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Laboratory and Field Studies Related to the Radionuclide Migration Project

October 1, 1983—September 30, 1984

Compiled and Edited by Joseph L. Thompson

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CONTENTS

	<u>Page</u>
ABSTRACT.	1
I. INTRODUCTION	2
II. CAMBRIC STUDIES.	3
A. Tritium Movement from RNM-1 to RNM-2S	3
B. Krypton Migration	7
C. Anion Migration	7
D. Cation Migration.	14
III. CHESHIRE STUDIES	16
A. Lithium Concentration	19
B. Tritium Concentration	20
C. Fission Product and Other Radioactive Element Concentrations. .	22
D. Radionuclide Migration from Cheshire.	25
IV. NASH STUDIES	26
V. LABORATORY AND COMPUTATIONAL WORK.	28
A. Sorption of Radionuclides on Tuff	28
B. Solubility and Speciation	30
C. Studies of Colloids	31
D. High-Precision Isotopic Analysis of Small Quantities of Plutonium.	31
VI. REFERENCES	32

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ABSTRACT

Laboratory and field work performed in FY 1984 in connection with the Radionuclide Migration Project are reviewed in this report. We have continued to monitor the migration of tritium, krypton, and iodine from the Cambric cavity region to the pumped satellite well RMM-2S at the Nevada Test Site. So far, no radioactive cations have appeared in the RMM-2S water. The concentrations of lithium, tritium, and a number of fission product and other radioactive elements have been measured at the Cheshire site. The tritium concentration at Cheshire is anomalously low. It appears that retention of radionuclides by the rhyolite of Pahute Mesa is comparable to that by the alluvium of Frenchman Flat. We are continuing our studies of sorption phenomena, chemical speciation, and colloid behavior. Computational work on chemical equilibria and colloid transport is progressing. We have improved our capabilities in the areas of gamma spectroscopy and mass spectrometry.

I. INTRODUCTION

In 1973, the Radionuclide Migration (RMM) project was started at the Nevada Test Site (NTS) to determine the potential for movement, both on and off the NTS, of radioactivity from underground nuclear explosions. Particular emphasis has been placed on measuring the rates of migration of radionuclides from explosion-modified zones in various geologic media. This program is a unique and vital part of the Department of Energy's efforts to ensure that nuclear tests do not endanger the public or NTS personnel because of the spread of radioactive material through underground routes. Organizations participating in this program include Los Alamos National Laboratory, Lawrence Livermore National Laboratory, the US Geological Survey, the Desert Research Institute, and various support organizations. Personnel from Los Alamos National Laboratory play an important role in the RMM project by providing expertise in radionuclide detection, by defining the interactions of radionuclides with geologic media, and by evaluating the importance of geochemical factors in radionuclide movement. There is a strong synergistic relationship between the RMM project and the Nevada Nuclear Waste Storage Investigations project at the Laboratory.

During FY 1984, analytical work at the Laboratory for the RMM program has focused largely on samples derived from two test sites at the NTS: Cambric in area 5 and Cheshire in area 20. The Cambric site is the location of one of the few large-scale field studies of radionuclide migration conducted anywhere in the world; it has been the principal source of data concerning the mobility of radioactive elements through tuff under field conditions. The Cheshire site is located on Pahute Mesa and provides an opportunity to evaluate the effectiveness of rhyolite in retarding the movement of radionuclides. However, natural hydrologic gradients at Cheshire complicate interpretation of data on the concentrations of radioactive elements in the cavity region.

A wide variety of laboratory studies relevant to the RMM program are under way at Los Alamos. In particular, there is a continuing effort to define the importance of chemical speciation in rock/solute interactions. It appears that, especially for the actinides, the presence of charged complexes or colloidal material strongly influences the movement of the radioactive elements through crushed or fractured rock. There is also a continuing effort to improve analytical sensitivity for detecting various radionuclides and to develop new methods for treating samples without changing critical properties

such as pH and Eh. Finally, a significant effort has been made this year to outline the RNM program for the next 5 years; we hope to secure a funding commitment that will allow for an orderly integration of continuing projects and new initiatives.

II. CAMBRIC STUDIES

The 0.75-kt nuclear test Cambric was conducted May 14, 1965, beneath the water table in tuffaceous alluvium at Frenchman Flat on the NTS. When the RNM project was started in 1973, the Cambric site was selected for initial study, and it continues to be a source of unique and interesting data. The Cambric detonation point was 294 m below the ground surface and 73 m below the water table. There is very little water movement at this depth in the alluvium that underlies this playa, and the tritium and fission products were still in the Cambric cavity region at the time the study was initiated. Samples collected on re-entry of the cavity in 1974 allowed us to measure distributions of radionuclides between solid and water and yielded information about the spatial location of certain elements relative to the detonation point (refractory elements tended to collect at the bottom of the cavity, whereas volatile elements were more concentrated in the rubble chimney above the cavity). In 1975, a hydraulic gradient was introduced at the Cambric site by pumping water from a satellite well (RNM-2S) located 91 m from the re-entry well (RNM-1). Since 1975, concentrations of dissolved radionuclides and tritium (which is present as tritiated water) have been monitored from both RNM-1 and RNM-2S to observe their transport through the alluvium between these wells. Details of the early work at Cambric are given in Refs. 1 and 2; more recent activities are described in Refs. 3 through 6. During the period covered by this report, we have continued to monitor the concentrations of radionuclides in water samples from both RNM-1 and RNM-2S.

A. Tritium Movement from RNM-1 to RNM-2S (J. L. Thompson, S. Maestas, and K. S. Kundberg)

The pump at RNM-2S has operated during FY 1984 at about 600 gal. per minute without interruption. Tritium concentrations in the water at RNM-2S for FY 1984 are given in Table 1. Figures 1 and 2 show cumulative data from the time pumping began; tritium activity levels are referenced to the time

TABLE I
TRITIUM CONCENTRATION IN WATER PUMPED FROM KMI-2S

Identification Number	Gallons Pumped ($\times 10^6$)	Date	Tritium ^a (10^3 pCi/ml)
G1400	2190.4	10/14/83	1.81
G1401	2199.6	10/27/83	1.79
G1402	2206.6	11/02/83	1.81
G1403	2213.5	11/10/83	1.81
G1404	2218.6	11/16/83	1.81
G1405	2223.8	11/22/83	1.75
G1406	2231.3	12/01/83	1.74
G1407	2238.1	12/09/83	1.74
G1408	2242.4	12/14/83	1.74
G1409	2249.1	12/22/83	1.72
G1410	2255.1	12/29/83	1.70
G1411	2266.9	01/12/84	1.69
G1412	2272.9	01/18/84	1.69
G1413	2278.7	01/26/84	1.70
G1414	2284.7	02/02/84	1.70
G1415	2290.7	02/09/84	1.70
G1416	2296.7	02/16/84	1.68
G1417	2302.8	02/23/84	1.67
G1418	2308.8	03/01/84	1.67
G1419	2314.6	03/08/84	1.66
G1420	2321.5	03/16/84	1.60
G1421	2326.6	03/22/84	1.61
G1422	2332.6	03/29/84	1.60
G1423	2338.6	04/05/84	1.61
G1424	2344.5	04/12/84	1.58
G1425	2351.3	04/20/84	1.55
G1426	2356.4	04/26/84	1.56
G1427	2362.4	05/03/84	1.55
G1428	2369.1	05/11/84	1.56
G1429	2375.1	05/18/84	1.56
G1430	2381.1	05/25/84	1.55
G1431	2387.1	06/01/84	1.54
G1432	2392.3	06/07/84	1.53
G1433	2398.2	06/14/84	1.50
G1434	2426.2	07/18/84	1.50
G1435	2449.1	08/17/84	1.46
G1436	2476.5	09/19/84	1.44

^aStandard deviation of counting data <0.1%.

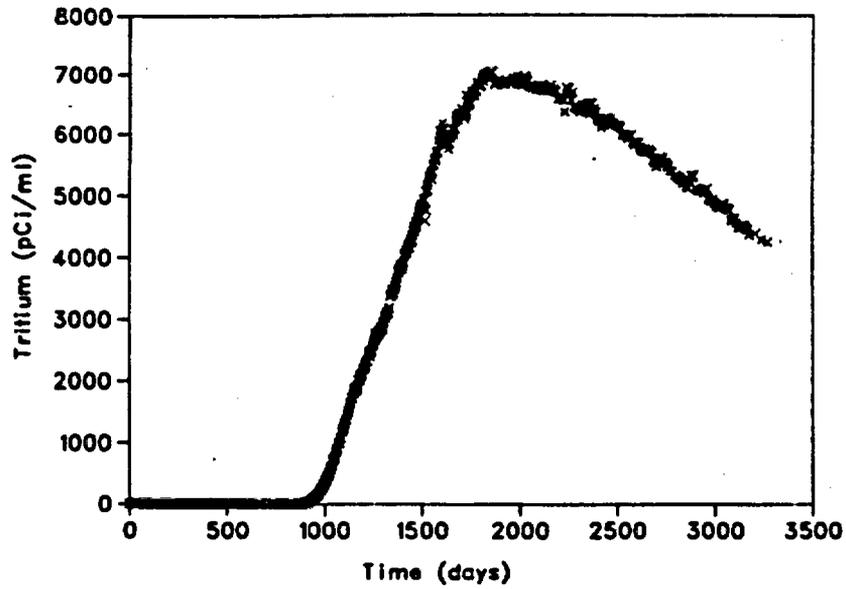


Fig. 1. Tritium concentration in water pumped from KM-2S vs time. Values are corrected to Cambrian zero time.

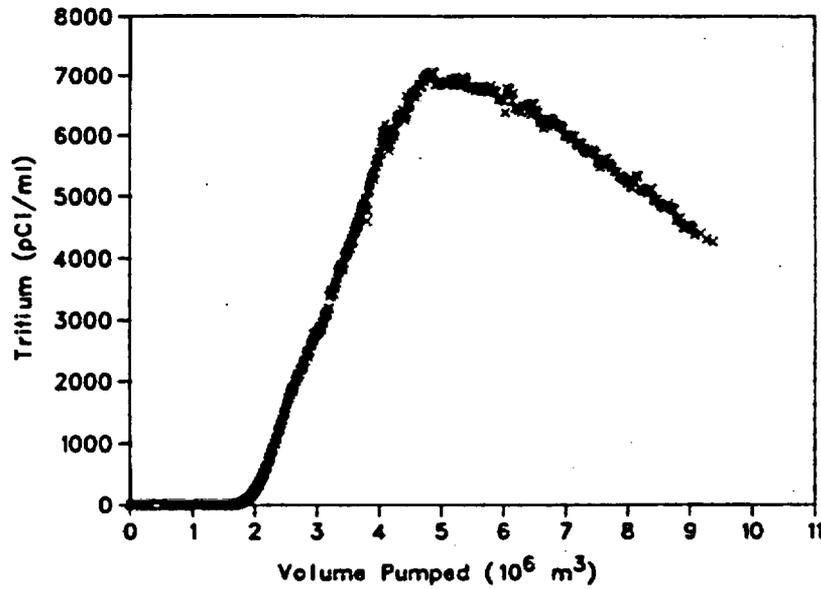


Fig. 2. Tritium concentration in water pumped from KM-2S vs volume pumped. Values are corrected to Cambrian zero time.

of the Cambric detonation. Samples from KMM-2S are collected in polyethylene bottles by personnel from Reynolds Electrical and Engineering Company (REECO); both REECO and Los Alamos perform analyses using liquid scintillation counting. The data in this report are from Los Alamos; however, the agreement between the two organizations' data is quite good. In July 1984, the sampling frequency was changed from weekly to monthly.

The original amount of tritium present at Cambric after the detonation was about 6×10^4 Ci (Ref. 1). By the end of September 1984, slightly more than 3.7×10^4 Ci of tritium had been pumped out through KMM-2S (about 60% of the initial inventory). Several efforts have been made to model the movement of tritium at Cambric. The general problem is discussed in Ref. 7, and the application of the computer code TRACK3D is described in Ref. 5.

In our annual progress report last year,⁶ we compared the tritium elution at KMM-2S with calculations that were based on Sauty's model⁸ for a two-dimensional, radial, converging flow field. At that time the best fit to the data was obtained using a Peclet number of 10. When the experimental values from the current year are included, the best fit is achieved with a Peclet number of 8, as is shown in Fig. 3. Nevertheless, the most recent data still

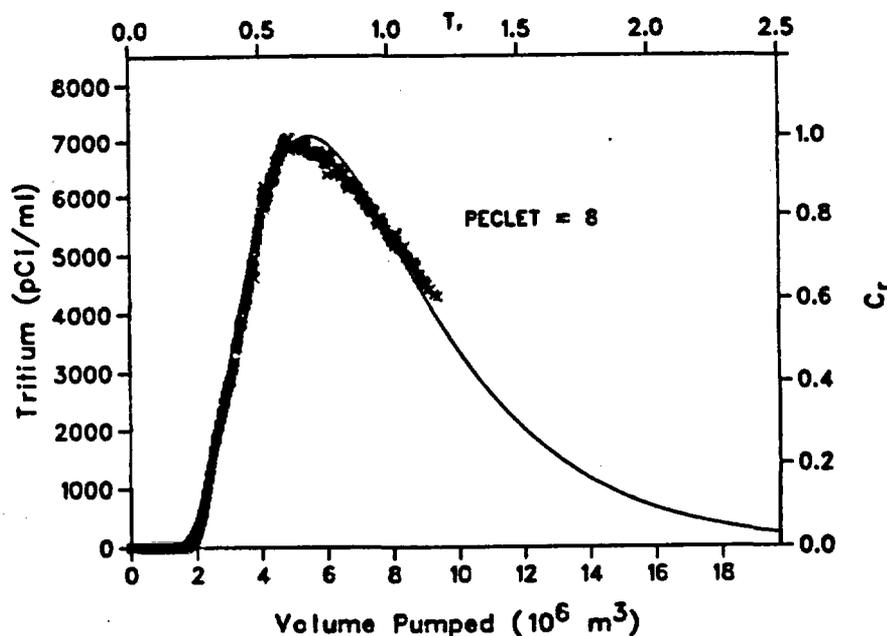


Fig. 3. Tritium concentration data (x) for KMM-2S water and the calculated elution of tracer after instantaneous tracer injection in a radially converging flow field for Peclet number 8.

tends to diverge from the predicted curve. We will continue to monitor this trend as more data are acquired.

B. Krypton Migration (J. L. Thompson, S. Maestas, and F. O. Lawrence)

Monthly collections of water from KMM-2S are taken in evacuated stainless steel tubes so that no gas exchange with the atmosphere can occur. These "pressurized" samples are analyzed for their ^{85}Kr content, as well as for tritium content. Current data are given in Table II, and cumulative data are displayed in Figs. 4 and 5. It is apparent that the krypton concentrations in water pumped from KMM-2S are no longer increasing; they may, in fact, now be decreasing. Because of the scatter in the data, it is hard to define the precise trace of the krypton elution, but it appears to follow the same general pattern of the tritium elution except that it is somewhat delayed. The krypton/tritium atom ratio seems to trend upward as more water is pumped. These data are compatible with the hypothesis that some krypton may be sorbed on the alluvium, and thus its movement is slower than that of water. It should be noted that the krypton/tritium ratio in KMM-2S water has remained significantly lower than the calculated source term ratio of 1.22×10^{-4} .

Samples of water from KMM-1 are also collected and analyzed, though less frequently than at KMM-2S. Data pertaining to the 1984 samples are given in Table III, and cumulative data for tritium and krypton in KMM-1 water are given in Table IV. Zone IV and V refer to regions in or adjacent to the chimney of the Cambrian Cavity.¹ We believe water pumped from KMM-1 during sampling is derived largely from Zone IV. Both the tritium and krypton contents of these water samples have diminished considerably as water has been pumped from the satellite well. However, the krypton/tritium ratio has remained above the calculated value of 1.22×10^{-4} . If krypton initially sorbed by the alluvium (perhaps in zeolite minerals) is slowly being leached out and is partially replacing the krypton removed by pumping at KMM-2S, the observed krypton/tritium ratios could be generated.

C. Anion Migration (K. Wolfsberg and K. S. Daniels)

Both ^{36}Cl and ^{129}I are present in solution at KMM-1, though at very low concentration levels. Iodine and chlorine normally exist as anionic species in groundwater and thus may be transported with minimal sorption through geologic media (for example, aluminosilicates), which generally have negative

TABLE II
TRITIUM AND ^{85}Kr ANALYSES IN PRESSURIZED
WATER SAMPLES FROM RNM-2S^a

Identification Number	Date Collected	Total Volume from RNM-2S (10^6 m^3)	Tritium Concentration		^{85}Kr Concentration		$^{85}\text{Kr}/\text{Tritium}$	
			(nCi/ml)	(10^{10} atoms/ml)	(dpm/ml)	(10^6 atoms/ml)	(Atom Ratio $\times 10^5$)	Ratio ^b
434-1-83-016 ^c	08/03/83	8.062	5.17	10.7	0.841	6.85	6.40	0.52
434-1-83-018 ^c	09/02/83	8.155	5.37	11.1	0.864	7.04	6.34	0.52
434-1-83-019 ^c	10/14/83	0.290	4.96	10.3	0.862	7.02	6.82	0.56
434-1-83-022 ^c	12/01/83	8.446	4.78	9.94	0.963	7.85	7.93	0.65
434-1-84-002	02/02/84	8.649	4.78	9.94	0.730	5.95	6.01	0.49
434-1-84-004	03/01/84	8.740	4.79	9.96	0.731	5.96	5.98	0.49
434-1-84-006	04/05/84	8.853	4.35	9.04	0.649	5.29	5.85	0.48
434-1-84-008	05/03/84	8.943	4.56	9.48	0.775	6.32	6.67	0.55
434-1-84-010	06/01/84	9.036	4.44	9.24	0.750	6.10	6.60	0.54
434-1-84-012	07/05/84	9.144	4.33	9.00	0.936	7.62	8.47	0.69
434-1-84-015	08/10/84	9.250	4.43	9.21	0.934	7.60	8.25	0.68

^aAll activity levels corrected to Cambrian zero time (May 14, 1965).

^bRatio of measured to calculated $^{85}\text{Kr}/\text{tritium}$ atom ratio of 1.22×10^{-4} at Cambrian zero time.

^cSamples were significantly smaller than usual.

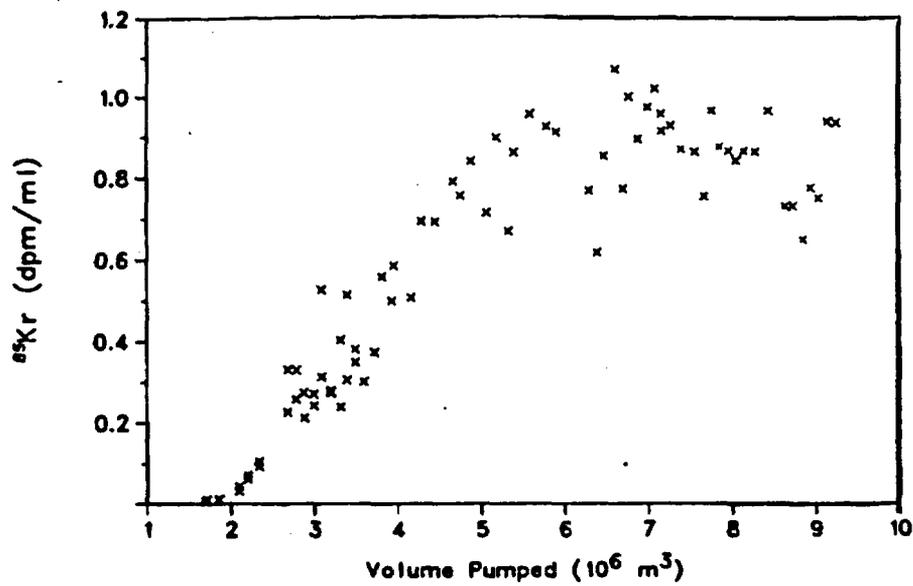


Fig. 4. The ^{85}Kr concentration in water pumped from KMM-2S. Values are corrected to Cambrian zero time.

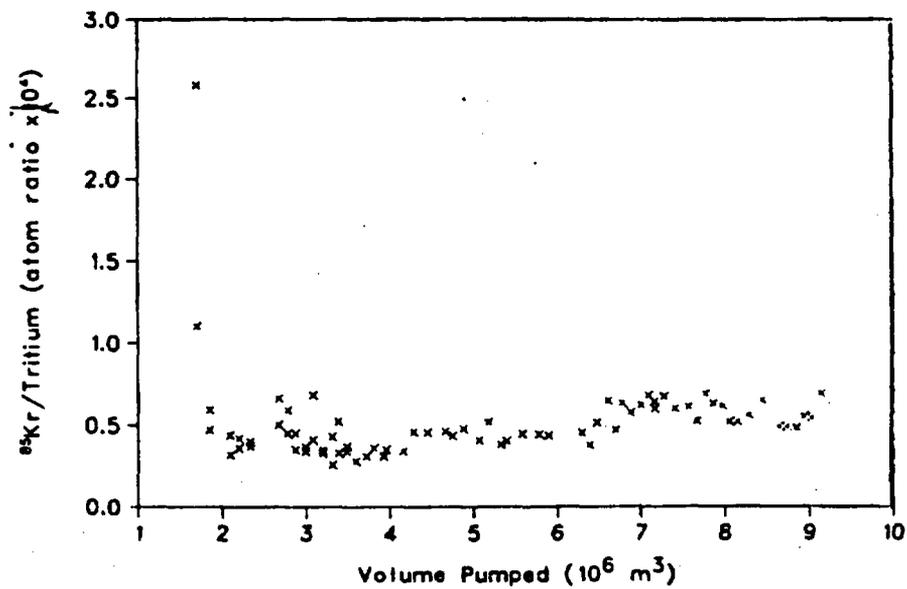


Fig. 5. Atom ratio of ^{85}Kr to tritium in water pumped from KMM-2S. Values are corrected to Cambrian zero time.

TABLE III
TRITIUM CONCENTRATION IN RNM-1 WATER (1984)

Identification Number	Volume Pumped (m ³)	Tritium Concentration (pCi/ml)	
		On Collection Date 4/24/84	Corrected to Cambric to 5/14/65
Q-1	11.0	7.7	22
Q-2	20.8	7.3	21
Q-3	36.7	6.9	20
Q-4	53.4	6.6	20
Q-5	62.8	7.5	22
434-3-84-001 ^a	67.8	8.5	25
434-3-84-003 ^a	70.0	7.3	21
Q-6	71.9	7.2	21
		Average	22

^aCollected in gas-tight pressurized tubes.

surface charges. Both ³⁶Cl and ¹²⁹I have been observed at RNM-2S. Details concerning the methods of detection (tandem-accelerator mass spectrometry and neutron activation analysis) have been given in previous reports.^{5,6} No new ³⁶Cl data were obtained in FY 1984, but several additional measurements were made of ¹²⁹I concentrations in RNM-2S water. These data are given in Table V in addition to several corrected values from a more extensive data set published previously.⁶ Figure 6 shows cumulative data comparing the concentration of ¹²⁹I with that of tritium in RNM-2S water. We recently estimated the fraction of initial iodine inventory in the Cambric cavity, which has now been pumped out of RNM-2S, and the distribution of that initial iodine relative to the distribution of tritium at the explosion site.

When RNM-1 was drilled, a series of perforations were made in each of the zones, and their coordinates were recorded in the whipstocker's log. The original water samples from Zones II to V were pumped from these perforations. Using the locations of the perforations in each zone, we calculated the concentrations of iodine and tritium at Cambric in 1974 (almost a decade after the detonation). Figure 7 shows the concentrations of ¹²⁹I and tritium as a function of the distance between the bottom of the cavity and the perforations.

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

Zone	Date	Water Volume ^a (10^6 m^3)	Concentration ^b		^{85}Kr /tritium Atom Ratio ^c	
			Tritium (10^9 atoms/ml)	^{85}Kr (10^6 atoms/ml)	($\times 10^4$)	R ^c
Original-Zone IV	08/08/75	0	3100	570	1.8	1.5
Original-Zone V	08/14/75	0	790	110	1.4	1.2
Zone IV + V	10/04/77	1.17	66	610	92	75
Zone IV + V	11/30/77	1.34	41	49	12	10
Zone IV + V	09/04/79	3.50	5.4	4.6	8.5	7
Zone IV + V	10/05/81	5.89	3.0	1.5	5.0	4
Zone IV + V	04/01/82	6.48	1.6	0.55	3.3	3
Zone IV + V	04/06/83	7.67	0.70	0.24	3.4	3
Zone IV + V	04/24/84	8.91	0.46	0.19	4.1	3

^aTotal volume of water removed from RNM-2S by indicated date.

^bValues corrected to Cambrian zero time.

^cMeasured ^{85}Kr /tritium divided by ^{85}Kr /tritium calculated for Cambrian (1.22×10^{-4}).

TABLE V
¹²⁹I CONCENTRATIONS IN RNM-2S WATERS^a

Identification Number	Total Volume Pumped (10 ⁶ m ³)	¹²⁹ I Concentration (10 ⁷ atoms/ml)
434-9-83-002 ^b	7.46	4.7 ± 0.6
434-A ^{b,c}	7.51	5.1 ± 0.6
434-B ^b	7.51	5.1 ± 0.6
434-9-83-005	7.77	3.0 ± 0.3
434-9-84-001	8.58	2.3 ± 0.2
434-9-84-005	8.94	2.2 ± 0.2

^aMeasurement by neutron activation analysis.

^bCorrected from Table IV, Ref. 6. The iodine carrier was added to sample 434-A. The volume pumped for samples 434-A and 434-B was 7.51 x 10⁶ m³.

^cThe iodine carrier was added to the sample at the well. For all other samples, including duplicates, the carrier was added at Los Alamos when the samples were purified.

Iodine concentration decreases more rapidly than tritium concentration because iodine's precursors are less volatile.

Our estimate of the source term for ¹²⁹I in the RNM-1 water before pumping at RNM-2S is based on a very limited data set (four points). We assume that the ¹²⁹I and tritium activities are distributed in a spherical sector; its vertex is at the bottom of the cavity and its radius extends outward to the perforations for Pumping Zone V. Because there was no pumping at the bottom of the cavity, we assume that the pumping from Zone II produced a sample that is representative of the volume from the vertex to the perforations. Likewise, we assume that the pumpings from the subsequent zones are representative of shell-like portions of the spherical sector, which extend from the perforations of the previous zone out to those of the zone being considered. (We do not know how far out the last pumping really sampled.) We then multiply the volume of each shell by the ¹²⁹I or tritium concentration in that shell to calculate the total for that nuclide in that spherical sector. The results of these calculations--normalized to 100%--are shown in Table VI.

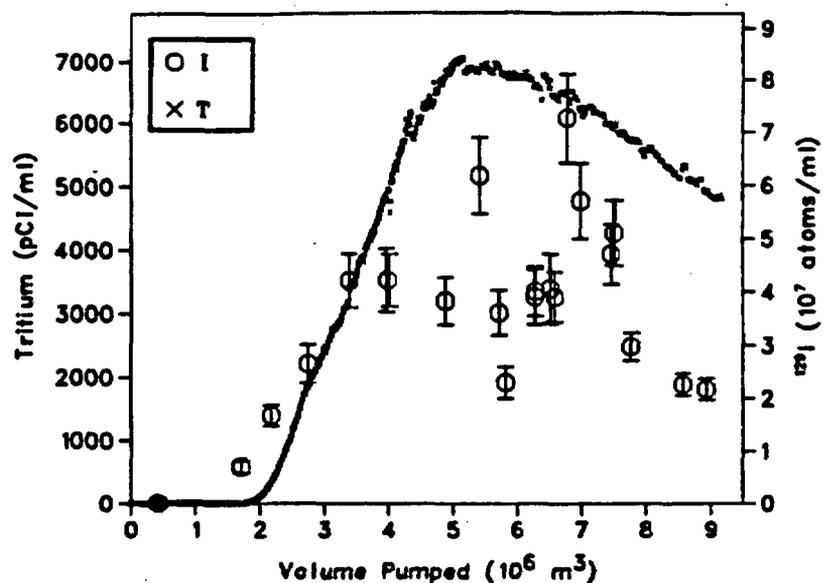


Fig. 6. Tritium and ¹²⁹I concentrations in KM-2S water. The error bars are the standard deviations for single measurements; they were obtained from the errors associated with measurements and estimated uncertainties for various parameters that enter into the calculation. These estimated uncertainties were propagated in quadrature.

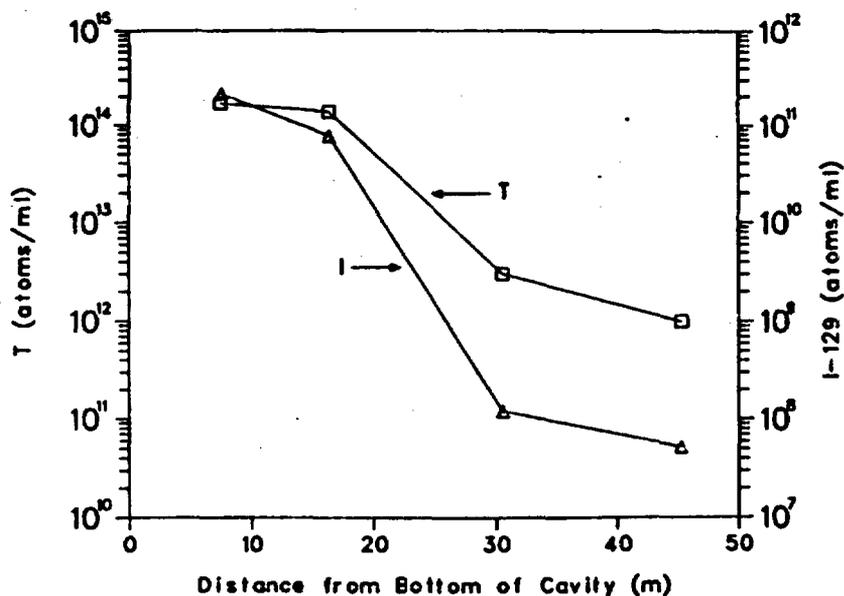


Fig. 7. Distribution of tritium and ¹²⁹I as a function of the distance from the bottom of the Cambrian cavity.

TABLE VI
DISTRIBUTION OF ^{129}I AND TRITIUM IN
SHELLS OF SPHERICAL SECTORS

Zone	Radius (m)	Activity in the Shell (%)	
		Tritium	^{129}I
II (core)	7.5	9.3	22.3
III	16.4	72.5	76.1
IV	30.6	9.6	0.7
V	45.3	8.5	0.8

Because these spherical sectors contain solids as well as solution, the number of atoms calculated for the sectors must be normalized against measured experimental data. We do this by using the tritium data because we know the number of tritium atoms in the source term.¹ If we apply the same factor to the ^{129}I , our calculations for the number of atoms in the spherical sector yield a value of 7.21×10^{20} atoms of ^{129}I dissolved in the water in the Cambic cavity. Because we calculated that the yield of this nuclide produced in the event is 1.77×10^{21} atoms, it appears that approximately 40% of the ^{129}I produced has dissolved in the groundwater. The remainder presumably is contained either in fused material in locations not accessible to water or in insoluble forms.

Having calculated the source term of dissolved ^{129}I , we are in a position to estimate the fraction of this radionuclide that has been pumped out of KMM-2S to date. The data for iodine elution from KMM-2S contain a good deal of scatter, so error bands were included with the assumed elution curve (see Fig. 8). Integrating these curves yields a value of $2.8 \pm 0.8 \times 10^{20}$ atoms. (If one draws histograms using the actual determinations and sums these, the result is also 2.8×10^{20} atoms.) Therefore, it appears that $(39 \pm 11)\%$ of the ^{129}I has been eluted during the time that about 60% of the tritium was eluted.

D. Cation Migration (J. L. Thompson, S. Maestas, J. D. Gallagher, G. W. Knobeloch, J. Drake, and V. M. Armijo)

We routinely collect large-volume (55-gal.) samples in plastic-lined barrels from KMM-2S and KMM-1. These samples are taken to dryness, and the

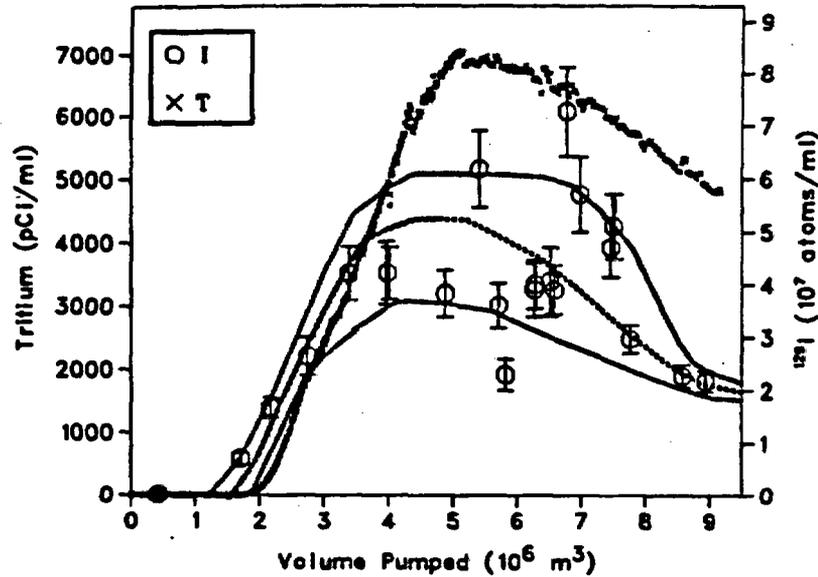


Fig. 8. Concentrations of ^{129}I in water pumped from KM-2S. The heavy dashed line is the estimated elution curve for iodine, and the light dashed lines define error bands to encompass most of the scattered data.

residue is placed in a low-background gamma-ray spectrometer. This procedure involves distilling the sample in a Corning AG-1 glass still with a small amount of EDTA until the volume is reduced to about 2 l. This concentrate and a hydrochloric acid wash from the still are evaporated in a clean-room environment. The residue, wrapped in a plastic bag, is compressed by hydraulic press into a highly compacted cylinder about 5.5 cm in diameter and 2.5 to 4 cm thick. We place the samples over a well-shielded intrinsic germanium detector and count them for several days. The resulting spectra are compared with background spectra obtained from samples collected at Well 5B at the NTS, which contain no fission products.

During FY 1984, we improved the calibration of our spectrometer for environmental samples of the type described above. A concentrated distillate of Well 5B water was doped with a known amount of a mixed radionuclide gamma-ray reference standard before final drying. We used the resulting compressed cylinder to determine the counter efficiencies for gamma rays (over an energy range of 10^2 to 2×10^3 keV) as they originated from a source that is typical of our environmental samples in both composition and geometry. The sensitivity for detection of ^{137}Cs in our 55-gal. samples is approximately 10^6 atoms/l.

In addition to the 55-gal. samples just described, 4-2 samples of water from RM-1 and RM-2S are periodically analyzed for ^{137}Cs and ^{90}Sr by a radiochemical procedure.⁵ The sensitivity of this analysis for both radionuclides is $\sim 10^8$ atoms/l. Table VII contains cumulative data showing how the concentrations of ^{137}Cs and ^{90}Sr in RM-1 water have decreased in the years since pumping at RM-2S began. Of particular interest is the fact that the cesium and strontium concentrations in this water have diminished less rapidly than has the tritium concentration. This probably indicates that some cesium and strontium are leaching from the alluvium in the cavity region, thus adding slightly to the concentrations of these ions. To date we have not detected ^{137}Cs or ^{90}Sr in RM-2S water. The absence of these cationic elements is not surprising because laboratory measurements have shown that they are strongly sorbed on the tuffaceous rock that is characteristic of the NTS.⁹

From the Cambric study it appears that the original volume of dissolved fission products has moved from the cavity under the force of the hydraulic gradient, but the rates of movement of individual radionuclides have varied considerably. In general, those species that moved through the alluvium with the water (though slightly behind or ahead) were anionic or neutral, whereas the cationic species were significantly retarded in their movement. This is consistent with what we have learned from laboratory studies of radionuclide interactions with geologic media. A great deal of detailed information concerning water chemistry, flow rates, and geochemical parameters is required before we can hope to successfully predict how a particular radionuclide in a given underground explosion zone will behave. Because most of our data to date have been derived from laboratory experiments, it is particularly important to conduct field studies such as that at Cambric to verify that our laboratory work is relevant to field situations.

III. CHESHIRE STUDIES

As noted above, the Cambric studies have provided a good deal of information concerning radionuclide behavior in an underground explosion zone that is located in tuffaceous alluvium. We would like to know what similarities and differences occur when the explosion zone is in a different geological environment. The Cheshire test conducted on Pahute Mesa (area 20 of the NTS) in February 1976 provides a study site that contrasts with Cambric in some

TABLE VII
TRITIUM, ⁹⁰Sr, AND ¹³⁷Cs CONCENTRATIONS
IN RNM-1 WATER

Zone	Date	Water Volume ^a (10 ⁶ m ³)	Concentration ^b			Atom Ratio (x 10 ⁴)	
			Tritium (10 ⁹ atoms/ml)	⁹⁰ Sr (10 ⁶ atoms/ml)	¹³⁷ Cs (10 ⁶ atoms/ml)	⁹⁰ Sr/T	¹³⁷ Cs/T
Original-Zone IV	08/08/75	0	3100	130	23	0.4	0.07
Original-Zone V	08/14/75	0	790	5.5	4.6	0.07	0.06
Zone IV + V	10/04/77	1.17	66	22	5.5	3	0.8
Zone IV + V	11/30/77	1.34	41	13	11	3	3
Zone IV + V	09/04/79	3.50	5.4	4.4	2.3	8	4
Zone IV + V	10/05/81	5.89	3.0	1.5	1.3 (1.6) ^c	5	4 (5) ^c
Zone IV + V	04/01/82	6.48	1.6	1.3	1.5 (1.5) ^c	8	9 (8) ^c
Zone IV + V	04/06/83	7.67	0.70	--	1.3 (1.1) ^c	--	19 (16) ^c
Zone IV + V	04/24/84	8.91	0.46	0.81	1.0	17	23

^aTotal volume of water removed from RNM-2S by indicated date.

^bValues corrected to Cambrian zero time.

^cValues in parentheses are based on gamma-spectral analyses of 55-gal. (evaporated) samples.

interesting ways. The Cheshire device was fired at a depth of 1174 m, about 544 m below water level, in brecciated rhyolitic lava. Hydraulic tests conducted at hole U20a-2, which is near the Cheshire site, indicate the presence of several relatively permeable zones in the rhyolite at depths around 1150, 910, and 775 m; there is also a small increase in the hydrostatic head with depth.¹⁰ These data suggest that at U20n, the Cheshire site, water may be moving upward through the cavity and chimney regions and then horizontally through a permeable zone. The general direction of water movement in area 20 is south and west.¹¹ Because the NTS boundary is a few miles southwest of U20n, we are particularly interested in determining the extent of radionuclide migration from this site.

The Cheshire cavity region was re-entered in late 1976. About 5000 gal. of water were pumped from the re-entry hole. We believe that most of this water came from below the cavity because the tritium concentration was much lower than we might have expected following an explosion with the observed yield. However, the pumped water did contain detectable amounts of fission products and plutonium. Also, some water samples were extracted from sidewall core material; these were used for tritium and krypton analyses. After these initial samples were taken, the pump became stuck and no further water samples were obtained until 1983. (Details of the 1976 work at Cheshire are given in Ref. 12.) By 1983, the obstructing pump had been pushed to the bottom of the hole and a bridge plug had been set above the original perforations in the casing. In August 1983, new perforations were made at a depth close to that of the Cheshire detonation, and several pressurized samples and a 55-gal. water sample were obtained. In September 1983, we pumped about 137 000 gal. of water from U20n and collected a large number of samples. An attempt to start pumping again in June 1984 was unsuccessful; the pump burned out and had to be replaced. The new pump was inserted July 31, 1984, and operated with a number of interruptions until October 26, 1984. Weekly sample collections were made by REECO personnel during this period, and both pressurized samples and 55-gal. samples were taken by Los Alamos workers on August 1 and October 23. The volume of water pumped during the August to October pumping must be estimated because the flow meter malfunctioned and was replaced during this time; we believe this volume was 3.1×10^6 gal. In this report, we discuss the results of analyses of the September 1983 samples (plus a few from the August to October 1984 sampling) and compare them with the 1976 data. We are

also able to draw some conclusions about the behavior of several radionuclides in the Cheshire environment compared with their behavior in the Cambrian environment.

A. Lithium Concentration (J. L. Thompson, S. Maestas, A. J. Mitchell, G. E. Bentley, and W. A. Taylor)

It is a common procedure at the NTS to add LiCl to fluids used in testing well casings. When the well is pumped, the decreasing levels of lithium in the pumped water indicate the extent to which the well has been cleared of the test fluids. Because LiCl was used at the Cambrian site during re-entry in 1976 and during remedial work in the spring of 1981, we monitored its concentration in our collected water samples. Table VIII contains these data for the 1983 and 1984 pumpings and also shows the range of values measured during the 1976 pumping. It appears that after some 10^4 gal. of water was pumped from the hole, the lithium content stabilized. (The last four values in the table were obtained by a somewhat different analytical technique, and probably do not represent sample increases in lithium content.) Our values agree with those obtained by KEECU¹³ for the 1983 pumping.

The apparent lithium content of the pumped water is substantially above that of ambient groundwater in Pahute Mesa. The USGS analyses of water from U20a-2 (Ref. 14) range from 0.026 to 0.06 mg/l, and KEECU measured lithium in water from U19c at 0.009 mg/l (Ref. 13). At first we thought that the Cheshire device might have left lithium residue in the immediate explosion zone. However, the lithium associated with the Cheshire device was highly enriched in ⁶Li, whereas our samples showed a ⁶Li content close to the normal 7.5% value. We now believe that the above-ambient concentration of lithium at the Cheshire site is caused by leaching of this element from fused debris in the cavity region. The lithium content of rhyolitic lava in the area is around 45 mg/kg of rock. Estimates based on the amount of rock fused and the rate at which it could be leached indicate that this is a plausible source for the observed lithium. Furthermore, data from the Bilby site (area 3) and from the Nash site (area 2) show that there was an increase in the lithium content of the water at these sites after the tests. Our experience at Cheshire indicates that if LiCl is to be used to "tag" water in re-entry wells at test sites, the concentration should be substantially larger than the few mg/ml frequently used in water wells.

TABLE VIII
LITHIUM ANALYSES OF CHESHIRE WATER

<u>Identification Number</u>	<u>Date Collected</u>	<u>Total^a Volume Pumped (10³ gal.)</u>	<u>Lithium Concentration^b (mg/l)</u>
8521 to 8529	9/76	1.3 to 4.3	0.19 to 1.7
852-9-83-001	8/83	~5	0.26
B-4	9/83	9	0.18
B-13	9/83	18	0.16
B-27	9/83	32	0.15
B-41	9/83	46	0.16
B-53	9/83	58	0.16
B-53	9/83	58	0.16
B-61	9/83	72	0.16
B-76	9/83	116	0.14
B-80	9/83	128	0.15
B-61 (repeat)	9/83	72	0.24
C-1	8/84	413	0.22
C-5	8/84	889	0.20
C-9	9/84	1380	0.20

^aTotal volume, based on an approximate pumping of 5×10^3 gal. in 1976.

^bStandard error approximately 10% of stated value.

B. Tritium Concentration (J. L. Thompson and S. Maestas)

We know the yield of the Cheshire device and have calculated the quantity of tritium produced. Based on these values and an assumed water content of the postshot region (taken to be equal to the measured preshot value), we can estimate the tritium concentration in the Cheshire cavity after infilling: 2×10^4 nCi/ml. When the first water samples were measured after the re-entry in 1976, the highest concentration of tritium observed was 2×10^3 nCi/ml. Because this sample was drawn from a depth below that of the detonation and contained so much less tritium than expected for the cavity water, we felt that the sample probably contained only a small fraction of water directly from the cavity. Seven years later, when the hole was next sampled--this time

from a depth close to that of the detonation point, the measured tritium concentration was lower by more than a factor of 3. As shown in Table IX, the tritium concentration remained essentially constant during the 1983 pumping of 1.4×10^5 gal. and diminished somewhat during the 1984 pumping of 2×10^6 gal. The total volume pumped from U20n through the end of September 1984 was a few per cent of the volume calculated for the cavity water.

TABLE IX
TRITIUM CONCENTRATION IN WATER PUMPED FROM CHESHIRE

<u>Identification Number</u>	<u>Date Collected</u>	<u>Total Volume Pumped (10^3 gal.)</u>	<u>Tritium Concentration^a (10^2 nCi/ml)</u>
852-1-83-003	08/06/83	5	5.91
852-9-83-001	08/07/83	5	5.89
B-4	09/07/83	9	5.95
B-13	09/07/83	18	5.95
B-27	09/07/83	32	5.97
B-41	09/08/83	46	5.98
B-53	09/08/83	58	6.00
B-61	09/08/83	72	5.95
B-76	09/09/83	116	5.89
B-80	09/09/83	128	5.92
852-1-83-008	09/09/83	136	5.76
852-1-83-009	09/09/83	136	5.58
C-1	08/01/84	0.2×10^3	5.41
C-2	08/01/84	0.2×10^3	5.35
C-4	08/15/84	0.6×10^3	5.31
C-5	08/22/84	0.9×10^3	5.29
C-7	09/05/84	1.3×10^3	5.05
C-8	09/12/84	1.6×10^3	5.26
C-9	09/19/84	1.8×10^3	5.18
C-10	09/26/84	2.1×10^3	5.20

^aActivity levels corrected to Cheshire zero time (February 14, 1976).

C. Fission Product and Other Radioactive Element Concentrations

(J. L. Thompson, S. Maestas, G. W. Knobeloch, D. W. Eford, V. M. Armijo, J. Drake, A. J. Mitchell, P. L. Wanek, M. R. Cisneros, F. O. Lawrence, J. D. Gallagher, J. H. Cappis, R. E. Perrin, and W. R. Daniels)

Several types of water samples are routinely taken at the Cheshire site. These include large-volume samples collected in 55-gal. plastic-lined barrels, pressurized samples in 2-l stainless steel tubes that are collected either at depth in the hole or at a surface hose bib, and grab samples collected in plastic bottles at the surface. The 55-gal. samples may be evaporated to dryness, and this "boildown" residue can be counted in a gamma-ray spectrometer (see Sec. II.D. above), or portions of the sample may be used to analyze elements such as strontium and plutonium by radiochemical procedures. Using vacuum-line techniques, we analyze the pressurized samples for tritium and ^{85}Kr . Grab samples are usually analyzed only for tritium; the analysis is by liquid scintillation counting. Table X shows the concentrations of those radionuclides detected in water samples from the Cheshire site September 1983 and August 1984 pumpings. Agreement between the two sets of analyses is generally within the estimated precision of the data. With its 312-day half-life, ^{54}Mn was no longer detectable at the time of the second pumping. Data for ^{85}Kr , ^{90}Sr , and ^{239}Pu are not yet available from the August pumping.

Because the absolute concentrations of these radionuclides are affected as water moves in and out of the cavity region, it is instructive to focus on the concentration of the nuclide relative to that of tritium (which is in the form of tritiated water). Such relative concentrations are shown in the first column of Table XI. The observed relative concentrations may be compared with the radionuclides actually produced by the nuclear event, that is, the source-term ratios, which are given in the second column. A radionuclide that is incorporated in the fused debris or sorbed by the rock will have an observed atom ratio much smaller than the source-term atom ratio. Thus the magnitude of the number in the third column of Table XI indicates the amount of retention by the rock for that particular radionuclide. The retention at Cheshire may be compared with that at Cambric (data given in the fourth column). Because the Cambric samples were pumped from specific zones ranging from the bottom of the cavity to a region adjacent to the chimney, there is a corresponding range of retention values. We do not know from exactly which region the water samples at Cheshire are drawn, but most of the Cheshire retention

TABLE X
RADIONUCLIDES IN WATER AT CHESHIRE

Radionuclide	Concentration ^a (atoms/ml)		Method of Analysis
	(9/83)	(8/84)	
³ H	1.23 x 10 ¹³	1.12 x 10 ¹³	liquid scintillation counting
²² Na	2 x 10 ⁴	2 x 10 ⁴	boildown, gamma spectroscopy
⁵⁴ Mn	2 x 10 ⁴	not detected	boildown, gamma spectroscopy
⁶⁰ Co	2 x 10 ³	2 x 10 ³	boildown, gamma spectroscopy
⁸⁵ Kr	5.7 x 10 ⁹	---	vac line separation, beta counting
⁹⁰ Sr	4 x 10 ⁶	---	radiochemistry, count ⁹⁰ Y gamma
¹⁰⁶ Ru	4 x 10 ⁶	4 x 10 ⁶	boildown, gamma spectroscopy
¹²⁵ Sb	2 x 10 ⁷	1 x 10 ⁷	boildown, gamma spectroscopy
¹³⁴ Cs	3 x 10 ⁴	4 x 10 ⁴	boildown, gamma spectroscopy
¹³⁷ Cs	5 x 10 ⁷	---	radiochemistry, gamma counting
¹³⁷ Cs	5 x 10 ⁷	7 x 10 ⁷	boildown, gamma spectroscopy
¹⁵² Eu	1 x 10 ⁴	1 x 10 ⁴	boildown, gamma spectroscopy
¹⁵⁴ Eu	1 x 10 ⁴	2 x 10 ⁴	boildown, gamma spectroscopy
¹⁵⁵ Eu	6 x 10 ³	1 x 10 ⁴	boildown, gamma spectroscopy
²³⁹ Pu	1 x 10 ⁷	---	radiochemistry, alpha counting

^aCorrected to t₀ values as of February 14, 1976.

values are comparable to or slightly higher than those from Cambric. This suggests that the rhyolite at Pahute Mesa is at least as effective as the alluvium at Frenchman Flat for retaining fission products. The retention of ²³⁹Pu appears to be higher in alluvium; however, the retention factor at Cambric may be in error as the source term of plutonium was rather small, and the sample concentrations were quite close to the limit of detection.

The water samples pumped from Cheshire contain a small amount of particulate matter, which may be removed by filtering or centrifuging. We have examined samples of such particulate material qualitatively to determine if there are any radionuclides that were not detectable as dissolved species. In general, the same radionuclides are present in the particulate material as in solution, with one exception. Both the centrifuged and filtered material

TABLE XI
OBSERVED AND SOURCE-TERM CONCENTRATIONS:
CHESHIRE AND CAMBRIC

	Cheshire			Cambric	
	$(N_X/N_T)_{obs}$ ^a	$(N_X/N_T)_{st}$ ^b	$(N_X/N_T)_{st} / (N_X/N_T)_{obs}$ ^c	$(N_X/N_T)_{st} / (N_X/N_T)_{obs}$ ^d	$(N_X/N_T)_{obs}$ ^d
⁸⁵ Kr	4.6×10^{-4}	5.9×10^{-4}	1.3	1.1 - 1.5	
⁹⁰ Sr	3×10^{-7}	1.1×10^{-4}	3×10^2	$4 \times 10^1 - 2 \times 10^3$	
¹⁰⁶ Ru	3×10^{-7}	6.3×10^{-3}	2×10^4	$1 \times 10^2 - 2 \times 10^2$	
¹²⁵ Sb	1×10^{-6}	1.0×10^{-3}	1×10^3	$3 \times 10^2 - 4 \times 10^2$	
¹³⁷ Cs	4×10^{-6}	1.6×10^{-2}	4×10^3	$7 \times 10^2 - 2 \times 10^4$	
²³⁹ Pu	1×10^{-6}	1.2×10^{-1}	1×10^5	$2 \times 10^7 - 3 \times 10^7$	

^aRatio of atoms of element x to atoms of tritium (from TABLE X).

^bAtom ratio as calculated for the source term, based on fission yield data from the literature (Refs. 15, 16).

^cThis ratio is a measure of the retention of the radionuclide in or on solids in the cavity region (see "retention factor E_d " in Ref. 17).

^dData from Ref. 17, ranging over all regions pumped.

contained small amounts of ¹⁴⁴Ce. Also, the August 1984 filter retained a detectable amount of ⁵⁴Mn, although this nuclide was not identified as a dissolved species in 1984. We dissolved some of the particulate material and analyzed its uranium isotopic content by mass spectrometry; significant amounts of ²³⁶U indicated that this material came from the explosion zone at Cheshire.

In the course of our work with filters, we became aware that Nuclepore polycarbonate filters may contain small amounts of fission products in quantities that vary from filter to filter. Furthermore, some of this fission product material may be leached from the filter as large quantities of water pass through the membrane. Although the activity levels in the filters are normally quite low, the solution being filtered can be contaminated, and of course, the activity of the filters themselves may be erroneously ascribed to

the material caught by the filters. We no longer use Nuclepore filters in situations where low-level contamination could be a problem.

D. Radionuclide Migration from Cheshire

Using the information available to date, we can make the following generalizations concerning the Cheshire site:

- (1) Both the water samples and the associated particulate samples contain the radionuclides expected from the cavity region of this test device.
- (2) The ratio of fission product nuclei (and plutonium) to tritium is reasonable, considering the source-term values and the retention factors observed at the Cambric site.
- (3) Concentrations of dissolved radioactive species are consistent between the early, limited pumping and the more extensive pumping 11 months later.
- (4) The concentration of tritium is about a factor of 30 less than it should be, according to the source-term calculations.

There are several possible explanations for the observation concerning tritium. The tritium yield calculation might be in error, or most of the tritium might not have been distributed in the cavity water. These unlikely scenarios also would require that the retention of fission products by rhyolite be much higher than by alluvium because the observed atom ratios of fission products to tritium are similar for the two geologic media. Another explanation could be that in the sampling (pumping) operation, water was drawn partially from the cavity and partially from an uncontaminated source. A third possible explanation is based on the hypothesis that the original cavity water has been diluted by natural water flow during which the major fraction of dissolved material migrated away. We believe this hypothesis is likely to be true. We anticipate that future work at the Cheshire site will enable us to determine why the tritium levels detected thus far are so much lower than expected.

At present, for all radionuclides detected except tritium and ^{85}Kr , the sample activity levels are below the US Department of Energy concentration guide limits¹⁸ for water in an uncontrolled area. Even if the concentrations

of all the radionuclides were a factor of 30 higher, Cheshire would not constitute a serious hazard from the point of view of health physics.

IV. NASH STUDIES (J. L. Thompson, S. Maestas, G. W. Knobloch, V. M. Armijo, J. Drake, and D. W. Eford)

The UE2ce hole adjacent to the Nash test in area 2 of the NTS is cased so as to produce water only from the carbonate rocks that underlie the alluvial valley fill. Because the Nash detonation occurred in alluvium above the water table, we thought that water samples drawn from the carbonate rocks below the water table might reveal transport of radioactive species from the unsaturated zone into the saturated zone. However, we do not know whether the activity detected to date in the water samples originated in the cavity region or represents material driven by the explosion into fractures in the carbonate rocks. There have been numerous pump shutdowns at UE2ce; as a result, no samples were collected in February, March, May, August, and September 1984. In those samples that were collected, the tritium varied considerably. The tritium concentrations in 1984 water samples from the Nash site are given in Table XII.

The ^{85}Kr concentration in Nash samples measured in 1978 was 1.5×10^9 to 2.4×10^9 atoms/ml (corrected to the zero time of January 19, 1967), and the ^{85}Kr /tritium atom ratio was 1.5×10^{-3} to 2.3×10^{-3} . In sample 508-1-84-002 taken April 25, 1984, we measured the ^{85}Kr concentration as 3.6×10^9 at t_0 , and the ^{85}Kr /tritium atom ratio as 3.5×10^{-3} . This latter value may be compared to the calculated source-term atom ratio of 5.5×10^{-3} . The 1984 ^{85}Kr /tritium atom ratio is 65% of the calculated value, whereas the 1978 measurements were 28 to 42% of the calculated value. These differences may not be significant, but the ^{85}Kr /tritium ratio does appear to have an upward trend with time. A similar trend was seen in the Cambric data.

Before 1983, we detected no ^{90}Sr or ^{137}Cs in water samples from the Nash site. In 1983, a water sample from Nash analyzed by our radiochemical procedure had a substantial amount of ^{137}Cs , but no ^{90}Sr . Because this sample had been filtered through a 0.05- μm Nuclepore filter, we suspected that ^{137}Cs might have been leached from the filter. We analyzed the 1983 sample again in 1984 as well as a recent sample, and our counting data are shown in Table XIII. This time, the filtration was through a 0.05- μm Millipore filter,

TABLE XII
TRITIUM CONCENTRATION IN WATER PUMPED FROM NASH

<u>Identification Number</u>		<u>Meter Reading (gal.)</u>	<u>Date</u>	<u>Tritium^a (nCi/mg)</u>
<u>Los Alamos</u>	<u>NTS</u>			
UE2ce-69	17175	4,758,999	10/20/83	19.2
UE2ce-70	17176	4,817,849	10/28/83	15.0
UE2ce-71	17177	4,859,128	11/01/83	15.5
UE2ce-72	17178	4,930,333	11/08/83	13.4
UE2ce-73	17179	5,011,313	11/17/83	13.9
UE2ce-74	17180	5,063,702	11/23/83	13.9
UE2ce-75	17181	5,109,808	11/29/83	14.4
UE2ce-76	17182	5,166,155	12/07/83	14.0
UE2ce-77	17183	5,302,611	12/30/83	13.8
UE2ce-78	17184	5,366,300	01/06/84	13.3
UE2ce-79	17185	5,402,570	01/10/84	13.1
UE2ce-80	17186	5,478,010	01/19/84	13.3
UE2ce-81	17187	5,528,820	01/25/84	13.4
UE2ce-82	17188	5,566,600	04/12/84	33.5
UE2ce-83	17194	5,697,932	06/14/84	25.0
UE2ce-84	17195	5,930,300	07/17/84	19.3
UE2ce-85	17196	6,058,347	08/07/84	17.3

^aStandard deviations of counting data <1%.

which does not contain fission products. Gross counting data are included in Table XIII to convey a sense of the signal magnitude compared with the background. These data suggest that there may be a small amount of ⁹⁰Sr and an even smaller amount of ¹³⁷Cs in both the 1983 and 1984 water samples from the Nash site. It will be interesting to see if analyses of future samples confirm the presence of these radionuclides.

TABLE XIII
RADIOCHEMICAL ANALYSES OF NASH WATER SAMPLES

Identification Number	⁹⁰ Sr			¹³⁷ Cs		
	Gross Activity (cpm)	Back- ground (cpm)	Concen- tration ^a (atoms/ml)	Gross Activity (cpm)	Back- ground (cpm)	Concen- tration ^a (atoms/ml)
DE2ce 59,60, and 69,70 (1983)	8.36	3.23	1.1 x 10 ⁵	3.73	2.47	4.5 x 10 ⁴
508-9-84-001 (1984)	10.49	3.23	1.9 x 10 ⁵	3.27	2.47	8.6 x 10 ⁴

^aThese values were adjusted for blank, decay, and chemical yield corrections.

V. LABORATORY AND COMPUTATIONAL WORK

Los Alamos has an extensive laboratory research program in support of the Nevada Nuclear Waste Storage Investigations (NNWSI) project. Part of the data collected in pursuit of NNWSI research goals is directly pertinent to the RNM project. In this section, we review some of this fiscal year's laboratory experimental and computational work that has relevance for both the NNWSI and the RNM projects. More detailed information is available from the reports referenced.¹⁹⁻²²

A. Sorption of Radionuclides on Tuff (B. P. Bayhurst, M. R. Cisneros, F. O. Lawrence, S. D. Knight, R. S. Kundberg, K. W. Thomas, and J. L. Thompson)

Batch sorption ratios for technetium and neptunium on crushed tuff have been close to zero (technetium) and between zero and ten (neptunium) at contact times of 3 to 6 weeks (Ref. 19). Long-term experiments with contact times up to 15 months are in progress; little change in the sorption ratio has been observed over a 12-month period.²² Using six tuffs of varying composition, we completed batch sorption experiments for uranium and selenium; there was apparent correlation between the uranium sorption ratio and the amount of zeolite (clinoptilolite) in the tuff.²⁰ We studied the effect of concentra-

tion on sorption²¹ for neptunium over a concentration range of 10^{-3} to 5×10^{-9} M; few changes in sorption ratio were observed. Most sorption studies conducted at Los Alamos have employed water from Well J-13 at the NTS. Recently, we have measured the effect of water composition on sorption ratios^{20,22} by using either distilled water or groundwater from Well UK25p#1, which has relatively high concentrations of calcium, magnesium, strontium, barium, sodium, bicarbonate, and sulfate. The water with the higher salt content gave lower sorption ratios for elements like cesium, strontium, and barium, which sorb by ion exchange, but salt content had little effect on the sorption of europium. Batch sorption studies of uranium, which are conducted in glove boxes with a controlled atmosphere of CO_2 , show²² that at higher pH conditions (lower CO_3^{2-}), there is less complexing of the uranyl ion with carbonate, and thus, higher sorption ratios are obtained than at a pH around 8 to 9. There was no corresponding effect on selenium sorption ratios. Tin and thorium have been added to the list of elements whose sorption ratios have been determined by batch methods.²¹

The sorption of simple cations in tuff is dominated by adsorption on aluminosilicates that have charged surfaces, such as zeolites and clays. We determined the kinetics of sorption on tuffs containing the minerals clinoptilolite and montmorillonite¹⁹ by studying the uptake of strontium, cesium, and barium on thin tuff wafers. The rate constants for uptake of these elements on tuff are consistent with a model of sorption that is diffusion limited and in which diffusion occurs in two stages. First, the cations diffuse into the rock through the water-filled pore space, and then they must diffuse into the much narrower channels within the aluminosilicate crystals. After they are within the zeolite framework or between the clay planes, the cations may rapidly sorb on the negatively charged surfaces. Actinide elements have a time constant for apparent sorption that is inconsistent with this model and may have a radically different mechanism of removal from solution.

We have observed an apparent kinetic effect in sorption experiments with plutonium and americium in which the actinide solution was flowing through columns of crushed tuff.²¹ This effect was later confirmed in batch sorption experiments that terminated at varying times. In column experiments, the kinetic effect is manifested by a significant fraction of the input activity passing through the column with the solvent front. In batch experiments, the kinetic effect results in very marked increases in the sorption ratio as

contact times are extended from hours to days to weeks. It is not clear whether the kinetic effect is caused by speciation changes in the dissolved actinide, colloidal transport, time dependence of the sorption process itself, or some other phenomenon. It is important that the underlying cause of this kinetic effect be discovered if we are to predict the extent of actinide transport from an underground nuclear waste repository or from an underground nuclear explosion cavity.

B. Solubility and Speciation (M. R. Cisneros, L. S. Hersman, D. E. Hobart, J. F. Kerrisk, F. O. Lawrence, T. W. Newton, V. L. Kundberg, and K. W. Thomas)

We have completed a thermodynamic data file for americium¹⁹ for the EQ3/6 chemical equilibrium computer program. There is still considerable uncertainty about the identity and formation constants of some americium species. From these data, we calculate that the solubility of americium in Well J-13 water is 1.0×10^{-8} M. Thermodynamic data for barium and radium have also been added to the EQ3/6 program.²⁰ By using the EQ3/6 computer code,²¹ we compared five waste elements (americium, plutonium, uranium, strontium, and radium) for solubility in waters from the tuffaceous aquifer and carbonate aquifer at the NTS. The solubilities of uranium, plutonium, and americium are higher in the water from the carbonate aquifer; the solubilities of strontium and radium are lower. Two methods of determining the solubility product of hydrous plutonium oxide ($\text{PuO}_2 \cdot n\text{H}_2\text{O}$) are being pursued.²⁰ Both methods involve relations among hydrous plutonium oxide solid and Pu(IV), Pu(V), and Pu(VI) in solution. Measurement of total plutonium in solution and use of the oxidation-reduction relation between Pu(VI) and Pu(IV) yielded a solubility product of 2×10^{-57} , as did the measurement of Pu(V) and Pu(VI). We have studied the rates of polymerization and disproportionation of Pu(IV) (Ref. 19) and determined the solubility of Pu(IV) polymer at pH = 5.3 (Ref. 20). Experiments using spectrometry to study the plutonium carbonate system indicate the presence of at least three different complexes.²¹ We have begun similar work to study the americium carbonate system. A continuing effort is being made to determine the effect of bacteria on the mobility of radioisotopes (especially plutonium) in tuff. In a recent experiment,²⁰ we observed that bacteria caused an increase in the measured sorption ratio for plutonium on a crushed tuff.

C. Studies of Colloids (L. F. Brown, S. W. Hodsen, A. J. Mitchell, E. J. Mroz, H. E. Nuttall, K. S. Kundberg, and B. J. Travis)

Several types of colloids could pose a hazard in the geologic disposal of high-level radioactive waste and in the confinement of radionuclides at an underground explosion site. These colloid types include natural colloids that sorb radionuclides, colloids formed by the radionuclides themselves, and colloidal material leached from waste forms such as borosilicate glass or fused debris. The role of colloids in radionuclide transport is not well understood, and much needed experimental data are just now forthcoming. We have made a preliminary examination of natural colloids, including their size distribution, sorption capacity, and other important properties.²⁰ Natural colloids are relatively large and arise from the partial dissolution of clays in the rock matrix. Measured concentrations in groundwater range from 1 to 200 ppb. They are composed of various clay minerals and have high ion exchange capacities. Natural colloids are expected to move at pore water velocities. Adsorbed species will, to some extent, escape the retardation affecting species in the groundwater that are not bound to particulates. We have combined population balance equations with transport equations in the TRACK3D computer code to model the transport of natural colloids.²⁰ Calculations done with the computer code compare well with analytic data from field measurements.²¹ The use of population balance equations coupled with transport codes is reviewed in Ref. 22.

A system has been assembled with which the particle-size distribution of colloids may be determined by means of autocorrelated photon spectroscopy. We tested this system on a gold colloid with both a helium-neon laser and a more powerful argon laser.²⁰ A computer program was written that inverts the autocorrelated photon spectroscopy data and allows good resolution of the particle-size distribution.²¹ We are testing the system further by using monodisperse polystyrene particles in the mean size range of 60 to 1000 nm (Ref. 22).

D. High-Precision Isotopic Analysis of Small Quantities of Plutonium (K. E. Perrin, G. W. Knobeloch, V. M. Armijo, and D. W. Efurd)

We are frequently asked to analyze samples of test debris or environmental samples that contain very small quantities of plutonium. The final measurement of plutonium from such samples is done with a thermal-ionization

mass spectrometer operating in the pulse-counting mode. We have recently developed an ionization technique that has high precision and accuracy.²³ It employs a surface-ionization diffusion-type source consisting of a rhenium filament overplated with platinum. With this technique, we routinely analyze samples containing a few femtograms of plutonium; the detection limit for plutonium is 2×10^5 atoms. Any contaminant that might coplate on the filament with plutonium or platinum must be eliminated before the sample is electroplated, so an extensive dissolution and purification scheme is needed for the sample preparation. The chemical procedure is described in detail as part of our discussion of the plutonium analysis. We have used the platinum overcoating method to measure neptunium, americium, uranium, and ruthenium, as well as plutonium.

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