℓ) On Collection Date 5/7/86	Corrected to Cambric t_o 5/14/65
T-1	2	1.19	4.07
T-2	19	1.14	3.90
T-3	39	1.15	3.93
T-4	72	1.21	4.14
T-5	77	1.16	3.97
T-6	78	1.24	4.24
434-3-87-002[a]	73	1.05	3.59
			Average 3.98

[a] Collected in a gas-tight pressurized tube.

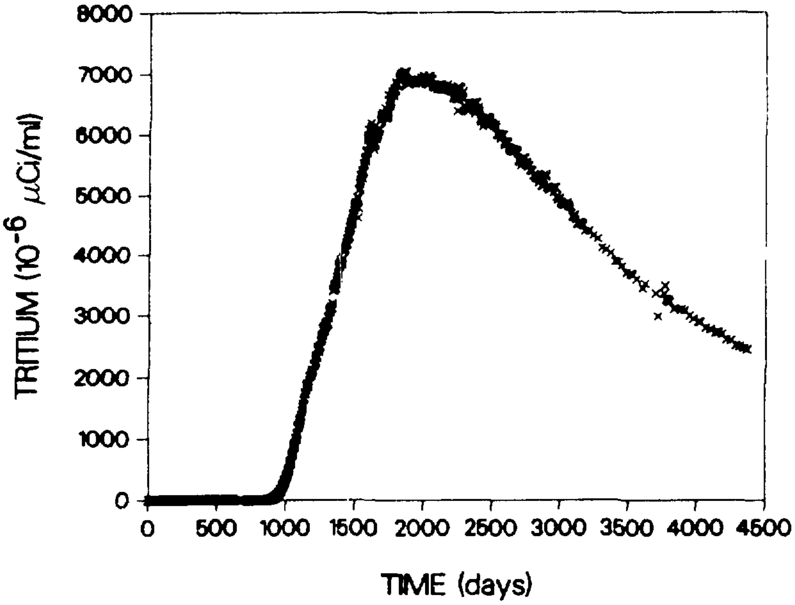

Fig. 1. Tritium concentration in water pumped from RNM2-2S *vs* time.

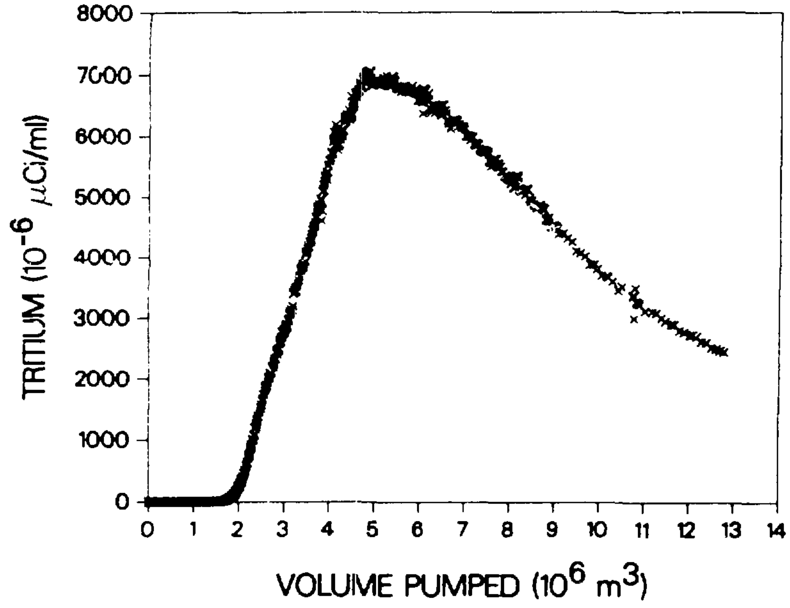

Fig. 2. Tritium concentration in water pumped from RNM-2S *vs* volume pumped.

TABLE III. TRITIUM AND ^{85}Kr ANALYSES OF PRESSURIZED WATER SAMPLES FROM RNM-2S[a]

Identification Number	Date Collected	Volume Pumped (10^6 m^3)	Tritium Concentration (10^{-3} μCi/mℓ)	^{85}Kr Concentration (10^{-7} μCi/mℓ)	^{85}Kr/Tritium Atom Ratio[b] ($\times 10^5$)	^{85}Kr/Tritium Ratio[c]
434-1-86-019	10/06/86	11.634	2.90	2.25	6.8	0.56
434-1-86-022	11/07/86	11.737	2.84	2.04	6.3	0.52
434-1-86-023	12/03/86	11.824	2.80	1.58	4.9	0.40
434-1-87-003	01/30/87	12.018	2.72	2.11	6.7	0.55
434-1-87-005	02/20/87	12.088	2.72	1.87	6.0	0.49
434-1-87-007	03/17/87	12.171	2.69	1.77	5.7	0.47
434-1-87-010	04/09/87	12.247	2.67	2.00	6.5	0.53
434-1-87-013	06/04/87	12.431	2.57	2.02	6.8	0.56
434-1-87-015	07/10/87	12.561	2.51	1.92	6.7	0.55
434-1-87-017	08/04/87	12.634	2.49	2.18	7.6	0.62
434-1-87-019	09/03/87	12.730	2.47	1.93	6.8	0.56

[a] All activity levels corrected to Cambric zero time (May 14, 1965).

[b] 1.81×10^{13} atoms ^{85}Kr = 1 μCi; 2.08×10^{13} atoms tritium = 1 μCi.

[c] Measured ^{85}Kr/tritium atom ratio divided by ^{85}Kr/tritium atom ratio calculated for Cambric zero time (1.22×10^{-4}).

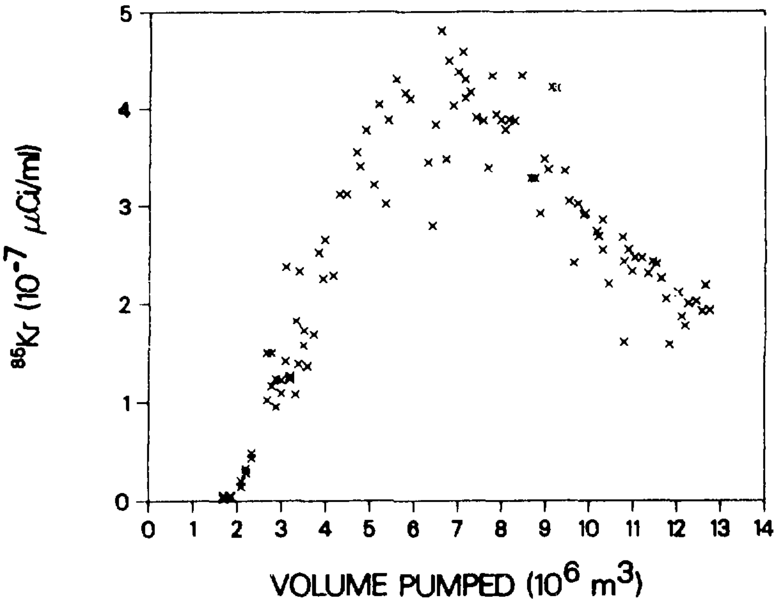

Fig. 3. The ^{85}Kr concentration in water pumped from RNM-2S.

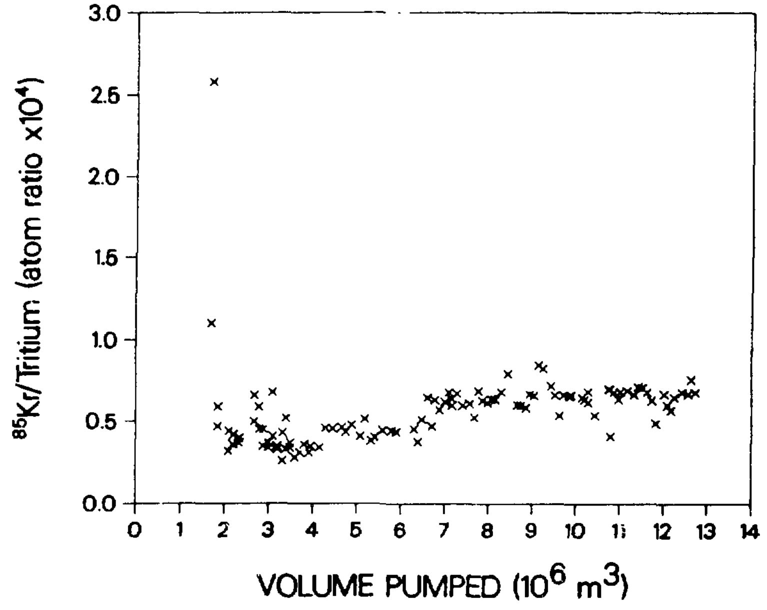

Fig. 4. Atom ratio of ^{85}Kr to tritium in water pumped from RNM-2S.

slowly (see Fig. 4), but it remains much lower than the source term value of 1.22 × 10^-4^. Correspondingly, the ^{85}Kr/tritium ratio for RNM-1 water is higher than the source term value (see Table IV). These facts indicate that the krypton is not moving away from the cavity region quite as rapidly as is the tritium, although in general the elution of these two radionuclides is rather similar, as can be seen by comparing Figs. 2 and 3.

TABLE IV. TRITIUM AND ^{85}Kr CONCENTRATIONS IN RNM-1 WATER

		Volume	Concentration[b]		^{85}Kr/Tritium	
Zone	Date	Pumped[a] (10^6 m^3)	Tritium (μCi/mℓ)	^{85}Kr (μCi/mℓ)	Atom Ratio[c] ($\times 10^4$)	Ratio[d]
Original-Zone IV	08/08/75	0.	1.5×10^{-1}	3.1×10^{-5}	1.8	1.5
Original-Zone V	08/14/75	0.	3.8×10^{-2}	6.1×10^{-6}	1.4	1.2
Zone IV + V	10/04/77	1.17	3.2×10^{-3}	3.4×10^{-5}	92	75
Zone IV + V	11/30/77	1.34	2.0×10^{-3}	2.7×10^{-6}	12	10
Zone IV + V	09/04/79	3.50	2.6×10^{-4}	2.5×10^{-7}	8.5	7
Zone IV + V	10/05/81	5.89	1.4×10^{-4}	8.3×10^{-8}	5.0	4
Zone IV + V	04/01/82	6.48	7.7×10^{-5}	3.0×10^{-8}	3.3	3
Zone IV + V	04/06/83	7.67	3.3×10^{-5}	1.3×10^{-8}	3.4	3
Zone IV + V	04/24/84	8.91	2.2×10^{-5}	1.0×10^{-8}	4.1	3
Zone IV + V	04/10/85	10.0	1.3×10^{-5}	1.2×10^{-8}	7.8	6
Zone IV + V	05/07/86	11.1	5.8×10^{-6}	2.1×10^{-9}	3.2	3
Zone IV + V	03/25/87	12.2	3.6×10^{-6}	1.7×10^{-9}	4.0	3

[a] Total volume of water removed from RNM-2S by indicated date.

[b] Values corrected to Cambric zero time.

[c] 1.81×10^{13} atoms ^{85}Kr = 1 μCi; 2.08×10^{13} atoms tritium = 1 μCi.

[d] Measured ^{85}Kr/tritium divided by ^{85}Kr/tritium calculated for Cambric (1.22×10^{-4}).

In Table V, we have included our entire data set for ^{90}Sr and ^{137}Cs concentrations in RNM-1 water so that trends in the data may be observed. The concentration of ^{90}Sr is so low that detection is difficult. The ^{137}Cs seems to be changing only a little and may have reached the point where desorption is balancing the removal of dissolved species.

TABLE V. TRITIUM, ^{90}Sr, AND ^{137}Cs CONCENTRATIONS IN RNM-1 WATER

		Volume Pumped[a]	Concentration[b]			Atom Ratio[c] ($\times 10^4$)	
Zone	Date	(10^6 m^3)	Tritium (μCi/mℓ)	^{90}Sr (μCi/mℓ)	^{137}Cs (μCi/mℓ)	^{90}Sr/T	^{137}Cs/T
Original-Zone IV	08/08/75	0.	1.5×10^{-1}	2.7×10^{-6}	4.5×10^{-7}	0.4	0.07
Original-Zone V	08/14/75	0.	3.8×10^{-2}	1.1×10^{-7}	9.0×10^{-8}	0.07	0.06
Zone IV + V	10/04/77	1.17	3.2×10^{-3}	4.6×10^{-7}	1.1×10^{-7}	3	0.8
Zone IV + V	11/30/77	1.34	2.0×10^{-3}	2.7×10^{-7}	2.2×10^{-7}	3	3
Zone IV + V	09/04/79	3.50	2.6×10^{-4}	9.1×10^{-8}	4.5×10^{-8}	8	4
Zone IV + V	10/05/81	5.89	1.4×10^{-4}	3.1×10^{-8}	2.6×10^{-8}	5	5
Zone IV + V	04/01/82	6.48	7.7×10^{-5}	2.7×10^{-8}	3.0×10^{-8}	8	9
Zone IV + V	04/06/83	7.67	3.3×10^{-5}	—	2.6×10^{-8}	-	19
Zone IV + V	04/24/84	8.91	2.2×10^{-5}	1.7×10^{-8}	2.0×10^{-8}	18	22
Zone IV + V	04/10/85	10.0	1.3×10^{-5}	1.1×10^{-8}	2.0×10^{-8}	20	38
Zone IV + V	05/07/86	11.1	5.8×10^{-6}	1.8×10^{-8}	2.0×10^{-8}	72	100
Zone IV + V	03/25/87	12.2	3.6×10^{-6}	3×10^{-9}	1.9×10^{-8}	20	130

[a] Total volume of water removed from RNM-2S by indicated date.

[b] Values corrected to Cambric zero time.

[c] 4.81×10^{13} atoms ^{90}Sr = 1 μCi; 5.09×10^{13} atoms ^{137}Cs = 1 μCi.

So far, we have not observed the migration of ^{90}Sr or ^{137}Cs from the cavity region to the RNM-2S well. This is in accord with laboratory measurements,[11] which show that these nuclides, present as cationic species, have very large sorption coefficients and adhere strongly to tuffaceous rock. It is probably also significant that we do not detect either of these nuclides migrating as colloids. The natural colloid content of the RNM-2S water is quite low, indicating that the alluvial soil is an efficient filter.

C. Chlorine-36 Migration (H. W. Bentley, D. Elmore, P. W. Kubik, A. E. Ogard, R. S. Rundberg, J. L. Thompson, and K. Wolfsberg)

We have recently analyzed a number of samples of RNM-2S water for the ^{36}Cl-to-chlorine ratio and can now define the elution of this radionuclide more completely than when we first discussed this subject.[7] The analyses were done by accelerator mass spectrometry at the University of Rochester, Rochester, New York. A complete description of the analytical method can be found in Elmore *et al.*[12] In Table VI we give the ^{36}Cl concentrations at various volumes of pumped effluent, and in Fig. 5 we compare the elution of ^{36}Cl with that of tritium. It is apparent that the breakthrough of the ^{36}Cl appears first and the maximum in the ^{36}Cl data also occurs before that of tritium. In soil chemistry studies, Thomas and Swoboda[13] observed that anions such as chloride were eluted before cations or neutral species such as tritiated water. This phenomenon has the descriptive name of anion exclusion. Anions, being of the same charge as the clays and zeolites in the soil, are repelled and effectively prevented from entering into the intragranular porosity of the soil particles. To calculate the value of anion exclusion in our ongoing experiment, it is necessary to fit separately the elution data for ^{36}Cl and tritium to a numerical equation (such as the two-dimensional solutions of Sauty[14]) for instantaneous tracer injection in a radial converging flow field. The difference in the two generated curves is then used to calculate an exclusion volume.

The early part of the ^{36}Cl and tritium elution curves through the maxima in Fig. 5 has been modeled by several methods. In Daniels,[6] the transport of tritiated water and ^{36}Cl away from the Cambric event was compared with the two-dimensional calculations of Sauty.[14] At that time, curves based on a Peclet number of 10 gave excellent fits to the

TABLE VI. CHLORINE-36 CONCENTRATIONS IN RNM-2S WATER SAMPLES

Identification Number	Volume Pumped (10^6 m^3)	^{36}Cl Concentration (10^{11} atoms/ℓ)
G 331	0.41	0.01 ± 0.002
G 556	1.40	0.03 ± 0.006
G 800	2.63	1.74 ± 0.11
434-9-78-009	2.61	2.03 ± 0.17
434-9-79-004	2.99	2.89 ± 0.16
G 912	3.18	3.04 ± 0.27
434-9-79-008	3.39	4.04 ± 0.20
434-9-79-012	3.81	3.95 ± 0.26
434-9-80-004	4.17	5.12 ± 0.39
G 1119	4.20	3.94 ± 0.37
G 1203	4.64	3.66 ± 0.26
G 1203	4.64	3.61 ± 0.33
434-9-80-009	4.88	3.87 ± 0.29
G 1269	5.23	3.56 ± 0.25
434-9-81-008	5.58	2.96 ± 0.26
G 1299	5.92	2.86 ± 0.26
434-9-82-005	6.59	2.73 ± 0.24
434-9-83-005	7.77	2.22 ± 0.20
434-9-84-005	8.94	1.64 ± 0.17
434-9-85-006	10.19	1.18 ± 0.10
434-9-86-002	10.87	1.10 ± 0.06
434-9-87-001	11.96	1.01 ± 0.05

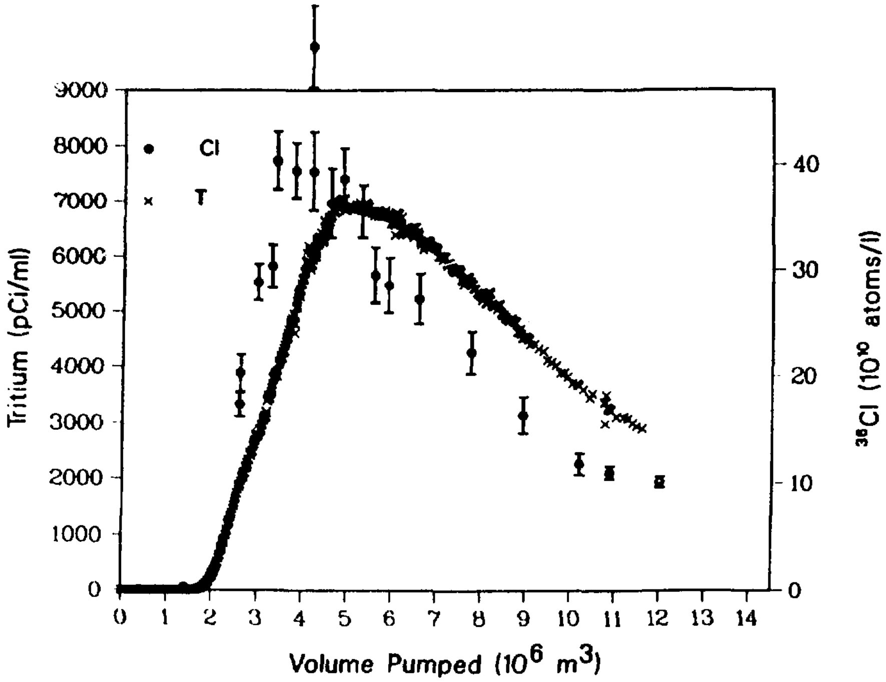

Fig. 5. Elution of tritium and ^{36}Cl from RNM-2S.

data through the maxima, but they also indicated that the data would diverge from the curves for both tritium and ^{36}Cl at longer elution times. The excellent fit could only be achieved by allowing the tritium source term to float; the best fit was a value that was 70% of the calculated source term. In the same report,[6] Travis presented a three-dimensional numerical simulation of the transport at Cambric that employed the TRACR3D model.[15] Both the leading edge of the elution front and the time of the peak concentration of tritium agreed well with the observed data. There were insufficient results at that time to model the tail of the elution curve.

Using the Sauty model and additional data from 1983 to the present, we have reexamined the results. Although a curve with a Peclet number of 10 still fits the tritium data through the maximum, a better fit to the tailing portion of the data can be made when a curve with a Peclet number of 6 (Fig. 6) is used. A similar fit to the ^{36}Cl data is shown in Fig. 7. However, the difference in slope between the data and the Sauty curve at longer

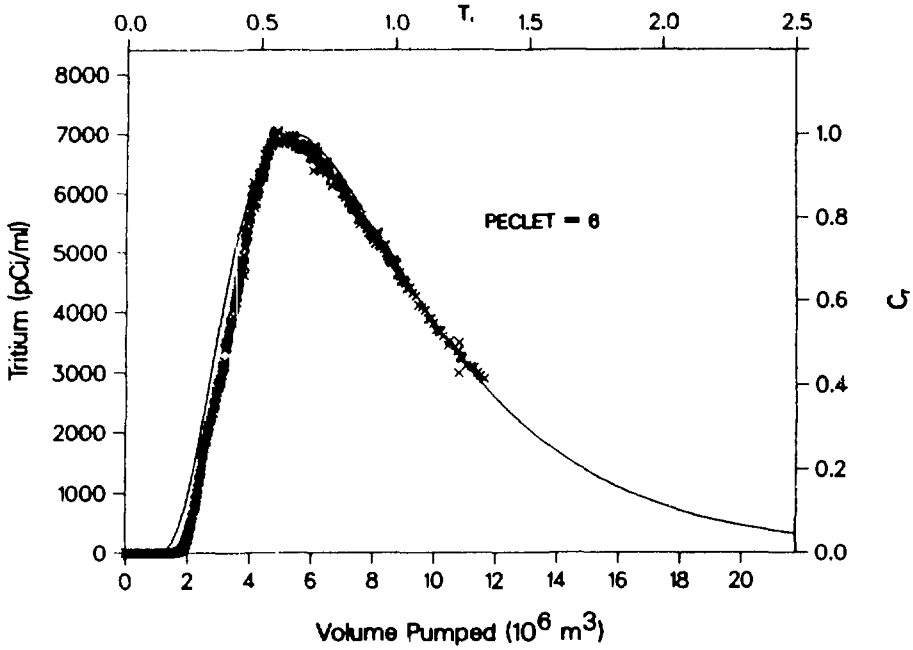

Fig. 6. Elution of tritium compared with Sauty Model.

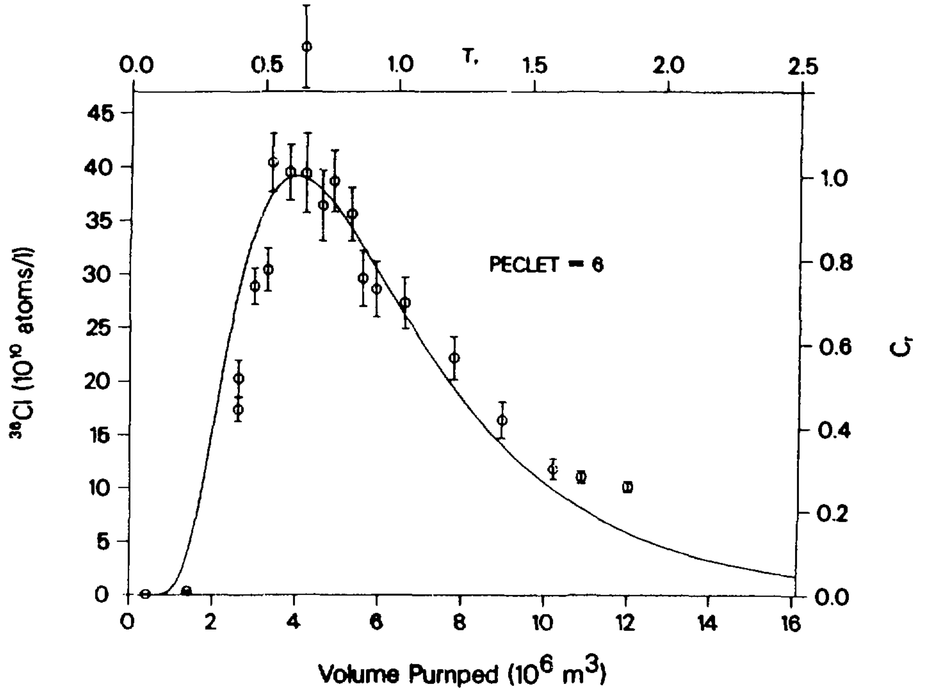

Fig. 7. Elution of ^{36}Cl compared with Sauty Model.

pumping times is still evident for both ^{36}Cl and tritium, which indicates that a curve with a still lower Peclet number may be needed to fit subsequent data.

The dimensionless time (T_r) of the Sauty curves, given in the upper abscissa in Figs. 6 and 7, equals 1 for the time required to pump the volume of water that would be contained in an imaginary cylinder whose radius is equal to the distance from the source term to the well. The volume of water from which the chloride ion is excluded is the difference in volumes for $T_r = 1$ on the ^{36}Cl curve (6.5×10^6 m^3) and on the tritium curve (8.6×10^6 m^3). Using these values, we can calculate that the chloride exclusion volume is 2.1×10^6 m^3. The mass of the alluvium contained in the same imaginary cylinder can be estimated from the properties of the alluvium. The bulk density of the alluvium is about 1.46 g/cm^3 and the estimated porosity is 0.42; thus, the mass of alluvium in the cylinder is 2.99×10^{10} kg. Anion exclusion is given in units of milliliters of liquid excluded by 100 g of soil, so the anion exclusion of the alluvium at the NTS is 7.0 mℓ/100 g. Thomas and Swoboda[13] found that anion exclusion for various soils varies between 3.7 mℓ/100 g for sandy loam soil and 20 mℓ/100 g for clay that was 40% montmorillonite. An alluvium had an anion exclusion of 3.9 mℓ/100 g—a value somewhat lower but comparable to the one we calculate.

A Peclet number of 6 corresponds to a dispersivity of 15.1 m for the geometry of this experiment. This value can be compared to the longitudinal dispersivities reported by Borg *et al.*,[16] which were estimated by calibrating mathematical models of transport against observed transport in field studies. Dispersivities were in the range of 11.6 to 91 m for a wide variety of lithologies. A sand or gravel deposit, which probably most closely approximates the tuffaceous alluvium of the NTS, had a calculated dispersivity of 21.3 m.

It appears that as pumping is continued with time, a Sauty curve with a lower Peclet number best fits the latest portion of the elution data. The calculated dispersivity correspondingly increases with time of pumping—an effect that has sometimes been called a "scaling effect" of dispersivities in field operations. Matheron and de Marsily [17] propose that the scaling effect observed in field experiments is an artifact of the model. They suggest that the convection-diffusion equation will not fit the transport of solutes (except for large distances or long times) because diffusion behavior is not homogeneous in three dimensions. They further suggest that all media are layered to some extent and that the different dispersivities of each of the horizontal layers as well as the vertical velocities must be considered.

The present field experiment presents an opportunity to model the transport of solutes in a relatively homogeneous media. Methods are being developed to calculate dispersivities as a function of concentration of the solute on the Sauty curve at different times. Such calculations will show if the asymptotic macrodispersion of Matheron and de Marsily is ever reached as the experiment is continued. An additional important benefit will be obtained by continuing this experiment until it is successfully modeled; it can then be used for validating codes to be used in the calculations of transport away from a high-level nuclear waste repository.

III. CHESHIRE STUDIES (S. Maestas, A. E. Ogard, and J. L. Thompson)

The Cheshire site in Area 20 affords us the opportunity to study radionuclide migration in a setting geologically less homogeneous than that of Cambric. The presence of natural hydraulic gradients and the likelihood of fracture flow add considerably to the complexity of analyzing the movement of tritium and fission products away from the shot cavity. The Cheshire test was conducted in February 1976 at a depth of 1174 m, which is about 544 m below the water table. The rock in this area is brecciated rhyolitic lava; there are zones of relatively permeable fractured material and relatively impermeable nonwelded or zeolitized tuff. We took water samples from near the cavity region in 1976 and again in 1983 and 1984. In 1985 we packed off the sampling perforations in the casing at 1200 m and, at a depth of 820 m, made new perforations from which we collected more samples. Our procedures for analyzing tritium and fission products in these water samples have been described in detail in an earlier report.[9] We experienced difficulty in interpreting our analytical data because the concentrations of tritium were not as large as expected for the cavity region and because both the tritium and fission product concentrations were nearly as great in samples withdrawn from the perforations at 820 m as they were from those taken at 1200 m. These problems are discussed in detail in earlier reports.[9,10]

During the past year, another hole, UE20n #1, was drilled vertically about 300 m from the Cheshire test site. This hole is 1000 m in depth and penetrates several relatively permeable zones that may serve as pathways for water flowing away from the cavity. Temperature logging in the hole indicated that water movement had occurred in the uppermost of these zones (roughly 700 to 820 m); tritium activity as monitored during the drilling was highest in this zone. The hole was cased to 696 m and a Moyno pump with a pumping speed of about 0.05 m^3/min (14 gals./min) was set just above the bottom of the casing. The pump was emplaced 06/22/87 and has operated intermittently since then. We collected several barrels and pressure tubes of water on 07/27/87 to measure tritium, ^{85}Kr, and fission products by our usual procedures. However, the water contained so much detergent from the drilling fluid and such a large amount of particulate material that we actually processed only about 80 ℓ. At the time of sampling, about 270 m^3 of water had been pumped from the hole; we anticipate that natural water flow and intermittent pumping will improve the quality of water for future samples. The results of our analysis of this sample from UE20n #1 are given in Table VII. For purposes of comparison, we have included data from the last two samplings of U20n. It appears that the tritium concentration in our sample from UE20n #1 is appreciably higher than that in the earlier samples from U20n. In fact, the tritium concentration is approximately the same as that of samples from U20n obtained in August 1984 (Ref. 9). The ^{85}Kr and ^{125}Sb are somewhat lower than in the earlier samples, and the ^{137}Cs is dramatically lower. These data are not unreasonable because we know that tritium, ^{85}Kr, and ^{125}Sb move with the groundwater, and ^{137}Cs tends to sorb on the rock. It is interesting that a major fraction of the ^{137}Cs in our sample passed through both 0.6- and 0.05-μm filters, which suggests that the cesium is either dissolved or in the form of rather small particulates. We expect to investigate the size distribution of particulates in future samples that may be more representative of formation water.

TABLE VII. RADIONUCLIDES IN WATER AT CHESHIRE[a]

Identification	Date	Concentration (μCi/mℓ)			
Number	Collected	Tritium	^{85}Kr	^{125}Sb	^{137}Cs
852-9-85-004	06/18/85	4.1×10^{-1}	2.6×10^{-4}	3.2×10^{-6}	4.5×10^{-7}
852-9-85-005	11/04/85	3.9×10^{-1}	2.4×10^{-4}	4.1×10^{-6}	6.9×10^{-7}
853-9-87-001	07/21/87	5.4×10^{-1}	1.3×10^{-4}	7×10^{-7}	5×10^{-10}

[a] All activities are corrected to t_o = 02/14/76.

IV. ALEMAN AND RELATED STUDIES (G. W. Butler, W. R. Daniels, J. Drake, W. D. Efurd, J. D. Gallagher, J. S. Gilmore, G. W. Knobeloch, S. Maestas, A. E. Ogard, R. S. Rundberg, K. W. Thomas, J. L. Thompson, and K. Wolfsberg)

In 1985 we became involved in an investigation of radionuclide movement that occurred in the layered tuffs of Areas 3 and 4 of the NTS. Water samples from an emplacement hole, U3kz, contained tritium; a more detailed analysis revealed that ^{85}Kr, ^{106}Ru, ^{125}Sb, ^{137}Cs, and plutonium were also present in water at this site, suggesting that there was movement of material from one of the expended test holes in the vicinity. We were able to identify the probable source of these radionuclides on the basis of an isotopic analysis of very small amounts of ^{101}Rh and ^{102}Rh. The source was the Sandreef event, which had been conducted in 1977 about 350 m north of U3kz. The plutonium found in the U3kz samples was shown to have come from airbourne contamination and was not connected with Sandreef. However, movement of tritium and fission products underground over such a large distance is an interesting phenomenon, and we are trying to learn how this took place. Before firing the test shot Aleman in U3kz, we drilled an auxillary hole, UE3e #1, 61 m north of U3kz. Water from this hole contained tritium and the same suite of fission products found in U3kz; gamma logging showed a narrow region of gamma activity at a depth of 658 m. Sidewall samples collected from this depth contained ^{137}Cs in measurable quantities. Before the Aleman test shot was fired, we added tracers to enable us to recognize samples associated with this event. We placed NaCl, cobalt, and ^{244}Cm in U3kz and NaBr in UE3e #1. In September 1986, UE3e #1 was stemmed and Aleman was fired. A detailed account of our work connected with the Aleman event up to this point is given in Ref. 10.

Early in 1987 we began drilling a hole, UE3e #2, 12 m north of UE3e #1. Our goal was to obtain core from the formation through which the radioactivity moved south from Sandreef. We hoped that by studying this core we might learn how the activity had moved (that is, by prompt injection, migration with groundwater, or transport as colloids). The hole was drilled with air foam to 594 m and then was cored to 657 m. Although core recovery was good and some tritium was found in the water during drilling, we were unable to locate any core sections with high gamma activity. The core was scanned with several types of survey meters, and selected portions were counted for extended times with a Ge(Li) detector. We believe that our failure to locate activity in the UE3e #2 core indicates that transport occurred through vertically oriented fractures that we did not intersect during this drilling. We expect to make another attempt in the next year to locate the path of radioactive movement. Meanwhile, we are monitoring the water level in this hole as part of a wider effort to gain information concerning the pressurized acquifier that exists in this region of the NTS.

We have analyzed water samples from another hole further north in Area 4. This hole, UE4t, was drilled during the first quarter of 1987 about 180 m from the location of a test called Gascon, which was conducted in November 1986. The hole was drilled in stages, interspersed with several-week intervals during which the water was monitored for tritium activity. Despite the proximity to the Gascon event and several older test sites, we have found no activity in water from UE4t. We are continuing to monitor the water in this hole and also are collecting data on water pressure at this location.

V. LABORATORY RESEARCH

Los Alamos personnel are engaged in a number of laboratory studies with direct bearing on radionuclide migration; many of these studies are part of our NNWSI research. In this report, we describe two laboratory projects related to colloids. Because there is the possibility that significant amounts of radioactive materials may be transported as colloids through groundwater systems, we have been seeking techniques for producing and characterizing radioactive colloids and determining the conditions under which they are mobile in rock/water systems. The studies described here are continuing, and these are interim reports.

A. Plutonium(IV) Colloid Characterization (A. J. Mitchell, R. S. Rundberg, J. F. Sledgianowski, J. L. Thompson, and I. R. Triay)

Plutonium may assume a quadravalent, polymeric form that can exist as a colloidal suspension for long periods of time. The possibility that plutonium colloid could move with groundwater interests us because in both the NNWSI and the RNM projects it is important to evaluate plutonium movement in the environment. As part of our attempt to better understand the behavior of plutonium in the environment, we are seeking to characterize plutonium colloids. Specifically, we have measured the size distribution and density of colloidal particulates in two plutonium(IV) suspensions prepared in very different ways. We achieved these measurements through a combination of filtration, ultracentrifugation, and photon auto-correlation spectroscopy. Our results indicate that different preparative methods may lead to very different size distributions; our data also suggest that plutonium(IV) colloids may have a lower density than is generally assumed.

We studied two plutonium(IV) colloid suspensions that had been prepared elsewhere in the Laboratory,* packaged in polyethylene bottles, and stored in our facilities for extended periods of time (34 months for Suspension A, 25 months for Suspension B). Several times per year the bottles were placed in an ultrasonic bath for several minutes and samples

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* We acknowledge with appreciation the work of D. E. Hobart, T. W. Newton, and P. D. Palmer in preparing these materials.

were withdrawn for plutonium assay by alpha counting. The radioactivities were constant with time during the storage period.

Suspension A was prepared by diluting a perchloric acid stock of ^{239}Pu with distilled water. The colloid was separated from other plutonium species by passing it through a column loaded with cation exchange resin; the eluate was further diluted with ammonium bicarbonate solution. Suspension A, as we received it, was approximately 3×10^{-6} M in ^{239}Pu and 3×10^{-3} M in bicarbonate ion; it had a pH of 8.4.

Suspension B was prepared originally as plutonium(V) in 10^{-3} M sodium bicarbonate solution. It was checked spectoscopically for several weeks; after a month there was no longer evidence of plutonium(V) or plutonium(VI), and the total plutonium assay was constant at about 8×10^{-6} M. Filtration data indicated that the plutonium was in the form of filterable material less than 50 nm and greater than 5 nm in diameter. The pH was 8.6.

To narrow the range of particulate diameters, we filtered both suspensions through Nuclepore filters with 30-nm-pore diameters. Less than 20% of the plutonium colloid in Suspension A passed through this filter, whereas almost 90% of the colloid in Suspension B passed through. None of Suspension A or B passed through an Amicon YMT filter. The Amicon YMT filter has a nominal molecular weight cutoff of 30 000 for globular molecules, which corresponds to a pore diameter of 4 to 5 nm. After filtration, our two study suspensions contained plutonium(IV) particulates in a diameter range of 30 to 5 nm; the plutonium concentrations were 5.2×10^{-7} M (Suspension A) and 7.6×10^{-6} M (Suspension B).

We used an ultracentrifuge (Sorvall, Model OTD65B) to further characterize the filtered plutonium suspensions. Following the centrifugation, we withdrew liquid by pipette from the centrifuge tubes to calibrated depths and measured the plutonium activity in each increment by liquid scintillation counting. We assumed that the movement of particles during centrifugation followed the equation

$$\ell n \frac{R_2}{R_1} = \frac{d^2 \omega^2 (\rho - \rho_{H_2O}) \Delta t}{18 \eta} ,$$

where

R_1 and R_2 = radial position of a particle relative to axis of rotation at times t_1 and t_2,
d = diameter of the particle (m),
ω = angular velocity = 2 π (frequency) (revolutions/s),
Δt = $t_2 - t_1$ (s),
η = viscosity of water at 20°C (1.00×10^{-3} kg/m · s),
ρ = density of the particle (kg/m^3), and
ρ_{H_2O} = density of water at 20°C (0.9982×10^3 kg/m^3).

Changes in plutonium activity as a function of depth were measured at various centrifuge speeds and times. From these data we can estimate values of R_1 and R_2 for a typical particle. Because the particles are in the diameter range of 30 to 5 nm, we can calculate a range of densities corresponding to these sizes. Density values must be larger than that of water, but smaller than that of PuO_2 (11.46 g/cm^3). If we centrifuged a suspension of plutonium particles of uniform density and size at the proper speed, we should get a sharp break in the plutonium distribution (that is, activity) as a function of depth in the centrifuge tube. In our experiments, the degree to which the observed data approximate such idealized data is a measure of the uniformity of the size and/or density of the plutonium(IV) particulates. For example, the activity change during the 30×10^3 rpm run (refer to Table VIII) indicates that although a large fraction of the plutonium particles moved 1 cm down the tube during centrifugation, some particles did not move this far. Presumably these latter particles were either smaller or less dense than the majority. When the centrifugation data indicate the movement of an appreciable fraction of the particles, we can calculate the density of these particles. The range of densities thus calculated is rather wide because the range of possible particle diameters extends from 30 to 5 nm. However, by examining the size distribution of particles with a photon auto-correlation spectrometer, we can narrow the limits of both the particle diameters and densities.

We measured the relative concentration of Pu(IV) colloid in the centrifuge tubes after centrifugation at varying speeds and times. In Tables VIII and IX, the liquid levels before

TABLE VIII. CONCENTRATION OF PLUTONIUM(IV) COLLOID AFTER CENTRIFUGATION AT VARYING DEPTHS IN THE TUBE – SUSPENSION A

Rotor Speed (10^3 rev/min)	Time (min)	Liquid Level Relative To Axis of Rotor (cm)	Relative Concentration (%)	
			1st Set	2nd Set
12	30	8.6 - 9.0	97	99
		9.0 - 9.4	97	100
		9.4 - 9.7	100	101
		9.7 - 10.1	95	101
		10.1 - 10.5	98	100
		10.5 - 10.8	100	103
		10.8 - 11.2	100	98
		11.2 - 11.8	96	100
18	30	9.4 - 9.8	35	39
		9.8 - 10.1	37	45
		10.1 - 10.5	50	53
		10.5 - 10.8	80	76
		10.8 - 11.2	71	87
		11.2 - 12.1	187	83
30	30	9.6 - 9.8	8	12
		9.8 - 10.1	14	14
		10.1 - 10.4	10	12
		10.4 - 10.7	23	19
		10.7 - 10.9	32	—
		10.9 - 11.2	51	35
		11.2 - 11.5	70	38
		11.5 - 11.8	107	252
		11.8 - 12.1	481	354
48	30	9.8 - 10.2	9	2
		10.2 - 10.4	12	2
		10.4 - 10.7	9	2
		10.7 - 11.0	9	2
		11.0 - 11.3	11	2
		11.3 - 11.6	15	4
		11.6 - 12.1	66	9

TABLE IX. CONCENTRATION OF PLUTONIUM(IV) COLLOID AFTER CENTRIFUGATION AT VARYING DEPTHS IN THE TUBE – SUSPENSION B

Rotor Speed (10^3 rev/min)	Time (min)	Liquid Level Relative To Axis of Rotor (cm)	Relative Concentration (%)	
			1st Set	2nd Set
6	30	9.3 - 9.7	87	
		9.7 - 10.0	88	
		10.0 - 10.4	75	
		10.4 - 10.7	92	
		10.7 - 11.0	110	
		11.0 - 11.4	84	
		11.4 - 11.7	107	
		11.7 - 12.1	122	
10	30	9.7 - 10.0	6	
		10.0 - 10.3	6	
		10.3 - 10.7	6	
		10.7 - 11.0	7	
		11.0 - 11.4	9	
		11.4 - 11.7	12	
		11.7 - 12.1	1210	
		9.4 - 9.8	10	
		9.8 - 10.1	9	
		10.1 - 10.4	10	
		10.4 - 10.8	10	
		10.8 - 11.1	11	
		11.1 - 11.4	20	
		11.4 - 11.7	27	
		11.7 - 12.1	946	
12	30	9.8 - 10.0	3	
		10.0 - 10.4	7	
		10.4 - 10.8	8	
		10.8 - 11.2	33	
		11.2 - 11.5	28	
		11.5 - 12.1	461	
18	15	9.2 - 10.2	4	2
		10.2 - 11.2	4	6

and after sampling are given relative to distance from the axis of rotation of the centrifuge. The data for Suspension A are given in Table VIII; the data for Suspension B are given in Table IX. It is apparent that the colloids in Suspension A and Suspension B are not of uniform size, but are distributed somewhat in diameter over the range of 30 to 5 nm. As noted above, it appears that the majority of particles in Suspension A moved about 1 cm during the 30 × 10^3 rpm run. A similar movement of the particles in Suspension B occurred at 12 x 10^3 rpm (Table IX). The fact that higher centrifuge speeds are required to move the majority of particles in Suspension A than those in Suspension B indicates that, on average, the particles in Suspension A are smaller or less dense. Centrifugation data alone are of no help in distinguishing between variations of particle size and density. However, because we have experimental limits on the size range of these plutonium colloids, we can calculate corresponding limits on their range of densities. For example, there appears to have been little movement of even the largest (that is, 30-nm) particles in Suspension B at 6 × 10^3 rpm; therefore, we can calculate that their maximum density must be about 6.7 g/cm^3. Of course, smaller particles could have had higher densities and still have shown no movement. Here, the additional information obtained by photon auto-correlation spectrometry becomes very helpful. We used this technique to determine that the colloid size distribution peak in Suspension B had a centriod value of 24 nm and a full width at half maximum of 8.6 nm. Using these values and the data from the runs at 12 × 10^3 and 10 × 10^3 rpm, we calculate that the density of the plutonium(IV) colloid particles in our Suspension B is about 3.2 gm/cm^3, and there is a range of 1.8 to 4.9 gm/cm^3.

We made similar calculations of the density of plutonium(IV) particles in Suspension A. In this case, we used the break in the concentration profiles at 30 × 10^3 and 18 × 10^3 rpm, but we have not yet obtained a size distribution from the auto-correlation spectrometer. Our limits of the density of the plutonium(IV) colloid in Suspension A are thus rather broad—ranging from 1.1 to about 6 g/cm^3.

We can observe two facts about these plutonium(IV) suspensions: (1) both are composed of particles with varying size/density values (Suspension A with a much wider range than Suspension B), and (2) Suspension B is composed of particles generally more dense than those of Suspension A. The range of particle sizes allows for a rather wide range of calculated particle densities, particularly for Suspension A, but in general the values are much less than the 11.46 g/cm^3 sometimes assumed in the literature.[18] It is apparent that the properties of plutonium(IV) colloids are strongly influenced by the conditions under which they form, and researchers should be wary of comparisons between colloid populations with different histories.

B. Colloid Transport (M. A. Ott, J. F. Sledgianowski, and J. L. Thompson)

Because colloid transport is generally recognized as one of the means by which radioactive materials may move through geologic media, we are developing a program to study this phenomenon. We had seen evidence of americium and plutonium colloid transport through small crushed-rock columns, and we decided to use similar columns for exploring the effects of colloid size on transmission through the column. The colloids we used in this case were polystyrene beads impregnated with a fluorescent dye (Polysciences, Inc.) that we could detect with very high sensitivity by using a fluorometer system (Spex, Model F222). Our procedure was to introduce colloids and tritiated water at the top of the column and collect elution fractions at a fixed flow of water through the column. Measurement of both the tritium and colloid content of each fraction enabled us to determine the total amount of colloid passing through the column as well as its elution rate relative to the solvent front.

We used columns 5 cm long and 0.45 cm in diameter that were filled with crushed tuff sieved to particle sizes between 75 and 500 μm. The column porosity was about 0.5 to 0.6 and the elution rate was 0.2 mℓ/h, which corresponds to an interstitial velocity of a few hundred m/yr. We selected polystyrene beads of 0.1-, 0.91-, and 9.55-μm diameter for this work; each size bead behaved differently. The 0.91-μm particles passed through the column with the water front in good yields (generally about 60 to 70% of the amount introduced). The 9.55-μm particles passed through the column with a much lower efficiency; there was often a small peak with the water front and a larger peak a short time later. The 0.1-μm particles apparently diffused into the pore spaces in the rock and were sorbed; they were not eluted after up to eight column volumes of water passed through the column. Attempts to elute these small particles with ionic solutions and organic solvents were not successful.

This study is obviously preliminary, but we believe it gives some indication of the size boundaries for colloid transport in geologic media. These results will be correlated with related information, such as sorption data, that we have gathered through other studies.

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