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Laboratory and Field Studies Related to the Radionuclide Migration Project

October 1, 1985—September 30, 1986

Compiled and Edited by Joseph L. Thompson

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LABORATORY AND FIELD STUDIES
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ABSTRACT

In this report we describe the work done at Los Alamos in support of the Radionuclide Migration project during fiscal year 1986. We have continued to monitor the transport of tritium and ^{85}Kr from the Cambrian explosion zone to the satellite well, which is pumped at 600 gal./min. Corresponding movement of cationic radionuclides such as ^{137}Cs and ^{90}Sr has not yet been observed after 12 yr of pumping, nor have we seen evidence that these strongly sorbing ions move in conjunction with colloids. We have analyzed more data from the Cheshire study site but have not resolved the uncertainties regarding the distribution and movement of radioactive materials at this location. Our attempts to improve our analytical capability for ^{36}Cl and ^{99}Tc have resulted in some progress. Similarly, we have increased our understanding of radionuclide transport phenomena such as channeling in fracture flow and anion exclusion in zeolites and clays. A sample exchange with Lawrence Livermore National Laboratory has helped us identify critical steps in our procedures for collecting and analyzing large-volume water samples. We have surveyed potential sites on Pahute Mesa at the Nevada Test Site for future radionuclide migration studies and conclude that there are none other than Cheshire presently available, and none are likely to be created in the near future. The Laboratory has engaged recently in radionuclide migration studies sponsored by our weapons program; we review this work in an appendix to the annual report.

I. INTRODUCTION

The Radionuclide Migration (RNM) project was initiated in 1973 to study the movement of radionuclides at the Nevada Test Site (NTS). The agencies involved in this project seek to understand how radioactive materials associated with underground nuclear tests may migrate through the groundwater system. The principal organizations involved in the RNM work are Los Alamos National Laboratory (LANL), Lawrence Livermore National Laboratory (LLNL), the US Geological Survey, the Desert Research Institute, and the Nevada Operations Office of the US Department of Energy; they are assisted by various support organizations at the NTS. Contributions to the program by LANL are generally in the areas of radionuclide detection, geochemistry, and radionuclide interactions with geologic media. Our principal study sites at the NTS are in Area 5 (the Cambric site) and in Area 20 (the Cheshire site). We have worked at the Cambric site since 1974 and have learned a good deal about the behavior of radionuclides in tuffaceous alluvium. The Cheshire site has been studied for a shorter time. It is located in brecciated rhyolite and is more complex geologically and hydrologically than the Cambric site is. We also examine other nuclear test sites as the opportunity arises; one such study is described in the Appendix to this report. Our goal is to develop an understanding of the basic phenomenology of radionuclide transport in the underground environment at the NTS. The opportunity to make field observations is an invaluable adjunct to our laboratory experimental programs, allowing us to verify predictions and validate mathematical models. Much of the RNM work is also of interest to the Nevada Nuclear Waste Storage Investigation project, and many Los Alamos personnel contribute to both programs.

In this report we review our accomplishments in the RNM project during the past year. New data are presented and often the entire data base is reproduced to show trends. Some subjects have been treated in detail in previous reports and in such cases references are given to the earlier documents. This year we have adopted $\mu\text{Ci}/\text{m}\ell$ as our standard unit of concentration, whereas $\text{atoms}/\text{m}\ell$ was often used in the past, so some tables and figures will appear altered from previous reports.

II. CAMBRIC STUDIES

The Cambric site is the location of a 0.75-kt nuclear test conducted in 1965 at a depth of 294 m in tuffaceous alluvium in Frenchman Flat at the NTS. The detonation point was 73 m below the water table, but there is little water movement at this depth, and when we re-entered the cavity and chimney regions in 1974 we found that the tritium and fission products associated with the test shot were still there. After we measured the distribution of the radionuclides between the soil and water, we began in 1974 testing to see what radioactive materials would move as the groundwater moved. We pumped water from a satellite well (RNM-2S) 91 m from the cavity, first at 300 gal./min and after 2 yr at 600 gal. min. We have continued to monitor the concentrations of radionuclides in the effluent water from RNM-2S and in the RNM-1 water. The work at the Cambric site is described in several articles¹⁻³ and annual reports.⁴⁻⁹ We present here new data acquired during the past year and discuss its relation to the existing data set.

A. Sampling and Counting Methodologies

Because our water samples from Cambric and other sites contain very small concentrations of radionuclides, we have developed sampling and counting protocols that enable us to measure the species of interest at or below the pCi/ml level. We described our procedures in some detail in our annual report for last year,⁹ so here we will only indicate the general method used and the level of detection routinely achieved.

Tritium analysis of pumped or bailed water samples is done by liquid scintillation counting. Our normal measurement limits are $\sim 2 \times 10^{-6}$ $\mu\text{Ci/ml}$ of water. Water samples containing ^{85}Kr are collected in gas-tight "pressurized tubes" and the ^{85}Kr is separated using a vacuum line. The ^{85}Kr is beta counted with a proportional counter over a period of several weeks. The detection limit for ^{85}Kr is $\sim 1 \times 10^{-8}$ $\mu\text{Ci/ml}$ of the water sample. We frequently measure 208- ℓ (55-gal.) water samples for the presence of gamma-emitting radionuclides. We concentrate these samples using a glass still, then evaporate them to dryness, and count them with a germanium detector. With this procedure we can detect ^{137}Cs at concentrations down to 4×10^{-11} $\mu\text{Ci/ml}$. We may separate ^{90}Sr or ^{137}Cs from water samples by using radiochemical procedures. If we start with 2- ℓ samples, our

measurement levels are ~ 1 to 2×10^{-8} $\mu\text{Ci}/\text{m}\ell$. We can chemically separate plutonium and alpha count the purified product. The counting limit for ^{239}Pu is $\sim 2 \times 10^{-11}$ $\mu\text{Ci}/\text{m}\ell$.

Nonroutine sample analyses for radionuclides such as ^{36}Cl , ^{99}Tc , and ^{129}I require more exotic procedures such as tandem-accelerator mass spectrometry, neutron activation analysis, and isotope dilution mass spectrometry. The use of such techniques is described for particular radionuclides in this and previous annual reports.

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

We have continued to monitor the decreasing levels of tritium in the effluent from the RNM-2S well. The latest data are given in Table I and the complete data set is displayed in Figs. 1 and 2. The shape of the tail of the elution curve will enable us to validate various models proposed to explain the movement of tritium between the RNM-1 and RNM-2S wells.^{5,8} The pump at RNM-2S was off from 12/05/85 to 01/21/86; the unusually large scatter in the data at about this time may be related to that fact. Through the end of September 1986, $\sim 75\%$ of the initial tritium inventory has been pumped out of RNM-2S.

C. Fission Product Migration (S. Maestas, A. E. Ogard, A. J. Mitchell, F. O. Lawrence, J. Drake, D. W. Eford, J. D. Gallagher, and J. L. Thompson)

We have listed in Table II the ^{85}Kr concentrations measured in RNM-2S water samples during the past year and in Fig. 3 have displayed the entire elution curve for this radionuclide. Although the elution pattern is generally similar, it is apparent that krypton is eluted somewhat after tritium. The ratio of ^{85}Kr /tritium as given in Table II and displayed in Fig. 4 shows a slowly rising trend but is significantly less than the source term ratio of 1.22×10^{-4} .

At RNM-1 the tritium and ^{85}Kr concentrations continue to decrease, as shown in Tables III and IV. However, the ^{85}Kr /tritium ratio remains higher than the source term ratio, again reflecting the fact that the krypton has not moved out of the cavity region as readily as has the tritium.

New data for ^{90}Sr and ^{137}Cs in RNM-1 water are given in Table V. We have included the complete data set for these radionuclides because we are using different units than in

TABLE I
TRITIUM ANALYSES OF RNM-2S WATER SAMPLES

Identification Number	Date Collected	Volume Pumped (10 ⁶ gals.)	Tritium ^a (10 ⁻³ μ Ci/ml)
G 1449	11/20/85	2837.3	1.06
G 1450	12/04/85	2847.0	0.94
b			
G 1451	01/22/86	2847.7	1.05
G 1452	01/28/86	2852.9	1.09
G 1453	02/04/86	2859.1	1.02
G 1454	02/10/86	2864.4	1.01
G 1455	02/19/86	2872.3	1.01
G 1456	02/27/86	2879.5	1.00
G 1457	04/03/86	2910.1	0.96
G 1458	05/22/86	2952.8	0.95
G 1459	06/20/86	2978.1	0.94
G 1460	07/23/86	3007.1	0.91
G 1461	08/19/86	3030.1	0.89
G 1462	09/27/86	3063.6	0.87

^aStandard deviation of counting data <1%.

^bNo pumping from 12/05/85 to 01/21/86; new pump installed 01/21/86.

previous years. The trend seen in recent years continues; namely the ⁹⁰Sr and ¹³⁷Cs concentrations are decreasing at a much slower rate than the concentration of the tritium. To date we have no evidence of either ⁹⁰Sr or ¹³⁷Cs in RNM-2S water. The large sorption ratios of these anions on tuffs, as measured in our laboratory,¹⁰ preclude their transport as dissolved species. We might anticipate that colloid-sized particles could carry either of these radionuclides over the 91-m distance between the two wells. However, our filtration studies of the RNM-2S water indicate that this water is very low in particulate content relative to other pumped water on the NTS. Apparently, the tuffaceous alluvium is a very effective filter, so colloid transport is not occurring to a measurable extent.

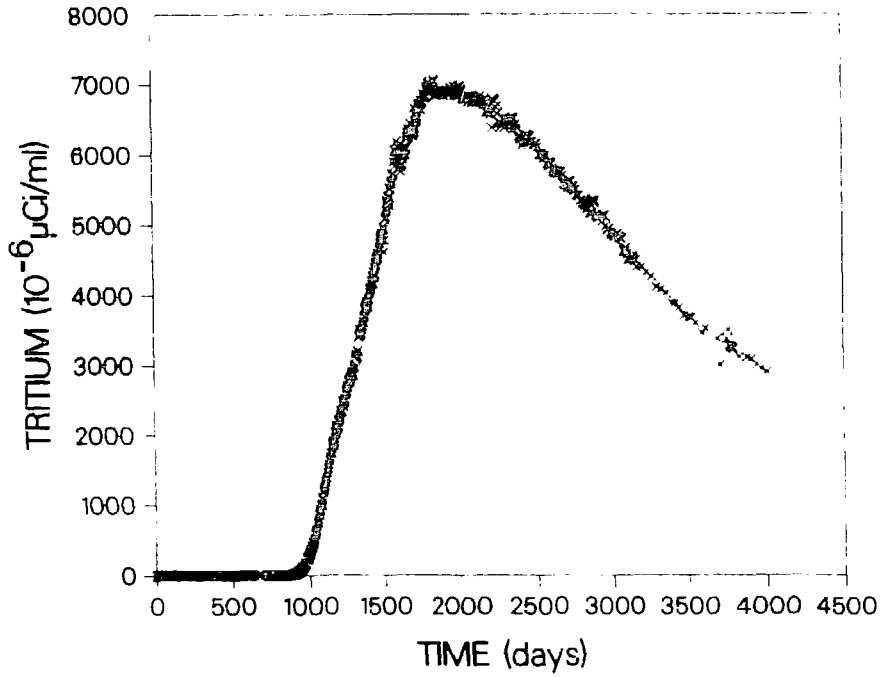


Fig. 1. Tritium concentration in water pumped from RNM-2S *vs* time.

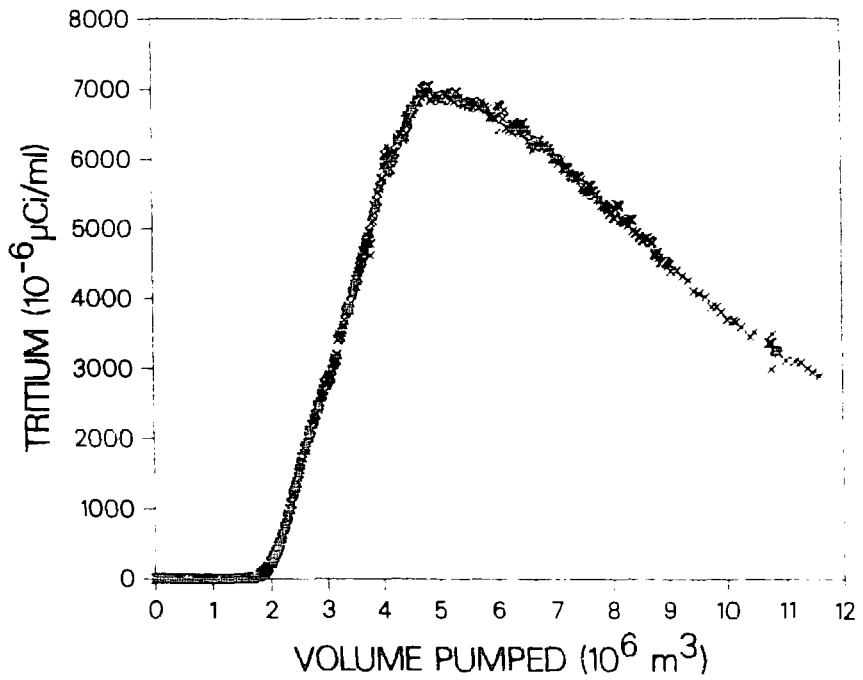


Fig. 2. Tritium concentration in water pumped from RNM-2S *vs* volume pumped.

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

Identification Number	Date Collected	Volume Pumped (10^6 m^3)	$^{85}\text{Kr}/\text{Tritium}$			
			Tritium Concentration $10^{-3} \mu\text{Ci}/\text{ml}$	^{85}Kr Concentration $10^{-7} \mu\text{Ci}/\text{ml}$	Atom Ratio ^b $\times 10^5$	Ratio ^c
434-1-85-019	11/20/85	10.740	3.32	2.67	7.00	0.57
434-1-85-021	12/04/85	10.777	3.01	2.42	7.00	0.57
434-1-86-001	01/24/86	10.787	3.38	1.60	4.11	0.34
434-1-86-003	02/19/86	10.873	3.24	2.54	6.82	0.56
434-1-86-005	03/19/86	10.966	3.17	2.32	6.36	0.52
434-1-86-007	04/03/86	11.014	3.13	2.46	6.84	0.56
434-1-86-009	05/22/86	11.176	3.10	2.46	6.91	0.57
434-1-86-013	07/08/86	11.333	3.01	2.30	6.65	0.54
434-1-86-015	08/05/86	11.424	2.95	2.42	7.14	0.58
434-1-86-017	09/03/86	11.521	2.94	2.40	7.10	0.58

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

^b 1.81×10^{13} atoms $^{85}\text{Kr} = 1 \mu\text{Ci}$; 2.08×10^{13} atoms tritium = $1 \mu\text{Ci}$.

^cMeasured $^{85}\text{Kr}/\text{tritium}$ atom ratio divided by $^{85}\text{Kr}/\text{tritium}$ atom ratio calculated for Cambic zero time (1.22×10^{-4})

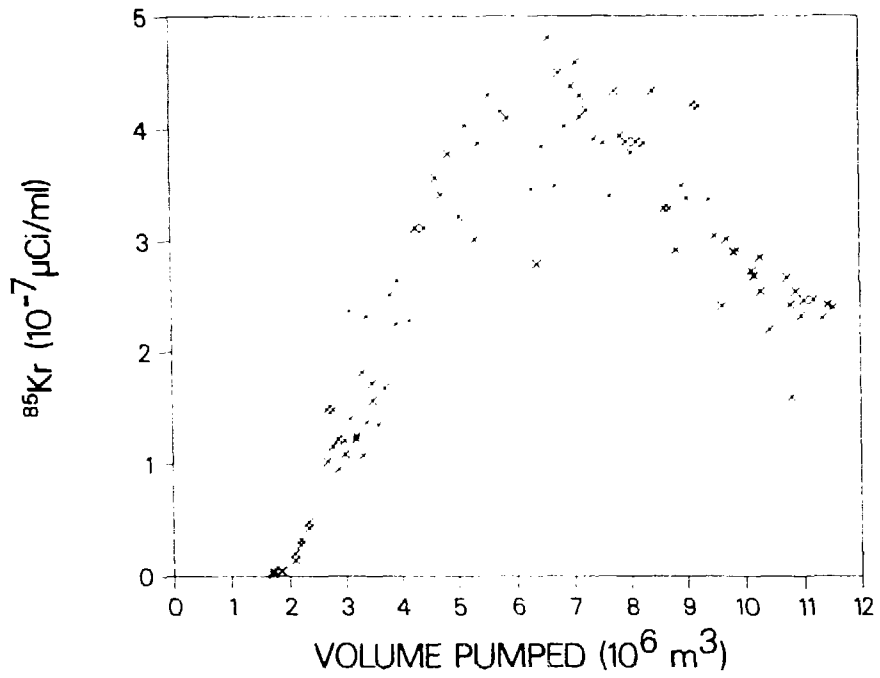


Fig. 3. The ^{85}Kr concentration in water pumped from RNM-2S.

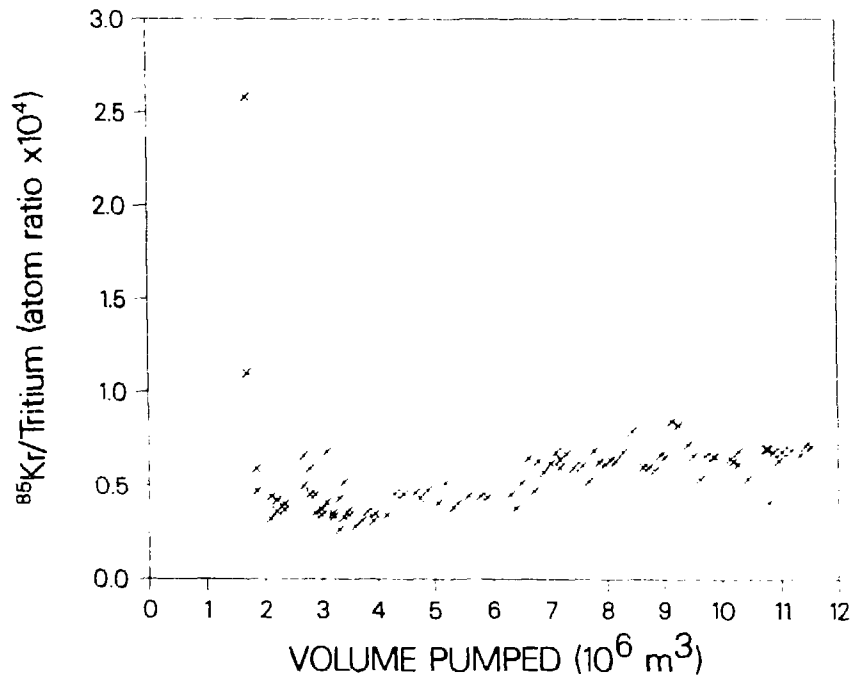


Fig. 4. Atom ratio of ^{85}Kr to tritium in water pumped from RNM-2S.

TABLE III
TRITIUM CONCENTRATION IN RNM-1 WATER (1986)

Identification Number	Volume Pumped (m ³)	Tritium Concentration (10 ⁻⁶ μCi/ml)	
		On Collection Date 5/7/86	Corrected to Cambric t ₀ 5/14/65
S-1	1.5	1.55	5.05
S-2	11.0	1.80	5.86
S-3	24.2	1.80	5.86
S-4	31.8	1.72	5.60
S-5	44.3	1.68	5.47
S-6	51.5	1.72	5.60
S-7	61.3	1.80	5.86
434-3-86-001 ^a	60.6	2.16	7.10
			Average 5.80

^aCollected in a gas-tight pressurized tube.

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

Zone	Date	Volume Pumped ^a (10 ⁶ m ³)	Concentration ^b		⁸⁵ Kr/Tritium	
			Tritium (μCi/ml)	⁸⁵ Kr (μCi/ml)	Atom Ratio ^c (× 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

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

^b Values corrected to Cambric zero time.

^c 1.81 × 10¹³ atoms ⁸⁵Kr = 1 μCi; 2.08 × 10¹³ atoms tritium = 1 μCi.

^d Measured ⁸⁵Kr/tritium divided by ⁸⁵Kr/tritium calculated for Cambric (1.22 × 10⁻⁴).

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

Zone	Date	Volume Pumped ^a (10^6 m^3)	Concentration ^b			Atom Ratio ^c ($\times 10^4$)	
			Tritium ($\mu\text{Ci}/\text{ml}$)	^{90}Sr ($\mu\text{Ci}/\text{ml}$)	^{137}Cs ($\mu\text{Ci}/\text{ml}$)	$^{90}\text{Sr}/\text{T}$	$^{137}\text{Cs}/\text{T}$
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

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

^b Values corrected to Cambrian zero time.

^c 4.81×10^{13} atoms $^{90}\text{Sr} = 1 \mu\text{Ci}$; 5.09×10^{13} atoms $^{137}\text{Cs} = 1 \mu\text{Ci}$.

III. CHESHIRE STUDIES (J. L. Thompson, S. Maestas, F. O. Lawrence, G. W. Knobeloch, D. W. Eford, J. Drake, and J. D. Gallagher)

As noted in the Introduction to this document, the Cheshire site is quite different from the Cambria site geologically, and it has hydraulic gradients that may cause movement of some of the radionuclides associated with the test. The test device was fired in the brecciated rhyolite of Pahute Mesa in February 1976 at a depth of 1174 m, ~544 m below the water table. We did limited sampling near the cavity region in late 1976; this effort was terminated when a pump became stuck in the re-entry hole. In 1983 and 1984 we collected water samples through perforations in the casing at a depth of about 1200 m. In 1985 we set a packer above 1200 m, made new perforations at 820 m, and collected more water samples. During the past year, we have analyzed a few water samples for tritium and ^{85}Kr and have boiled down and counted two 208- ℓ samples, one taken just before the 820-m perforations were made and one taken several months later. These analyses add to our data base but do not answer the questions concerning data interpretation that were discussed in our report from last year.⁹

Table VI contains tritium analyses results obtained since September 1985. These values, added to those in Table VI of Ref. 9 and Table IX of Ref. 8, complete our data set for tritium measurements for Cheshire samples. In Table VII we presented our complete data set for tritium and ^{85}Kr measured in pressurized samples from Cheshire. Finally, in Table VIII we list our most recent analyses of gamma-emitting radionuclides in evaporated 208- ℓ water samples. This latter group may be compared with the data in Table VIII of Ref. 9.

In general, the concentrations of all of the radionuclides sampled have decreased as water was pumped from the hole at Cheshire. This trend can be seen in Figs. 5 and 6. The surprising observation is that most species are present in about the same concentrations in samples from 820-m depth and those from 1200-m depth. We would have anticipated that in traveling 400 m through rhyolite, elements like cesium and strontium would be largely removed from solution because of their high sorption coefficients. Another difficulty in assessing our measurements at Cheshire is that we have never measured tritium concentrations as high as the value expected for the cavity region. These problems are

TABLE VI
TRITIUM CONCENTRATION IN WATER PUMPED FROM CHESHIRE

Identification Number	Date	Volume Pumped (10 ⁶ gals.)	Tritium (10 ² μCi/ml) ^a
C-25	10/01/85	7.4	3.82
852-1-85-008	11/04/85	9.1	3.94
C-26	11/07/85	9.3	3.97

^aStandard deviation of counting data <1%. Values are corrected to t₀ = 02/14/76.

TABLE VII
TRITIUM AND ⁸⁵Kr ANALYSES OF PRESSURIZED
WATER SAMPLES FROM CHESHIRE

Identification Number	Date	Volume Pumped (10 ⁶ gals.)	Concentration		⁸⁵ Kr/Tritium	
			⁸⁵ Kr (10 ⁻⁴ μCi/ml)	Tritium (10 ⁻¹ μCi/ml)	Atom Ratio ^a × 10 ⁴	Ratio ^b
852-1-83-008	09/09/83	0.06	3.0	5.77	4.5	0.76
852-1-83-009	09/09/83	0.06	3.3	5.58	5.2	0.88
852-1-84-001	08/01/84	0.17	3.2	5.38	5.2	0.88
852-1-84-003	10/23/84	3.0	2.9	5.19	4.9	0.83
852-1-84-005	10/23/84	3.0	2.4	5.14	4.1	0.70
852-1-85-001	05/09/85	3.4	3.1	4.95	5.4	0.92
852-1-85-002	05/09/85	3.4	3.0	5.00	5.2	0.88
852-1-85-003	05/14/85	3.5	3.0	4.6	5.7	0.97
852-1-85-004	05/14/85	3.5	3.2	4.7	5.9	1.00
852-1-85-005	06/18/85	4.8	2.6	4.1	5.5	0.93
852-1-85-008	11/04/85	9.1	2.4	3.9	5.4	0.92

^a1.81 × 10¹³ atoms ⁸⁵Kr = 1 μCi; 2.08 × 10¹³ atoms tritium = 1 μCi.

^bMeasured ⁸⁵Kr/tritium divided by ⁸⁵Kr/tritium atom ratio calculated for Cheshire zero time (5.90 × 10⁻⁴).

TABLE VIII
RADIONUCLIDES IN WATER AT CHESHIRE

Radionuclide	Concentration ($\mu\text{Ci/ml}$) ^a	
	852-9-85-001 ^b	852-9-85-005 ^c
³ H	4.98×10^{-1}	3.94×10^{-1}
²² Na	7×10^{-9}	2×10^{-9}
⁴⁰ K	5.8×10^{-9}	9.8×10^{-9}
⁶⁰ Co	1×10^{-10}	1×10^{-10}
⁸⁵ Kr	3.0×10^{-4}	2.4×10^{-4}
⁹⁰ Sr	1.5×10^{-7}	—
¹⁰⁶ Ru	1×10^{-8}	6×10^{-7}
¹²⁵ Sb	5.1×10^{-6}	4.1×10^{-6}
¹³⁴ Cs	1×10^{-8}	9×10^{-10}
¹³⁷ Cs	2.6×10^{-6}	—
(radiochem.) ¹³⁷ Cs	1.9×10^{-6}	6.9×10^{-7}
(gamma spec.) ¹⁵² Eu	not detected	not detected
¹⁵⁴ Eu	10^{-9}	10^{-9}
¹⁵⁵ Eu	10^{-9}	10^{-9}

^aConcentrations corrected to $t_0 = 02/14/76$.

^bCollected 05/09/85; 3.4×10^6 gals. pumped.

^cCollected 11/04/85; 9.1×10^6 gals. pumped.

discussed in more detail in Ref. 9. The information collected this past year has not resolved our problems with interpreting the data from Cheshire.

IV. ANALYTICAL DEVELOPMENT

A. Measurement of ³⁶Cl (A. E. Ogard and D. J. Rokop)

The concentration of ³⁶Cl in waters pumped from RNM-2S as analyzed on the University of Rochester tandem accelerator mass spectrometer was reported in Ref. 6. We

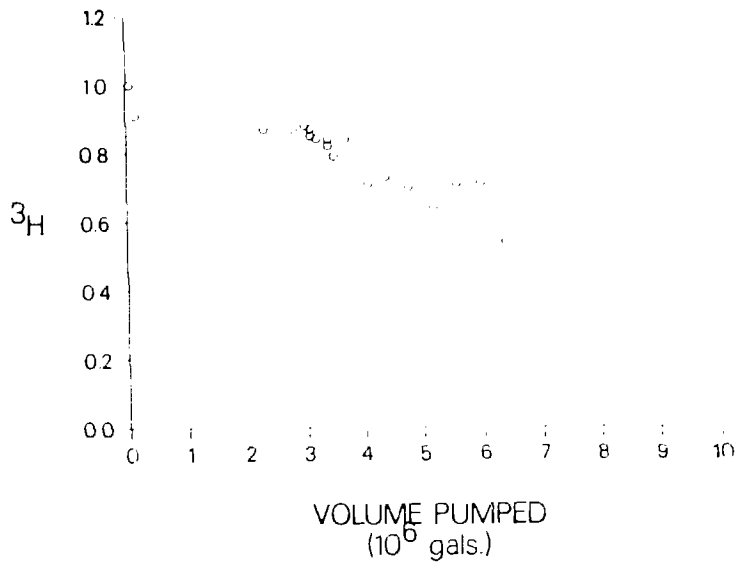


Fig. 5. Relative tritium concentration in water from Cheshire as a function of volume pumped.

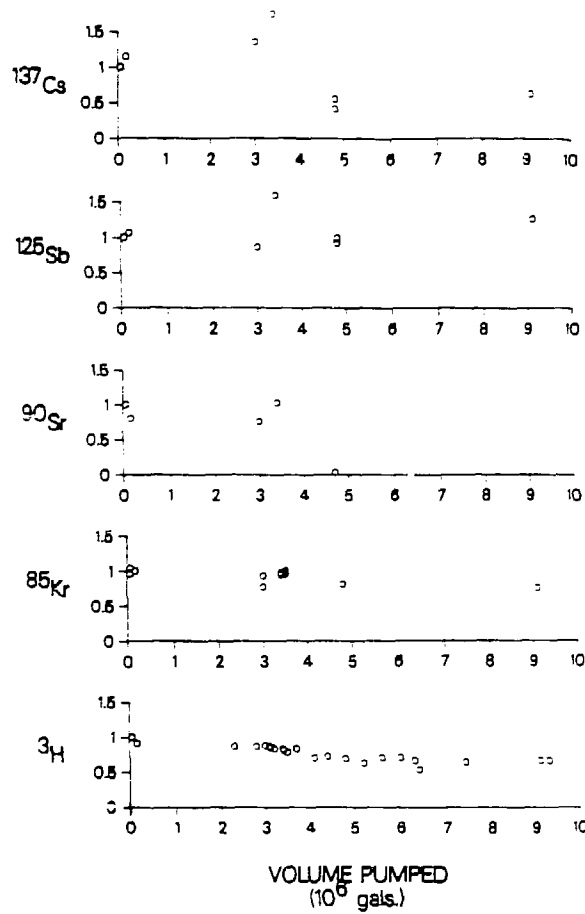


Fig. 6. Relative radionuclide concentrations in water from Cheshire as a function of volume pumped.

have recently prepared a new suite of samples that includes water taken during the previously measured period and extends the sampling period to January 1987. We prepared the ^{36}Cl samples by adding sufficient KCl to the RNM-2S water to give a $^{36}\text{Cl}/\text{Cl}$ ratio of $\sim 2 \times 10^{-12}$. We precipitated the chlorine as AgCl , purified the precipitate of any ^{36}S , and stored it in readiness for analysis sometime in early 1987.

The University of Rochester tandem accelerator mass spectrometer is the only facility in this country that can perform ^{36}Cl analyses at the level found in RNM-2S water. There are, however, circumstances in which the concentration of ^{36}Cl in the environment is higher because of anthropogenic sources and then standard mass spectrometric analysis is possible. We have prepared ^{36}Cl standards and analyzed their isotopic content with our tandem magnetic mass spectrometer to determine our lower limits of detection of this isotope. We use negative thermal ionization from a triple-filament source. The high dynamic range of measurement requires the use of a Faraday cup to collect the ^{35}Cl and single-ion counting to measure the ^{36}Cl . We obtained excellent agreement between measured and standard values for ^{36}Cl in concentration ratios of $^{36}\text{Cl}/\text{Cl}$ from 10^{-7} to 10^{-9} . The useful detection limit of our equipment as currently configured is $\sim 5 \times 10^{-10}$; the addition of an electrostatic analyzer to the tandem magnetic mass spectrometer should extend the limit to 5×10^{-11} . Although this is not sensitive enough for RNM samples, it may be sufficient for ^{36}Cl analyses of environmental samples derived from other locations.

B. Measurement of ^{99}Tc (A. E. Ogard, D. J. Rokop, D. B. Curtis, and N. C. Schroeder)

During the past year, we have continued to work on a procedure that uses the tandem magnetic mass spectrometer to measure ^{99}Tc in RNM waters. Our procedure involves adding a technetium tracer to the water sample, sorbing the technetium on an ion exchange resin, and washing it free of impurities. We then elute the technetium, remove most of the acid by evaporation, and distill the technetium to an ice-cooled surface. After dissolving the technetium in a minimum of water, we electroplate it onto a rhenium filament. We treat this filament with La_2O_3 and H_2O_2 , then with NH_4OH before introducing it into the spectrometer. The TcO_4^- ions are produced by negative ionization. The sensitivity of

this method is $\sim 5 \times 10^6$ atoms of technetium. We will apply this methodology to RNM samples during the coming year.

C. Radionuclide Transport (R. S. Rundberg, D. R. Janecky, and A. J. Mitchell)

We have made progress during the past year in understanding two aspects of radionuclide transport. The information we have acquired is only summarized here; some of it is presented in detail in another report.¹¹ We have observed that simple matrix diffusion models cannot explain our laboratory observations of radionuclide transport through fractures in natural tuff. Although nonsorbing radioactive tracers move through the fractures in reasonable correspondence with matrix diffusion model predictions, sorbing tracers produce an elution pulse earlier than expected. The size and shape of this pulse cannot be reproduced by simply reducing the distribution coefficient or adjusting the diffusivity in the model. However, by including channeling we can explain this early pulse. Channeling is caused by the irregular surface texture of the fractures and can be modeled using fractal geometry.

Another phenomenon we have been studying is anion exclusion, which results in anions moving through geologic media more rapidly than the reference water moves. We have been able to relate the magnitude of anion exclusion to the internal void volume of zeolites and clays. In the simplest terms, anions with radii larger than or close to the channel diameters of the zeolites or the interlayer spacing in the clays will be excluded from the zeolite intercrystalline pore space or the clay interlayer void. We observed good correlation between the experimentally measured anion exclusion in crushed-rock columns of tuff containing known amounts of mordenite, clinoptilolite, analcime, and smectite and the calculated interstitial and void volumes of these minerals. Anion exclusion may have a significant effect on the relative speed with which some anions travel in field situations, especially in rock that is not fully saturated with water.

D. Comparison of Los Alamos Samples with Those from LLNL (J. L. Thompson and J. D. Gallagher)

Both LLNL and LANL have reported analyses of water samples collected at essentially the same time from the same source (for example, see data in Refs. 9 and 12 about

U20n samples collected in September 1983). Direct comparison of these analyses is difficult because the laboratories chose different reference times (shot time *vs* collection time), but if appropriate corrections are made, it is apparent that there are significant disagreements in the reported concentrations of many radionuclides. A major source of these divergent results is the different sampling and sample treatments procedures employed by the two laboratories. These procedures are described in Ref. 8 for LANL and in Ref. 12 for LLNL. A critical step in sample treatment is the filtering done before the water is evaporated. The LLNL report presents data showing how sensitive the results are to the filtering protocol used.¹² A number of the radionuclides present in these samples appear to be associated with very small (that is, <50-nm-diam) particles that may or may not be retained on the filters—depending on the filter type and pore size. Another possible cause for differing results is the different counting techniques used by the two laboratories. To determine how important this might be, we exchanged dried samples. The sample received by LANL was identified as barrel 3, U20n, 166 ℓ, collected 10/23/83; it was accompanied by a gamma-ray analysis based on the computer code GAMANAL. We repackaged the sample to conform to the container type routinely used in our work and counted and analyzed it according to normal procedures. The computer codes we used were RAYGUN and SPECANL, which generally agree with each other within ~5%. In Table IX we have presented the LANL/LLNL activity ratios for nuclides, as determined by these two codes. It is apparent that although the counting results differ somewhat between the two laboratories, the major source of variation must reside in sample treatment before counting. We believe that part of the difference seen in the counting results can be attributed to the size difference between the LLNL sample and our usual samples. Sample size affects the source-counter geometry and, hence, the counting efficiency. This sample exchange has been helpful in that it caused us to review critically the steps in our sampling and analyzing procedures; we hope to continue and to expand interlaboratory exchanges.

V. SURVEY OF POSSIBLE SITES FOR RADIONUCLIDE MIGRATION STUDIES

Since the beginning of the RNM project, we have been aware of the need to examine the radionuclide migration in as many of the varied geological/hydrological environments

TABLE IX
SAMPLE COMPARISON

Nuclide	$\left(\frac{\text{Activity(LANL)}}{\text{Activity(LLNL)}} \right)$	
	Raygun	Specan1
⁴⁰ K	1.42	1.48
⁶⁰ Co	1.09	1.04
¹⁰⁶ Ru	1.00	1.21
¹²⁵ Sb	0.85	0.80
¹³⁴ Cs	0.93	1.01
¹³⁷ Cs	0.75	0.75
¹⁵² Eu	0.93	0.89
¹⁵⁴ Eu	1.15	1.12
¹⁵⁵ Eu	1.15	1.18

found on the NTS as possible. Our most intensively studied site, Cambric, is located in alluvial soil in which there is a low natural hydraulic gradient and little fracturing. We monitored wells drilled in the vicinity of nuclear test events in the Yucca Flat region of the NTS where there is layered tuff and where fracturing may be significant. We may have the opportunity to learn more about radionuclide movement in the Yucca Flat area in the near future (see Appendix). The brecciated rhyolites of Pahute Mesa provide yet another medium for our studies, and we are attempting to observe the movement of radionuclides in the vicinity of the Cheshire event in area 20 of the NTS. Because of the uncertainties associated with samples obtained from Cheshire (Refs. 8 and 9), we are continuing to look for other potential study sites on Pahute Mesa and have recently completed a survey of such locations.

Favorable criteria for an RNM study site include:

- (1) a test conducted below the water table so that the resulting cavity will be completely flooded with the infilling water. If appreciable amounts of postshot radioactive material are left in the unsaturated zone, it is very difficult to define the radionuclide source term because our knowledge of radioactive movement in unsaturated material is extremely limited. Much of our sampling is of water (either pumped or bailed),

and we need to know that the water is in contact with the radioactive materials of interest.

- (2) a test conducted within the past few years, preferably within less than 1 yr. A number of nuclides such as ^3H , ^{85}Kr , ^{90}Sr , and ^{137}Cs are sufficiently long-lived to be present many years after their production, but the variety of radionuclides available for sampling is much richer in the first year or two. Also, the isotopic distribution of certain shorter-lived radionuclides (for example, ^{89}Sr and ^{134}Cs) may give some clues about their initial mode of transport. Pairs of radionuclides in which one isotope has gaseous precursors and one does not (^{134}Cs and ^{137}Cs) or the isobaric precursors have differing half-lives (^{89}Sr and ^{90}Sr) are particularly useful in this regard.
- (3) a test conducted in a location for which the geologic and hydrologic features are well characterized. In particular, we would like to know the composition of the rock, the extent of fracturing, the transmissivity of the rock, and the direction and speed of water movement in the area.
- (4) a test located where there is no possibility of the presence of radioactive material from previous tests. Our understanding of radionuclide migration is too primitive to cope with the complexities associated with multiple-source terms.

Application of these criteria to tests conducted on Pahute Mesa narrows the choice of candidates for RNM studies. The majority of these tests were fired in the unsaturated zone or at the level of the water table. Only one test satisfied criteria 1 through 3. Unfortunately, it was located some 400 m from a previous test, which probably caused extensive fracturing in the area and is a potential source of radionuclides in the groundwater. It appears that Cheshire is the only site on Pahute Mesa presently available for RNM studies. We are exploring the possibility that a future test could be located in this area and thereby be suitable for our work.

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APPENDIX

RADIONUCLIDES AT U3kz

Early in 1984, tritium was discovered in water at an emplacement hole, U3kz, that was being readied for a test event scheduled for 1986. Subsequently, we detected the presence of fission products in water samples from this site. This discovery triggered an intensive investigation by personnel from INC, ESS, and J Divisions at LANL to discover the source and mode of travel of the observed radionuclides. This work is being funded by the weapons program and is not part of our regular RNM project. However, what we are learning from the U3kz effort is very pertinent to RNM studies and, therefore, we are including here a brief review of the U3kz work through October 1986. The review will focus largely on results obtained within the INC Division of the Laboratory.

Our initial sampling of the U3kz emplacement hole took place in April 1985 when we took two pressurized water samples. We found ^{85}Kr as well as tritium in both of them. We collected a 55-gal. sample in December 1985 during dewatering of the hole. We boiled down this barrel of water in May 1986 and detected ^{106}Ru , ^{125}Sb , ^{137}Cs , and Pu in the residue as well as on the 5- μm filters through which we filtered the water before evaporating it. Although the amount of plutonium present in the evaporated sample was quite small ($\sim 10^9$ atoms), we hoped to use the alpha activity ratio $^{238}\text{Pu}/\text{total Pu}$ to determine the source of the material. There are four expanded test holes in the vicinity of U3kz that are potential sites from which radionuclides might have moved to U3kz. The alpha activity ratio $^{238}\text{Pu}/\text{total Pu}$ ranges from 0.11 to 0.24 for these four sites, so it might have been possible to associate U3kz data with one of these sites. Unfortunately, we found the U3kz alpha activity ratio value is 0.68—an anomalously high value probably caused by ^{238}Pu that was windblown and contaminated the water samples at the site.

In May 1986, we collected another 55-gal. water sample from U3kz, filtered it through 0.05- μm Millipore filters, and then evaporated it. We detected tritium and ^{90}Sr in the filtered water as well as the fission products ^{106}Ru , ^{125}Sb , and ^{137}Cs in the residue. Also, we found these same fission products in the material retained on the filters. The major fraction of the ^{106}Ru and ^{137}Cs activities occurred with the material on the filter, whereas the major fraction of the ^{125}Sb occurred with the water. In addition, we detected the

presence of ^{102m}Rh on the filters. We dissolved the filters and radiochemically separated the rhodium. Then we compared the isotopic composition of this sample with similar archived samples from the four expended test holes around U3kz. These isotopic ratios were measured with very good precision, and we have considerable confidence in them. The data are presented in Table A-I. The agreement of the $^{101g}\text{Rh}/^{102m}\text{Rh}$ values and the absence of ^{102g}Rh indicated that the rhodium detected at U3kz was produced by the Sandreef test. Although this does not prove that all the other radioactive material detected at U3kz came from Sandreef, there are no anomolous quantities of any radionuclides that would indicate contamination from other, more recent tests. Because we had on hand some archival refractory material from Sandreef, we re-counted this material with a Ge(Li) detector system and compared the results with those from the U3kz material (see Table A-II). It is apparent that many of the refractory elements present in the Sandreef cavity are not present at U3kz. The absence of ^{106}Ru in the refractory Sandreef sample is due to both its short half-life and its volatility.

The observation that radionuclides had migrated some 350 m (1150 ft) from Sandreef evoked considerable interest at the NTS as well as at LANL. The NTS site manager convened an *ad hoc* Aleman Radionuclide Migration Panel to advise him about the test shot Aleman, which was scheduled to be fired in the hole U3kz. Of particular concern was the possibility that the test shot would alter the U3kz site so that further studies could not be carried on there. This problem was resolved when LANL (J Division) drilled an auxillary hole, UE3e, 61 m (200 ft) north of U3kz to intercept the transport path of the radionuclides from Sandreef. Our analysis of water from UE3e showed that the same radionuclides were present and in the same relative amounts as in the water from U3kz. Logs taken in UE3e indicated that the measured gamma activity was confined to a narrow band at 658 m (2160 ft) depth. Sidewall coring yielded a small amount of material in which ^{137}Cs was present but not ^{106}Ru or ^{125}Sb . The reason for this apparent separation of radionuclides is not clear. Observations of the water pressure at depth in both U3kz and UE3e indicate that below ~ 600 m the water is under a pressure ~ 20 atmospheres higher than expected. We do not know the relationship between the pressurized aquifer and the radionuclide migration.

TABLE A-I
RHODIUM ANALYSES

Shot	^{102g}Rh (in 1986)	$\left(\frac{^{101g}\text{Rh}/^{102m}\text{Rh} \text{ at shot time in shot debris}}{^{101g}\text{Rh}/^{102m}\text{Rh} \text{ at shot time in U3kz debris}} \right)$
Tortugas (1984)	measurable	1.96
Turquoise (1983)	measurable	1.03
Bouschet (1982)	measurable	1.13
Sandreef (1977)	not measurable	1.00
U3kz	not measurable	

TABLE A-II
RADIONUCLIDES PRESENT IN SAMPLES
FROM SANDREEF AND U3KZ AS OF JULY 1986 AS
DETERMINED BY GAMMA-RAY SPECTROSCOPY

	Sandreef (Refractory Soil)	U3kz (Filtered Particulates)
^{54}Mn	X ^a	O
^{60}Co	X	O
^{102m}Rh	X	X
^{106}Ru	O	X
^{125}Sb	X	X
^{134}Cs	X	O
^{137}Cs	X	X
^{144}Ce	X	O
^{150}Eu	X	O
^{152}Eu	X	O
^{154}Eu	X	O

^a X = measurable; O = not measurable.

To trace the postshot movement of radionuclides from Aleman, we added tracers to the Aleman event. These consisted of a small amount of ^{244}Cm , and large amounts of NaCl, and cobalt. The ^{36}Cl and ^{60}Co activation products, along with the ^{244}Cm , would provide a variety of radiochemical species—both anionic and cationic—that would be uniquely associated with the Aleman event. In addition, we placed NaBr in UE3e before it was stemmed so that water pumped from this region could also be recognized. A number of water samples were taken from U3kz during the last dewatering before the test device was inserted. Also, surface and subsurface soil samples were collected from the area before Aleman was fired (see Fig. A-1).

Aleman was fired 9/11/86. The low yield probably resulted in incomplete activation of the tracers and little dispersion of tracer materials. We plan to drill a hole in the U3kz/UE3e area during 1987 to obtain more information concerning the geology and hydrology of the formation(s) through which radionuclide migration from Sandreef occurred. In the meantime, we are studying the particulates present in the water samples collected from U3kz during the final dewatering. Our goal is to establish if any relationships exist between the composition of the particulates, their size, and the fission products associated with them. We filtered a 55-gal. water sample through a 10- μm prefilter and an Amicon porous filter membrane; after backflushing the Amicon filter, we obtained ~ 6 g of particulates with particle diameters >5 nm. These particulates contained $\sim 10^9$ - 10^{10} atoms of ^{106}Ru , ^{125}Sb , and ^{137}Cs per gram of solid. The composition of the particulates, as determined by x-ray diffraction, was clinoptilolite (50-60%), feldspar (25%), opal (10%), and smectite ($<10\%$). We separated the clinoptilolite and smectite fractions by a grinding and settling-rate technique and found that no large differences exist in the relative concentrations of ^{106}Ru , ^{125}Sb , and ^{137}Cs associated with these two minerals. Table A-III and A-IV report results for all the samples taken by personnel from INC Division from U3kz and UE3e, respectively.

The U3kz study is continuing, and may expand to include analyses of samples from other sites in Areas 3 and 4 of the NTS.

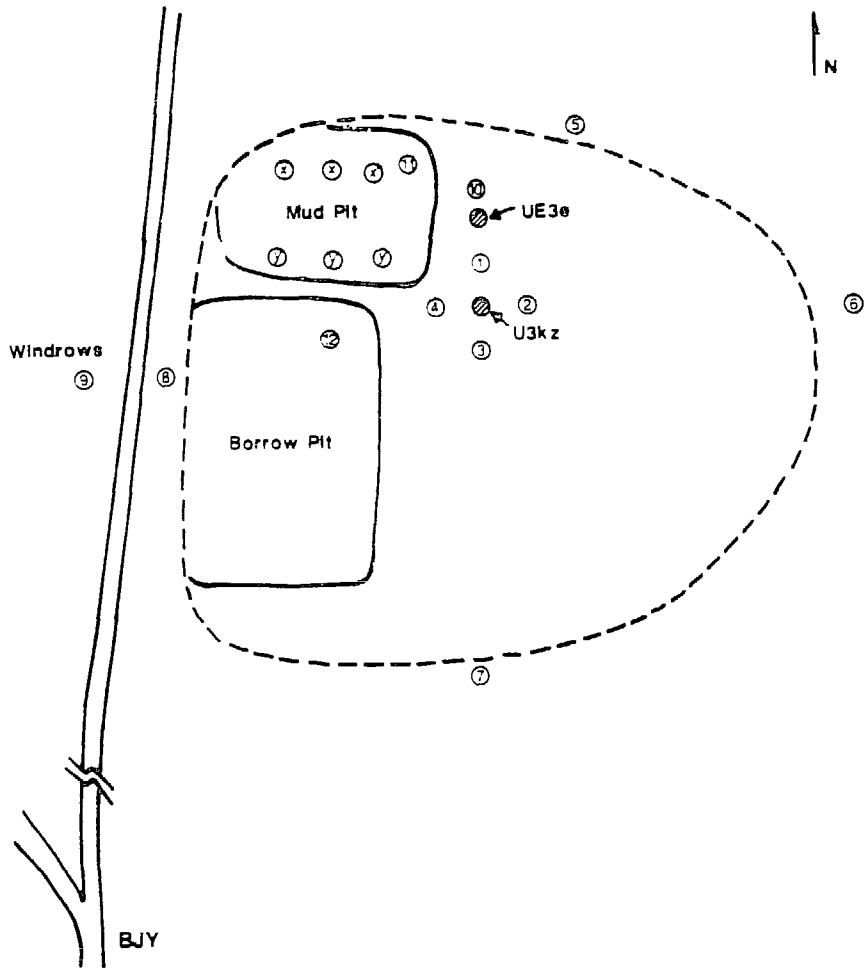


Fig. A-1. Soil Sampling at U3kz Area .

TABLE A-III
SAMPLE COLLECTIONS U3kz

Date	Identification Number	Type	Comments
04/09/85	1234-1-85-001	water, pressure bottles	at 2100 ft
04/09/85	1234-1-85-002	water, pressure bottles	at 2100 ft
12/18/85	1234-9-85-001	water, 55 gal.	during dewatering
05/29/86	1234-9-86-001	water, 55 gal.	barrel immersed
05/30/86	1234-9-86-002	water, 55 gal.	barrel immersed
07/16/86	1234-9-86-003	water, 55 gal.	during dewatering
07/16/86	1234-9-86-004	water, 55 gal.	during dewatering
07/22/86	No. 1 thru No. 12	soil, surface	~1 in. deep, ~100 sq. in.
08/21/86	No. 1 thru No. 3	soil, subsurface	~1 ft deep in mud pit
08/21/86	1234-1-86-001	water, pressure bottles	
08/21/86	1234-1-86-002	water, pressure bottles	
08/21/86	1234-1-86-003	water, pressure bottles	
08/22/86	No. 1 thru No. 20	water, 55 gals	during dewatering

TABLE A-IV
SAMPLE COLLECTIONS UE3e

Date	Identification Number	Type	Comments
07/14/86	1235-9-86-001	water, 55 gal.	lifted in drill stem
07/14/86	1235-9-86-002	water, 55 gal.	lifted in drill stem
07/18/86	1235-9-86-003	water, 55 gal.	lifted in drill stem
07/23/86	1235-1-86-001	water, pressure bottles	at 2160 ft
07/23/86	1235-1-86-002	water, pressure bottles	at 2160 ft
07/23/86	1235-1-86-003	water, pressure bottles	at 2160 ft
07/23/86	No. 1 thru No. 3	soil, subsurface	~1 ft deep in mud pit