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EVALUATION OF ISOTOPE MIGRATION - LAND BURIAL

WATER CHEMISTRY AT COMMERCIALLY OPERATED LOW-LEVEL RADIOACTIVE WASTE DISPOSAL SITES

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EXECUTIVE SUMMARY

The prime consideration for continued use of shallow land burial practices for the disposal of low-level radioactive waste is the containment of radionuclides. Before additional disposal sites for commercial low-level waste can be licensed, the existing sites must be evaluated in terms of their effectiveness for retaining radionuclides. A multi-disciplined approach is required in this effort; one part of which is the study reported here.

In cooperation with the U.S. Geological Survey, a field and laboratory program was initiated to study the existing commercial low-level radioactive waste disposal sites. This investigation will provide source term data for radionuclides and other solutes in trench waters at the sites and will describe the physical, chemical, and biological properties of the geochemical system that control the movement of radionuclides. This study was also initiated to provide experimental research support to the U.S. Nuclear Regulatory Commission for development of criteria for the selection, licensing and regulation of solid low-level radioactive waste disposal sites.

In the past year, the disposal sites at Maxey Flats, Kentucky, and Barnwell, South Carolina, were sampled, Maxey Flats for the fourth time, Barnwell for the second. Results of trench water inorganic, organic, and radiochemical analyses are similar to those reported for previous samplings. Trench water compositions reflect two processes; (1) interaction between the buried waste and infiltrating groundwaters and, (2) the effects of bacterial decomposition of organic material. Waters from Maxey Flats show a strongly developed anoxic, chemically reducing regime, while the Barnwell trench waters are relatively more oxidized regimes. Only trench 8 at Barnwell shows a water chemistry similar to the strongly developed anoxic regimes at Maxey Flats. Bacterial decomposition processes cause decreases in redox potential (Eh), sulfate and nitrate concentrations, as well as increases in alkalinity and ammonia relative to local groundwater composition. The extent to which groundwaters are changed reflects the length of time water accumulations persist in the trenches, which in turn is a function of the saturation state and permeability of the local geomedia.

No overall systematic changes in any disposal trenches were observed during the relatively brief sampling interval. However, changes in some radionuclide and inorganic components were observed in several trenches.

Tritium was the most abundant of the radionuclides and was found in all the trench waters. Chemically bound as HTO, tritium would be the most mobile radionuclide. ^{90}Sr, ^{238,239,240}Pu and ^{137}Cs were found as dissolved species in most trench waters. The radionuclide content of Barnwell trench waters is orders of magnitude lower than those at Maxey Flats.

Analyses of water collected from a series of experimental interceptor trenches at Maxey Flats showed them to have a chemical composition intermediate between disposal trench water and local groundwater. The presence of radionuclides in the experimental trench water suggests that radionculide migration from the disposal trenches may have proceeded beyond the experimental trench location.

Preliminary results are reported for continuing sorption studies by a batch technique using an improved experimental apparatus designed to maintain the anoxic nature of the trench waters during experiments. Activity in the liquid phase of the system continues to decrease with time. Steady-state conditions have not been established as yet, indicating that sorption in the anoxic water regimes may be kinetically much slower relative to more oxidized waters.

Preliminary results of batch sorption tests using site-specific materials from the Barnwell disposal site are reported. Batch sorption experiments with Maxey Flats shale, reference soil forming minerals, and oxic waters spiked with small amounts of various organic chelating agents showed a decreased experimental K_d relative to unspiked waters. Experiments with EDTA showed the largest differences; but the sorption of the reference smectite clay was least affected by the added organics.

An apparatus for single-pass flow-through column sorption experiments has been designed. Flow rate measurements on intact and repacked columns of Barnwell sediments are reported.

Tritium content as a function of depth has been determined in four sediment cores collected from beneath the disposal trenches at the Barnwell facility. A bi-modal distribution was observed, probably reflecting the downward movement of water from the trench. The tritium maxima probably represent the extent of movement of water which accumulates in the trenches periodically. The core recovered from beneath trench 2 contains detectable amounts of ^{60}Co down its length.

Gel filtration chromatography experiments using trench waters from the West Valley, New York, disposal site showed an association between ^{137}Cs and a portion of the trench water dissolved organic content (DOC). Experiments with spiked trench water (^{137}Cs and EDTA) indicated that the organic fraction referred to above was not EDTA.

Future efforts in the areas of trench water chemistry, sorption tests, and trench core analyses are described, along with applications for the results of these studies to regulatory concerns.

EVALUATION OF ISOTOPE MIGRATION - LAND BURIAL WATER CHEMISTRY AT COMMERCIALLY OPERATED LOW-LEVEL RADIOACTIVE WASTE DISPOSAL SITES

1. INTRODUCTION

This report summarizes the past year's effort in the shallow land burial program, as well as reports the work performed during the last quarter of the year. Not all of the data presented in the previous quarterly reports will be repeated here for the sake of brevity and clarity of presentation. However, all of this data is referenced through the text. This report updates the program status described more extensively elsewhere,(1) and describes the future program direction.

1.1 Purpose of the Study

This study is designed to provide an understanding of and to monitor the chemical behavior of existing low-level sites, and to provide experimental research support to the U.S. Nuclear Regulatory Commission (NRC) in developing criteria for the selection and licensing of solid low-level radioactive waste disposal sites. One of the significant factors in the development of these criteria is the ability to make predictions on the rate of movement of radionuclides along the groundwater flow path.

In cooperation with the U.S. Geological Survey (USGS), a field and laboratory program was initiated to study the existing commercial low-level radioactive waste disposal sites. This investigation will define the source terms (concentrations in solutions) of radionuclides and other solutes in trench waters at the sites and will describe the physical, chemical, and biological properties of the geochemical systems that control the movement of radionuclides.

1.2 Scope of the Study

1.2.1 Water Collection and Analyses

Water samples collected from selected disposal trenches and nearby test wells were analyzed for inorganic, organic, and radiochemical constituents. These analyses are part of the source term data base studies of the commercial disposal sites. The well waters were also sampled to, (1) detect and characterize any radionuclides that might be migrating along groundwater flow paths and, (2) compare and contrast local groundwater compositions to those of the trench waters. Procedures for the collection, preservation, and analysis of the trench waters have been developed to supplement standard methods when required. These procedures are continually updated as needed. Experiments to detect the existence of radionuclide complexes with organic chelating agents in selected trench waters were also performed.

1.2.2 Geochemical Considerations

The geochemical aspects of radionuclide migration and retention in this portion of the program are limited to, (i) laboratory sorption studies and, (ii) radiochemical analyses of cores obtained by the U.S. Geological Survey from beneath waste disposal trenches. Laboratory sorption studies involve batch and column experiments using site-specific materials and are performed under conditions which simulate the field situation. Data and ideas developed from these studies will be compared to the results of the core analyses for field verification. Conclusions derived from these studies are expected to have direct application to modeling studies of the sites and to establish siting criteria and improved burial practices at future sites.

1.3 Summary of Past Year's Activity

A brief outline of the past year's effort in the areas of water analyses, laboratory sorption studies, and core analyses are presented below. More detailed descriptions of the work performed and the results are contained in the main body of the report.

1.3.1 Trench Water Analyses

- Sampling trips to the Maxey Flats, Kentucky, and Barwell, South Carolina, disposal facilities were undertaken during the past year. Trench waters were collected for analyses as part of the source term investigations and were analyzed for inorganic, organic, and radiochemical components.

- A series of experimental trenches constructed at Maxey Flats were sampled, and the waters analyzed along with the disposal trench waters. An additional analysis for bromide ion was performed because bromide salts were added as tracers for the interceptor trench experiment.

- Additional laboratory and field analyses were performed to better characterize the trench waters and check the reliability of certain procedures currently in use. Field measurements were expanded to include sulfide ion measurements. Additional laboratory procedures included sulfate, chloride, and bromide determinations using an ion chromatographic procedure; Eh and pH measurements in the laboratory; measurements of bicarbonate ion using a carbon dioxide probe and titration alkalinity procedures; ferrous-ferric distribution by a colorimetric method.

- A series of gel-filtration chromatography experiments were performed using selected trench waters. These experiments were designed to detect the presence of organo-radionuclide complexes in the trench waters. Analyses of the amounts of

1.3.2 Laboratory Sorption Experiments and Core Analyses

complexes in the trench waters. Analyses of the amounts of free chelating agents present in selected trench waters have been performed.

- Experiments were performed to gauge the effect of organic complexing agents on sorption capacities. Selected organic complexing agents, including EDTA, were used in the experiments, along with samples of Maxey Flats shale and selected soil forming minerals.

- Sediments and trench waters from the Barnwell, South Carolina, disposal site were used in laboratory sorption experiments. A time study was initiated to measure the sorption capacity as a function of contact time for these site-specific materials. This work is part of the source term characterization studies, as well as the integrated sorption studies and trench core analyses effort.

- An improved experimental apparatus has been designed for use in sorption experiments where the anoxic character of the trench waters must be maintained during the experiment. Using this new apparatus, sorption experiments using Maxey Flats trench waters and soils have been initiated to measure the sorption capacity of these systems under anaerobic conditions. Previous studies have measured the sorption behavior relative to more oxidized trench waters for equivalent contact times. The new experiments are intended to measure the sorption behavior in a more absolute sense.

- Flow-through column experiments have been initiated using intact sediment cores from the Barnwell, South Carolina, disposal site. An apparatus was designed and built to control the water flow rate through the column. Experiments to measure flow rates as a function of the hydraulic head were performed.

- Sediment cores, obtained from beneath four disposal trenches at Barnwell and a holding lagoon at West Valley, were analyzed for their tritium content as a function of depth. Tritium content was measured in rainfall samples collected at Maxey Flats.

- The measurements of ^{60}Co distribution as a function of depth in the Barnwell trench cores are sediments are in progress. Some preliminary results are presented here for the trench 2 core.

2. TRENCH WATER SOURCE TERM INVESTIGATIONS AT THE MAXEY FLATS, KENTUCKY, AND BARNWELL, SOUTH CAROLINA, DISPOSAL SITES

(J. Clinton, M. Kinsley, B. Nine, P. Pietrzak, J. Smith, C. Anderson, K. Czyscinski, A. Weiss)

2.1 Introduction

A major portion of the disposal site source term investigations involves analyses of waters collected from disposal trenches and nearby observation wells. The water analysis scheme includes radiochemical, inorganic (major, as well as minor anions and cations), and organic components. Four disposal sites have been sampled to date; namely, Maxey Flats, Kentucky; West Valley, New York; Barnwell, South Carolina; and Sheffield, Illinois. Data from these sampling trips, as well as detailed collection and analytical procedures, have been reported previously.(1) In the past year, sampling trips were taken to the Maxey Flats and Barnwell disposal facilities. The Maxey Flats facility has been sampled four times over a four year period (1976-1979); the Barnwell site has been sampled twice (1979 and 1980). Analytical results for these sampling trips are presented here. For comparison purposes, data from earlier sampling trips are included.

In addition to routine sampling of the disposal trenches at Maxey Flats, water samples were also taken from a series of experimental trenches. These trenches were constructed for the purpose of intercepting groundwater flow paths along which radionuclides are believed to be migrating. Samples collected from these trenches were analyzed for radiochemical, inorganic, and organic components in a similar manner to the disposal trenches. A detailed description of the various aspects of this multi-disciplined experiment can be found elsewhere.(2)

2.2 Analyses of Waters Collected From the Maxey Flats, Kentucky, Disposal Site-October-November 1979

2.2.1 Field Measurements

Four disposal trenches were sampled along with one observation well and five experimental trenches.(3,4) Anaerobic sampling procedures(1) were used for the disposal trenches and one of the experimental trenches (2E). The four remaining experimental trenches did not contain sufficient water for the anaerobic sampling system. A specific-ion electrode(5) for the measurement of sulfide ion was added to the field measurements. The locations of the trenches and well are shown in Figure 2.1, and the field data presented in Table 2.1. In general, field data obtained in the latest sampling are similar to that observed in past samplings. Detectable sulfide ion was observed in trenches 27 and 32.

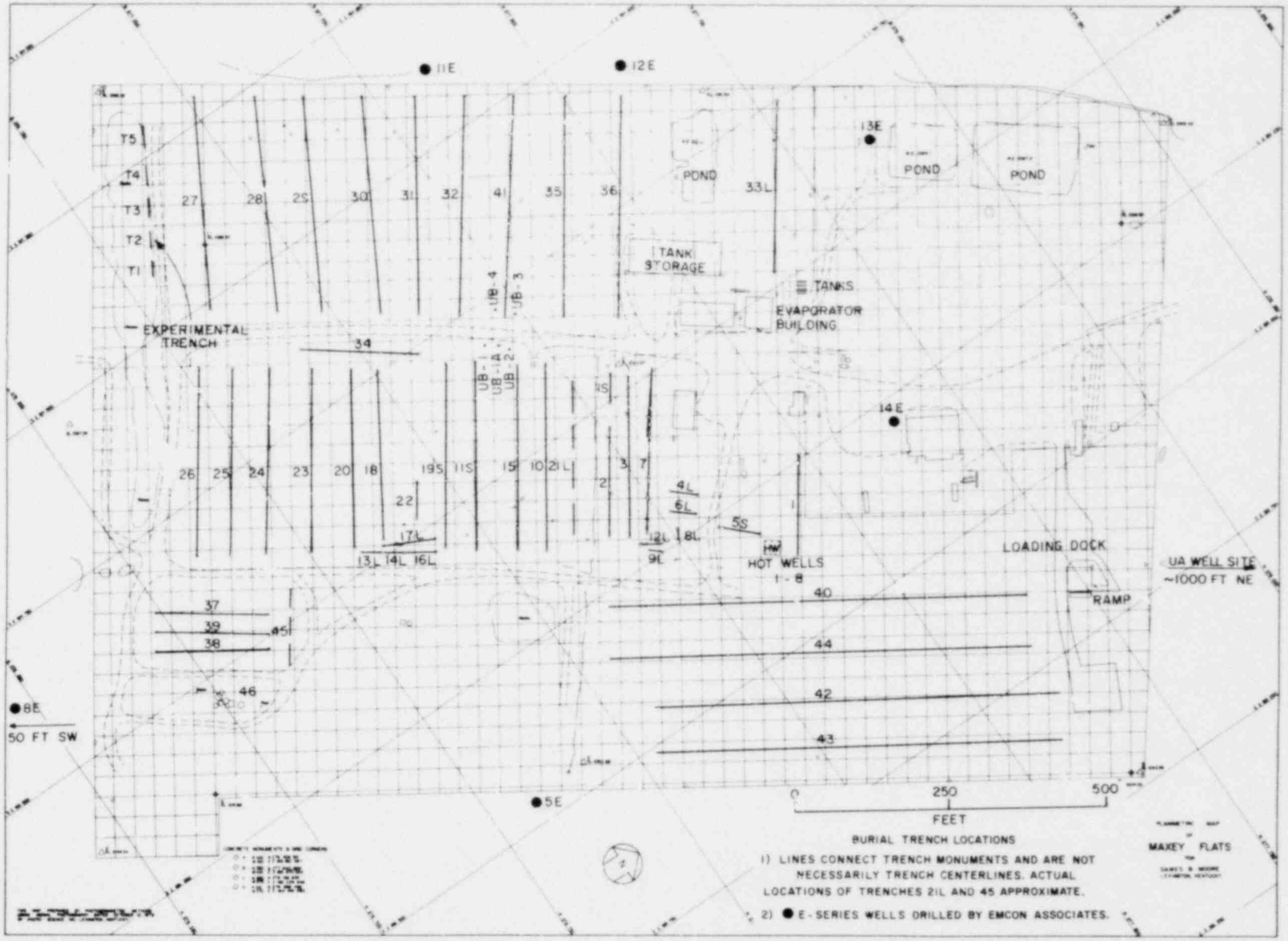

Figure 2.1 Locator map of the Maxey Flats, Kentucky, disopsal site.

Table 2.1

Field Measurements of Water Samples Collected at
Maxey Flats, Kentucky, Disposal Site

Sampling Location	Date	Temperature (°C)	Specific Conductance (μmho/cm)[a]	Dissolved Oxygen (mg/L)	Eh (mV, NHE)[b]	pH	Sulfide (mV)[c]
Trench 2	9/76[d]	20.0	3400	e	e	6.7	f
	7/77	15.0	3200	g	90	7.4	f
Trench 19S	9/76	21.0	2340	e	e	6.6	f
	5/78	12.4	2310	0.2	25	6.9	f
	11/79	16.0	1800	<0.1	57	e	430
Trench 26	9/76[d]	21.0	2910	e	e	6.8	f
	7/77	20.8	2680	g	130	7.3	f
Trench 27	9/76[d]	20.0	12000	e	e	6.0	f
	5/78	17.6	9370	0.05	17	6.6	f
	10/79	18.0	18000	0.15	140	5.9	-490
Trench 30	10/79	16.0	6900	0.1	140	6.5	-0.1
Trench 32	9/76	20.0	5750	e	e	7.3	f
	7/77	17.2	5650	g	10	7.9	f
	11/79	16.0	3500	<0.1	-56	5.6	-540
Trench 33L-4	9/76	20.0	7600	e	e	12.3	f
	5/78	12.0	5580	4.1	-7	12.1	f
Well UB1-A	5/78	12.4	2310	0.2	274	6.6	f
	11/79	h	h	h	h	h	h
Experimental Trench T-2E	10/79	14.5	4000	0.1	270	5.5	-79

[a] Specific conductance expressed as μmho/cm at 25 °C.

[b] Field measurements of Eh are reported relative to the normal hydrogen electrode (NHE).

[c] Field measurements in mV not yet converted to sulfide concentration.

[d] In September 1976, field measurements were made on separate aliquots of trench water within 30 minutes of collection. On subsequent trips, measurements were made with probes inserted directly into the flow stream.

[e] Redox potential (Eh) and dissolved oxygen were not measured in September 1976.

[f] Sulfide was not measured until 1979.

[g] Dissolved oxygen was not measured in July 1977.

[h] Field measurements not made.

2.2.2 Dissolved Radionuclides

Waters from the disposal trenches, experimental interceptor trenches, and well UB1-A, were analyzed for their dissolved radionuclide content. The water samples were analyzed after filtration through a 0.45 μm Millipore filter. Results of the radiochemical analyses are presented in Table 2.2, along with additional data from all the multiply sampled trenches.

In comparison against water samples obtained from these trenches in May 1978, all changes in concentration are within one order of magnitude. Trench 27 showed the largest increases in plutonium, while trench 19S showed an approximately equal decline. Compared to the earlier sampling (May 1978), results for well UB1-A show a slight increase in plutonium activity and decreases in strontium and cobalt activities.

Table 2.2

Concentrations of Dissolved Radionuclide in Waters From Multiply Sampled Disposal Trenches and Well UB1-A
Maxey Flats, Kentucky, Disposal Site
[pCi/L (±2σ%)][a]

Radionuclide	Date	Trench 2	Trench 19S	Trench 26	Trench 27	Trench 32	Trench 33L-4	Well UB1-A
Gross Alpha	9/76	1.2 E4 (4.3)	2.3 E5 (<1)	4.1 E4 (2.7)	4.8 E4 (2.3)	8.6 E4 (1.4)	7.6 E3 (5.2)	----[b]
	7/77	6.7 E3 (8.5)	----	2.7 E4 (4.0)	----	3.1 E4 (3.9)	----	----
	5/78	----	1.7 E5 (1.7)	----	4.9 E3 (11)	----	4.9 E3 (11)	<10
	10/79	----	6.3 E4 (1.2)	----	6.9 E4 (1.0)	9.7 E4 (<1)	----	<11
Gross Beta	9/76	2.8 E4 (3.6)	7.5 E5 (<1)	1.3 E5 (1.6)	7.2 E5 (<1)	1.2 E6 (<1)	7.0 E4 (1.9)	----
	7/77	2.4 E4 (5.5)	----	1.2 E5 (1.2)	----	1.8 E6 (<1)	----	----
	5/78	----	6.4 E5 (2.0)	----	4.0 E5 (2.6)	----	3.7 E4 (8.8)	3.1 E 2 (30)
	10/79	----	3.2 E4 (<1)	----	1.9 E5 (<1)	5.9 E5 (<1)	----	1.0 E 2 (34)
Tritium	9/76	2.5 E7 (<1)	6.9 E7 (<1)	2.0 E8 (<1)	3.1 E8 (<1)	2.1 E8 (<1)	6.2 E7 (<1)	----
	7/77	2.1 E7 (<1)	----	1.3 E8 (<1)	----	2.3 E9 (<1)	----	----
	5/78	----	6.8 E7 (<1)	----	5.9 E8 (<1)	----	2.9 E7 (<1)	5.8 E 6 (<1)
	10/79	----	8.7 E7 (<1)	----	5.1 E9 (<1)	2.1 E9 (<1)	----	4.9 E 6 (<1)
^{90}Sr[c]	9/76	6.8 E3 (<1)	2.6 E5 (<1)	3.5 E4 (<1)	2.0 E5 (<1)	3.8 E5 (<1)	2.4 E4 (<1)	----
	7/77	3.6 E3 (10)	----	3.0 E4 (10)	----	5.4 E5 (<10)	----	----
	5/78	----	2.9 E5 (10)	----	2.1 E5 (10)	----	1.7 E4 (10)	6.3 E 1 (10)
	10/79	----	2.2 E5 (10)	----	1.5 E5 (10)	3.3 E5 (10)	----	3.9 E 1 (20)
^{238}Pu[c]	9/76	3.8 E3 (2.7)	1.7 E5 (7.6)	3.1 E4 (6.8)	1.3 E4 (3.1)	3.6 E3 (4.2)	9.9 E3 (4.4)	----
	7/77	9.4 E3 (10)	----	1.3 E5 (10)	----	1.1 E5 (10)	----	----
	5/78	----	2.1 E5 (10)	----	4.1 E3 (10)	----	4.2 E2 (10)	1.4 E 1 (16)
	10/79	----	7.3 E4 (6.0)	----	2.6 E4 (10)	3.7 E4 (10)	----	2.6 E 1 (10)
^{239,240}Pu[c]	9/76	4.1 E2 (8.6)	2.1 E4 (24)	2.7 E3 (2.2)	1.7 E3 (13)	1.1 E2 (25)	8.4 E2 (40)	----
	7/77	2.9 E2 (10)	----	3.5 E3 (10)	----	2.9 E3 (10)	----	----
	5/78	----	3.4 E2 (10)	----	6.7 E2 (10)	----	6.6 E3 (10)	5.4 E-1 (110)
	10/79	----	2.6 E2 (6.0)	----	2.5 E3 (10)	8.1 E2 (10)	----	3.5 E-1 (134)
^{241}Am	9/76	4.2 E3 (3.9)	7.7 E2 (7.0)	1.00 E3 (5.7)	1.5 E4 (3.8)	<40	<20	----
	7/77	2.9 E3 (8.9)	----	N.D.[d]	----	N.D.	----	----
	5/78	----	1.5 E3 (17)	----	1.4 E3 (17)	----	N.D.	N.D.
	10/79	----	1.3 E3 (15)	----	4.7 E3 (3.0)	6.0 E3 (3.0)	----	N.D.
^{60}Co	9/76	1.4 E4 (1.9)	1.3 E3 (23)	1.3 E3 (6.8)	2.0 E4 (3.2)	6.0 E3 (5.6)	<300	----
	7/77	1.0 E4 (4.5)	----	1.4 E3 (14)	----	3.5 E3 (8.1)	----	----
	5/78	----	2.5 E3 (11)	----	1.3 E3 (21)	----	3.6 E1 (64)	2.5 E 2 (13)
	10/79	----	3.3 E3 (3.0)	----	4.0 E3 (2.6)	2.3 E3 (3.6)	----	1.1 E 2 (34)
^{134}Cs	9/76	<100	<100	3.1 E2 (18)	<100	4.2 E2 (24)	<100	----
	7/77	N.D.	----	N.D.	----	N.D.	----	----
	5/78	----	N.D.	----	N.D.	----	N.D.	N.D.
	10/79	----	N.D.	----	N.D.	1.1 E2 (23)	----	N.D.
^{137}Cs	9/76	<100	3.2 E3 (9.3)	7.5 E3 (2.0)	2.3 E4 (2.4)	6.0 E3 (4.6)	<100	----
	7/77	N.D.	----	5.3 E3 (5.7)	----	1.9 E3 (5.5)	----	----
	5/78	----	1.0 E4 (3.8)	----	8.0 E3 (4.6)	----	2.1 E2 (66)	N.D.
	10/79	----	2.7 E3 (2.8)	----	2.2 E3 (3.2)	3.2 E3 (2.4)	----	N.D.

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[a] Number in ( ) = 2σ % counting uncertainty.
[b] ---- = no sample collected.
[c] Analyses performed by LFE Laboratories, Richmond, California.
[d] N.D. = activity not detected.

2.2.3 Tritium Content in Rainfall Samples

Between March 1977 and September 1979, rainfall samples were collected by USGS personnel at the Maxey Flats, disposal site for the purpose of determining tritium levels. Results of these analyses are listed in Table 2.3. The samples were taken using rainfall collectors located adjacent to wells 11E, 13E, UA and UB, which are shown in Figure 2.1.

In general, a relative increase or decrease in the tritium content from one sampling period to the next is consistent at all the sampling locations. This would indicate that the relative changes are controlled by climatic variations at the site. A more quantitative evaluation of this data would require information concerning the amounts of rainfall during these time intervals, along with the quantities and tritium contents of trench waters processed through the evaporator.

Table 2.3

Tritium Content in Rainfall Samples Collected at the Maxey Flats, Kentucky, Disposal Site
[pCi/L (±2σ%)][a]

Date	11E	13E	UA	UB
3/9/77-4/20/77	3.87 E3 (4.2%)	1.53 E5 (1.3%)	<7 E2	-----
4/13/77-5/17/77	6.36 E3 (12%)	2.62 E4 (19%)	2.01 E3 (35%)	-----
5/77-6/21/77	2.75 E4 (2.3%)	2.85 E4 (2.1%)	4.27 E4 (1.8%)	-----
6/21/77-7/20/77	1.08 E4 (4.1%)	1.65 E4 (3.2%)	1.08 E4 (4.2%)	-----
7/20/77-8/25/77	2.99 E3 (13%)	4.96 E4 (1.8%)	1.47 E3 (20%)	-----
8/25/77-9/21/77	6.29 E3 (5.8%)	7.75 E3 (4.9%)	3.46 E3 (10%)	-----
9/21/77-10/14/77	7.28 E3 (5.3%)	4.36 E3 (9.0%)	<7 E2	-----
10/14/77-11/22/77	1.30 E4 (3.9%)	7.90 E3 (5.1%)	1.53 E4 (3.3%)	-----
11/22/77-12/20/77	1.04 E5 (<1)	4.68 E4 (1.7%)	4.91 E3 (8.1%)	-----
12/20/78-3/20/78	1.72 E4 (3.5%)	1.05 E5 (<1)	-----	4.6 E4 (2.0%)
3/22/78-4/19/78	4.28 E4 (1.9%)	5.55 E4 (1.6%)	1.65 E4 (3.0%)	6.96 E4 (1.4%)
4/19/78-5/15/78	8.66 E4 (1.2%)	4.93 E4 (1.8%)	1.70 E3 (40%)	2.74 E5 (<1%)
5/15/78-6/16/78	2.90 E4 (2.1%)	1.83 E5 (1.1%)	8.81 E4 (2.8%)	3.03 E4 (1.2%)
6/16/78-7/12/78	4.11 E3 (7.5%)	2.20 E4 (2.7%)	3.71 E3	7.41 E3 (6.0%)
7/12/78-8/9/78	4.25 E3 (3.8%)	3.38 E3 (10.1%)	5.91 E2 (38.0%)	------
8/9/78-9/5/78	5.71 E3 (6.0%)	6.50 E3 (5.5%)	2.63 E2 (86%)	3.12 E3 (9.9%)
9/5/78-10/5/78	3.82 E3 (10.2%)	5.28 E3 (6.3%)	<2.4 E2	2.92 E3 (10.6%)
10/5/78-11/9/78	8.70 E3 (4.5%)	7.50 E3 (5.2%)	6.54 E3 (6.1%)	2.72 E4 (2.6%)
11/8/78-12/5/78	1.03 E5 (<1%)	1.73 E4 (2.9%)	2.69 E4 (2.2%)	4.73 E4 (1.7%)
12/5/78-2/28/79	2.2 E4	6.3 E4	1.5 E4	1.6 E4
2/28/79-3/28/79	6.25 E3 (5.6%)	1.57 E5 (1.1%)	9.07 E3 (4.7%)	2.58 E3 (7.7%)
3/28/79-4/23/79	4.27 E4 (2.2%)	4.84 E4 (2.0%)	1.79 E4 (3.4%)	7.16 E3 (5.3%)
4/23/79-5/22/79	1.02 E4 (8.5%)	7.14 E3 (11.6%)	2.92 E3 (27%)	5.00 E3 (14%)
5/22/79-6/19/79	3.82 E4 (2.7%)	2.86 E4 (3.2%)	3.46 E3 (14%)	1.14 E4 (5.8%)
6/19/79--8/2/79	<6.2 E2	3.13 E3 (19%)	4.50 E3 (16%)	<6.2 E2
8/2/79-8/28/79	3.40 E3 (19%)	8.16 E2 (73%)	<6 E2	7.93 E2 (75%)
8/29/79-9/28/79	5.57 E3 (12%)	8.85 E4 (1.6%)	1.81 E5 (1.1%)	2.87 E4 (3.3%)

[a] Number in ( ) = 2σ% counting uncertainty.

2.2.4 Organic Compounds

Water samples collected from the disposal and experimental interceptor trenches were analyzed for organic constituents soluble in methylene chloride. Aliquots of the waters were extracted into methylene chloride, concentrated, and analyzed by GC-MS spectroscopic techniques for qualitative identification of the compounds present. Quantifications were performed by gas chromatographic techniques. Complete details of the procedures have been described previously.(1) Results for the disposal trenches and well UB1-A are presented in Tables 2.4-2.8. Concentrations of the organic compounds in the methylene chloride extract are reported as concentrations in the original trench water samples. The suite of organic compounds present is similar to those found in previous water samples taken from the Maxey Flats disposal trenches.(1) Major components in these waters are also similar to those found in West Valley trench water samples.(1)

2.2.5 Carbon Analyses

Aliquots of the trench waters were analyzed by means of a Beckman Total Carbon Analyser. The instrument measures total and inorganic carbon; the organic carbon is equal to the difference between these numbers. Results are presented in Table 2.9. For the disposal trenches, the results are similar to those obtained previously.

2.2.6 Inorganic Analyses

2.2.6.1 Procedures

Waters collected during the October-November 1979 sampling trip were analyzed for dissolved anions and cations as part of the source term investigation at the commercial low-level disposal site. In addition, water samples from the experimental interceptor trenches were also included. Detailed sample handling, preparation and analysis procedures have been described in detail in a previous report.(1)

2.2.6.2 Additional Analyses

In addition to those analyses performed previously, several additional analyses were performed to more thoroughly characterize these waters, and to check the reliability of previous results. These additional analyses are:

1) Analyses for total iron and ferrous iron by means of a colorimetric procedure.(6)

2) Additional pH and Eh measurements in the laboratory.

3) Sulfate analyses using an ion-chromatographic (I.C.) technique.(7)

Table 2.4

Compounds Identified in Trench 19S, Maxey Flats, Kentucky, Disposal Site (October-November, 1979)

Compound	Concentration (mg/L)
Acidic Fraction:	
2-Methylpropionic acid	0.12
2-Methylbutanoic acid	0.52
3-Methylbutanoic acid	0.80
Ethylene glycol	N.Q.[a]
3-Methylpentanoic acid	0.67
C_6 acid[b]	0.26
Phenol	0.04
2-Methylhexanoic acid	0.13
Cresol	1.2
2-Ethylhexanoic acid	1.9
C_8 acid[c]	0.96
C_8 acid[c]	1.1
Diethylene glycol	N.Q.
Phenylacetic acid	0.34
Nonanoic acid	0.08
Polyethylene glycol	N.Q.
Phenylhexanoic acid	N.Q.
Neutral Fraction:	
p-Dioxane	N.Q.
Methylisobutyl ketone	0.20
Toluene	9.5
Xylene	0.03
Cyclohexanol	0.10
Dibutyl ketone	N.Q.
Triethyl phosphate	0.28
Camphor	N.Q.
Naphthalene	0.03
Tributyl phosphate	0.17
Phthalate ester	N.Q.

[a] Not quantified.
[b] Quantified using 3-Methylpentanoic acid standard.
[c] Quantified using 2-Ethylhexanoic acid standard.

Table 2.5

Compounds Identified in Trench 27, Maxey Flats, Kentucky, Disposal Site (October-November, 1979)

Compound	Concentration (mg/L)
Acidic Fraction:	
2-Methylpropionic acid	0.24
2-Methylbutanoic acid	0.60
3-Methylbutanoic acid	0.76
Valeric acid	0.28
Ethylene glycol	N.Q.[a]
3-Methylpentanoic acid	0.45
C_6 acid[b]	0.16
Phenol	0.23
Hexanoic acid	0.64
2-Methylhexanoic acid	0.24
C_8 acid	N.Q.
Cresol (isomers)	0.56
2-Ethylhexanoic acid	9.7
C_8 acid[c]	0.08
C_8 acid[c]	0.06
Benzoic acid	0.24
Octanoic acid	0.10
Phenylacetic acid	0.16
Phenylpropionic acid	0.50
Polyethylene glycol	N.Q.
Phenylhexanoic acid	N.Q.
Neutral Fraction:	
p-Dioxane	N.Q.
Methylisobutyl ketone	1.8
Toluene	0.56
2-Ethyl 1-hexanol	0.17
Diethylene glycol diethyl ether	N.Q.
Fenchone	N.Q.
Triethyl phosphate	0.29
Camphor	N.Q.
Naphthalene	0.06

[a] Not quantified.
[b] Quantified using 3-Methylpentanoic acid standard.
[c] Quantified using 2-Ethylhexanoic acid standard.

Table 2.6

Compounds Identified in Trench 30, Maxey Flats, Kentucky, Disposal Site (October-November, 1979)

Compound	Concentration (mg/L)
Acidic Fraction:	
Ethylene glycol	N.Q.[a]
C_8 acid	N.Q.
2-Ethylhexanoic acid	1.1
C_8 acid[b]	1.8
Toluic acid	2.7
Neutral Fraction:	
Fenchone	0.08
Phthalate ester	N.Q.

[a] Not quantified.
[b] Quantified using 2-Ethylhexanoic acid standard.

Table 2.7

Compounds Identified in Trench 32, Maxey Flats, Kentucky, Disposal Site (October-November, 1979)

Compound	Concentration (mg/L)
Acidic Fraction:	
Ethylene glycol	N.Q.[a]
3-Methylpentanoic acid	0.98
Phenol	0.08
2-Methylhexanoic acid	0.57
Cresol	0.28
2-Ethylhexanoic acid	3.2
C_8 acid[b]	0.80
Octanoic acid	0.20
Toluic acid	2.1
Phenylbutyric acid	N.Q.
Phenylhexanoic acid	N.Q.
Neutral Fraction:	
p-Dioxane	N.Q.
Toluene	2.4
Xylene	0.13
Naphthalene	0.07
Tributyl phosphate	0.30
Phthalate ester	N.Q.

[a] Not quantified.

[b] Quantified using 2-Ethylhexanoic acid standard.

Table 2.8

Compounds Identified in Well UB1-A, Maxey Flats, Kentucky, Disposal Site (October-November, 1979)

Compound	Concentration (mg/L)
Acidic Fraction:	
Ethylene glycol	N.Q.[a]
Diethylene glycol	N.Q.[a]
Polyglycol	N.Q.[a]
Neutral Fraction:	
p-Dioxane	N.Q.

[a] These peaks are very small.

Table 2.9

Carbon Analyses of Multiply Sampled Trenches and Well UB1-A, Maxey Flats, Kentucky, Disposal Site

Sampling Location	Collection Date	Total Carbon (mg/L)	Inorganic Carbon (mg/L)	Organic Carbon (mg/L)
Trench 19S	9/76	700	78	620
	5/78	570	70	500
	11/79	470	170	300
Trench 26	9/76	1100	150	950
	7/77	870	100	770
Trench 27	9/76	730	<2	730
	5/78	540	<2	540
	10/79	580	70	510
Trench 30	10/79	1800	1500	300
Trench 32	9/76	1300	510	790
	7/77	1400	380	990
	10/79	1000	350	650
Trench 33L-4	9/76	1900	<2	1900
	5/78	1100	10	1100
Well UB1-A	5/78	15	7	8
	10/79	20	15	5

4) Field analyses for dissolved sulfide by means of an ion-selective electrode.(5)

5) Analyses for bromide and chloride using an ion-chromatographic technique.(7)

The ferrous iron determination is useful in evaluating redox equilibria in the trench waters, and the stability of the trench waters after collection and handling. Laboratory pH and Eh measurements are also required for these evaluations. Sulfide was detected in field measurements during collection of these waters(3) as would be expected in anoxic waters. Quantification of this procedure is in progress. The ion chromatographic analyses were performed to check the reliability of the colorimetric sulfate analyses. Bromide, present in the experimental interceptor trenches, interferes with chloride determinations when analyzed by the indirect colorimetric technique.(1) To circumvent this difficulty, an ion chromatographic technique was employed for both halogen ion determinations. Bromide salts were added as tracers to experimental interceptor trenches 1, 2, 3, and 5.(2)

2.2.6.3 Results

Results of anion and cation analyses are shown in Tables 2.10-2.11. Analytical results for the multiply sampled trenches are also included for comparison with the most recent data. Disposal trench 30 was also sampled recently (October 1979), but the results are not included here because it was only sampled once during the four year interval. Results for trench 30 have been reported previously.(4)

Results for the disposal trench waters are similar to those reported for waters collected during earlier sampling trips.(1) The waters frequently show low contents of sulfate and nitrate, high titration alkalinity, the presence of ammonia and sulfide, and low Eh values. These are characteristics of chemically reducing, anoxic water regimes frequently found in stagnant waters in natural environments, and typical of organic-laden waste waters. The observed trench water composition results from a combination of two processes; namely, (1) leaching of the waste by groundwaters percolating through the buried material and, (2) bacterial degradation of organic matter leached from the waste. The extent to which the local groundwater is changed by these two processes is a function of how long water accumulations persist in the trenches. A lengthy stay increases leaching, as well as the extent to which bacterial degradation processes modify the leachate composition. Sodium, potassium, and chloride concentrations in the trench waters are a good indicator of the extent of leaching since they are conservative relative to ensuring bacterial processes. Bacterial decomposition of organic material modified the trench water composition in the following manner. Dissolved oxygen in the water is consumed rapidly, followed by nitrate and sulfate reduction. Carbon dioxide and ammonia are generated continually during these stages, resulting in increased alkalinity and ammonia levels in the waters and decreased concentrations of sulfate and nitrate relative to uncontaminated groundwaters. In the absence of heavy metals, such a iron, sulfide ion concentrations can build to detectable levels. Concentrations of other ions

Table 2.10

Concentrations of Dissolved Nonmetals in Water From Multiply Sampled Trenches and Well UB1-A, Taken From Maxey Flats, Kentucky, Disposal Site
(Concentrations in mg/L)

Dissolved Component	Date	Disposal Trenches 2	19S	26	27	32	33L4	Well UB1A
Total Alkalinity[a] (as $CaCO_3$)	9/76	1560	980	1320	432	2720	1810	----[b]
	7/77	1370	----	860	----	2600	----	----
	5/78	----	910	----	330	----	1600	50
	10/79	----	900	----	300	1700	----	30
Hardness (Mg+Ca) (as $CaCO_3$)	9/76	400	680	590	3300	1200	3600	----
	7/77	170	----	360	----	1300	----	----
	5/78	----	810	----	1900	----	1600	1300
	10/79	----	650	----	4800	1400	----	1700
Inorganic Carbon	9/76	270	78	150	<2	510	<2	----
	7/77	330	----	100	----	380	----	----
	5/78	----	70	----	<2	----	9.3	74
	10/79	----	170	----	74	350	----	15
D.O.C.	9/76	210	620	950	730	790	1900	----
	7/77	90	----	770	----	990	----	----
	5/78	----	500	----	540	----	1070	7.3
	10/79	----	300	----	500	670	----	5.1
Nitrogen (N) (NH_3-probe)	9/76	c	c	c	c	c	c	----
	7/77	36	----	115	----	117	----	----
	5/78	----	4.1	----	80	----	18	<1
	10/79	----	30	----	60	90	----	<1
Nitrogen (N) (NH_4^+-color)	9/76	c	c	c	c	c	c	----
	7/77	39	----	99	----	99	----	----
	5/78	----	b	----	b	----	b	b
	10/79	----	34	----	75	88	----	<1
Chloride-color[d]	9/76	310	150	290	4200	37[illegible]	320	----
	7/77	230	----	210	----	580	----	----
	5/78	----	140	----	3900	----	168	300
	10/79	----	169	----	6180	508	----	364
Chloride-I.C.[e]	10/79	----	190	----	6100	330	----	350
Bromide-I.C.	10/79	----	1.3	----	180	3.3	----	8.2
Nitrogen (N) (NO_2^--color)	9/76	c	c	c	c	c	c	----
	7/77	c	----	c	----	c	----	----
	5/78	----	c	----	c	----	c	
	10/79	----	<0.04	----	<0.04	<0.04	----	<0.04
Nitrogen (N) ($NO_2^-+NO_3^-$-color)	9/76	<0.05	<0.05	<0.05	1.6	<0.05	21	----
	7/77	0.08	----	<0.04	----	<0.04	----	---
	5/78	----	<0.1	----	<0.1	----	10.6	<0.1
	10/79	----	0.12	----	0.75	0.8	----	
Phosphate	9/76	c	c	c	c	c	c	----
	7/77	<0.5	----	1.0	----	24	----	----
	5/78	----	<2	----	17	----	<2	<3
	10/79	----	<1	----	<1	1.1	----	<1
Silica	9/76	14	9.0	9.0	14	14	1.7	----
	7/77	13	----	6.5	----	10	----	----
	5/78	----	9.0	----	5	----	1	14
	10/79	---	15	----	19	29	----	19
Sulfate-color (Anaerobic)	9/76	11	<10	<10	69	11	<10	----
	7/77	<5	----	<1	----	<1	----	----
	5/78	----	<5	----	<5	----	<5	1200
	10/79	----	23[f]	----	1100	>60[g]	----	1700
Sulfate-I.C. (Anaerobic)	10/79	----	<0.5	----	2.2	9.6	----	1700
Sulfate-I.C. (Acidified)	10/79	----	h	----	62	64	----	1900
pH[a]	9/76	7.05	6.60	6.90	6.30	7.40	12.6	----
	7/77	7.70	----	6.20	----	7.50	----	----
	5/78	----	7.10	----	6.65	----	12.8	6.53
	10/79	----	7.15	----	5.6	7.5	----	6.4
Total Anions (meq/L)	9/76	40	24	34	130	65	47	----
	7/77	34	----	28	----	68	----	----
	5/78	----	22	----	120	----	38	35
	10/79	----	24[i]	----	180[i]	46[i]	----	50[i]

[a] Measurement was made immediately after anaerobic filtration.
[b] ---No sample was collected.
[c] Measurement was not made.
[d] Colorimetric method determines bromide and iodine as chloride.
[e] Ion chromatography(I.C.).
[f] Standard deviation ±20%.
[g] Interfering components.
[h] Nitrate interference.
[i] Used data for the acidified I.C. sulfate analyses in the calculations.

Table 2.11

Concentrations of Dissolved Metals in Waters From Multiply Sampled Trenches and Well UB1-A, Maxey Flats, Kentucky, Disposal Site (Concentrations in mg/L)

Metal	Date	Disposal Trenches						Well
		2	19S	26	27	32	33L4	UB1A
Barium	9/76	a	a	a	a	a	a	---[b]
	7/77	a	---	a	---	a	---	---
	5/78	---	a	---	a	---	a	a
	10/79	---	<2	---	17	19	---	<2
Calcium	9/76	29	58	31	600	75	1400	---
	7/77	20	---	45	---	65	---	---
	5/78	---	50	---	240	---	650	160
	10/79	---	42	---	740	42	---	180
Cesium	9/76	a	a	a	a	a	a	---
	7/77	<0.1	---	0.2	---	0.1	---	---
	5/78	---	0.1	---	<0.05	---	<0.05	<0.05
	10/79	---	<0.5	---	<0.5	<0.5	---	<0.5
Iron[c]	9/76	40	150	65	1200	16	<0.01	---
	7/77	28	---	110	---	32	---	---
	5/78	---	115	---	1150	---	0.3	<0.1
	10/79	---	60	---	1400	0.4	---	<0.1
Iron[d]	9/76	a	a	a	a	a	a	---
	7/77	a	---	a	---	a	---	---
	5/78	a	a	---	a	---	a	---
	10/79	---	58	---	1400	<0.5	---	<0.5
Fe^{+2}/Fe^{+3}	10/79	---	30	---	39	a	---	a
Lithium	9/76	0.99	9.23	0.34	1.9	0.15	0.23	---
	7/77	1.3	---	0.15	---	0.23	---	---
	5/78	---	0.38	---	1.85	---	0.16	0.44
	10/79	---	<0.5	---	2.3	<0.5	---	0.5
Magnesium	9/76	79	130	130	430	230	0.03	---
	7/77	41	---	87	---	320	---	---
	5/78	---	124	---	255	---	0.08	224
	10/79	---	130	---	720	300	---	300
Manganese	9/76	0.75	0.76	0.74	70	1.2	<0.01	---
	7/77	a	---	a	---	a	---	---
	5/78	---	0.42	a	88	---	<0.05	0.14
	10/79	---	0.19	---	190	0.34	---	<0.1
Potassium	9/76	66	25	39	120	210	160	---
	7/77	35	---	27	---	280	---	---
	5/78	---	12	---	36	---	30	4
	10/79	---	27	---	100	160	---	12
Sodium	9/76	700	100	240	670	700	160	---
	7/77	1300	---	270	---	1900	---	---
	5/78	---	650	---	450	---	180	500
	10/79	---	480	---	770	7200	---	530
Strontium	9/76	a	a	a	a	a	a	---
	7/77	a	---	a	---	a	---	---
	5/78	---	0.53	---	3.8	---	7.0	2.5
	10/79	---	0.65	---	6.7	0.52	---	2.6
Total Cations (mg/L)	9/76	42	24	26	140	59	83	---
	7/77	66	---	34	---	130	---	---
	5/78	---	45	---	100	---	41	49
	10/79	---	39	---	200	69	---	57

[a] Measurement was not made.
[b] ---No sample was collected.
[c] Atomic absorption method.
[d] Colorimetric method.

such as calcium, magnesium, and strontium are controlled by the changes in carbonate alkalinity developed from bacterial action. As reported previously,(1) the titration alkalinity shows an irregular behavior reflecting the complex nature and high buffering capacity typical of these anoxic trench waters. Presumably, the highly irregular shape of the titration curves is due to the presence of titratable components leached from the wastes.

The presence of high iron and sulfide ion concentrations in trench 27 (Table 2.1-strongly negative mV values indicate measurable sulfide concentrations) is puzzling in that a high iron concentration should keep free sulfide ion to extremely small and undetectable levels. Conflicting results were also obtained for sulfate concentrations (colorimetric vs ion chromatographic procedures) in trench 27 (Table 2.10). If the high sulfate concentration is correct (1100 mg/L, Table 2.10), this would also conflict with the observation of detectable sulfide found in the field measurements. We believe that the high sulfide field measurement (-490 mV, Table 2.1) may be in error due to equipment malfunctions. Field pH measurements of this trench required replacement of the electrodes due to malfunctions during the sampling. The anomalous chemistry of this particular trench requires more detailed investigation to resolve these apparently contradictory results.

For the multiply sampled trenches, no consistent pattern of change with time is evident. However, detecting an evolutionary change in trench water compositions is complicated by two factors. First, the four year sampling interval is short relative to the functional lifetime of the disposal site. Second, water accumulating in the trenches is pumped out periodically to prevent overflows, when the accumulation rate exceeds the rate at which the water migrates through the groundwater flow paths. After each pumping, the trench water-soil system may take some time to reestablish the anoxic nature of the system as it existed prior to the pumpout.

2.2.7 Redox Equilibria

Preserving the sample was a prime consideration in developing sampling and analytical procedures. Some shifts in the numerous chemical equilibria present in these complex waters are to be anticipated during the sample collection, transportation, and filtering processes prior to analysis. These changes result because the waters have been removed from contact with the soil media and have experienced temperature and gas phase changes. It is hoped that these alterations of the sample environment do not produce changes so drastic that the inorganic analyses are completely unrepresentative of in situ field conditions. One method of evaluating the extent of these changes is to examine Eh-pH relationships measured in the field, and later in the laboratory during subsequent sample manipulations.

Figure 2.2 presents an Eh-pH stability diagram for iron species frequently found in both oxidized and reduced natural environments. Field trench water Eh-pH measurements correlate well with those expected for equilibria between aqueous ferrous iron and limonitic iron oxide (a common soil component) and iron sulfides (commonly formed in anoxic sediment-water systems). After sampling, transporation and laboratory filtration, the Eh-pH values for

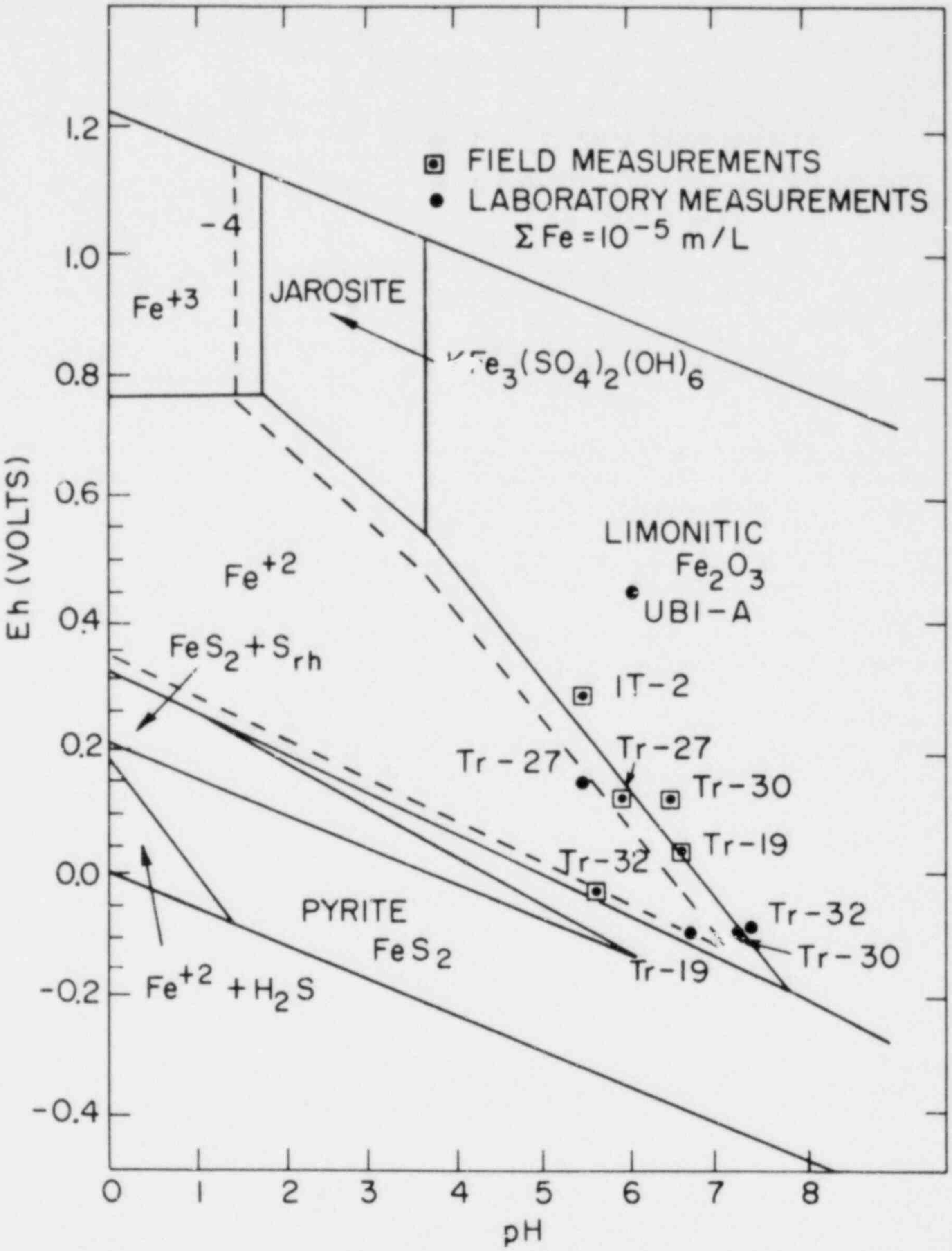

Figure 2.2 Eh-pH relationships for water samples collected from Maxey Flats, October-November 1979. Diagram modified after Garrels and Christ.(8)

the various trenches have shifted but are still in good agreement with the equilibria lines for these systems. This indicates that the water systems have not been drastically altered during sample handling. Waters from well UB1-A are drastically different than the trench waters in that the redox environment in the well is oxidizing and not controlled by iron equilibria.

A more detailed picture of the chemical systems for individual trenches can be seen on this diagram (Figure 2.2). Field data for trench 32 indicates an equilibrium with iron sulfide. Field measurements for sulfide ion activity(3) showed the highest readings for trench 32, and the color of the water drawn from the trench was black. Precipitated iron sulfide is black in color and is frequently observed forming in natural anoxic waters. The remaining waters appear to be controlled by ferrous iron and iron oxides commonly present in soils. In the trench 27 waters, total dissolved iron is in the range of 10^{-3} mg/L, however, chloride content in this water is also high so that the actual concentration of free ferrous iron is in the proper range for this diagram due to extensive iron-chloride ion pairing at these relatively high iron and chloride concentrations. The experimental interceptor trench 2E also shows an equilibrium of ferrous iron and iron oxide, although the redox state of this water is more oxidizing than the disposal trenches.

2.2.8 Experimental Interceptor Trenches

A series of five experimental trenches were constructed at Maxey Flats for the purpose of intercepting groundwater flow paths in the vicinity of disposal trenches 26 and 27. The location of these trenches is shown in Figure 2.1. Four of the trenches (Trenches 2-5) were sampled aerobically during the sampling trip in October-November 1979; experimental trench 2 was sampled both aerobically and anaerobically. Water samples collected were analyzed for organic, inorganic, and radiochemical components along with the waters collected from the disposal trenches during the same trip. An additional analysis for bromide ion was included because NaBr was used as a tracer in the interceptor trench experiment.

Analytical results for these samples are given in Table 2.12. Data from an earlier sampling (July 1977) of disposal trench 26 is included in Table 2.12 for comparison because this is the disposal trench closest to the experimental trenches.

Comparison of the disposal trench waters against the more typical groundwaters (well UB1-A) shows the contrast between ground waters and the anoxic trench waters (Table 2.12). The interceptor trench waters show a chemistry intermediate between the well and disposal trench waters. Results of DOC and extractable organic material (Tables 2.13 and 2.14) also show an intermediate composition between the complex disposal trenches and the well waters. This may reflect an increased influence of disposal trench waters on the interceptor trenches relative to their influence on the well waters.

The relatively low sulfate concentrations, high alkalinity, and predominance of ferrous iron in solution indicate an anoxic water chemistry in the experimental trenches.

Table 2.12

Analyses of Experimental and Disposal Trench and Well Waters -
Maxey Flats, Kentucky, Disposal Site (October-November, 1979)
(mg/L)[a]

Dissolved Component	Disposal			Experimental Interceptor Trenches			
	Trench 27	Trench 26[b]	Well UB-1A	T-2E	T-3W	T-4E	T-5
pH	5.9	7.3	6.[illegible]	5.5	6.8	7.1	7.5
Eh (mV, NHE)	140	130	d	270	d	d	d
Dissolved Oxygen	0.15	---	d	0.1	d	d	d
Specific Conductance (μmho/cm@25°C)	18000	2680	d	4000	d	d	d
Temperature(°C)	18.0	20.8	d	14.5	d	d	d
Chloride	6080	210	348	178	168	143	84
Bromide	178	---	8.2	1200	2210	2.4	4060
Total Alkalinity	300	860	30	300	450	300	320
Nitrogen (NO_3^-)	0.75	.09	0.50	0.39	0.51	<0.05	1.4
Nitrogen (NH_4^+)	68	99	<1	1.0	13	<1	<1
Phosphate	<1	1.0	<1	<1	<1	<1	<1
Silica	19	6.5	19	8.7	7.7	7.5	0.7
Sulfate[e]	1100/62	<1	1700/100	550/530	1000/1000	1500/1500	1300/1300
DOC	500	770	5.1	120	15	29	14
Calcium	740	45	180	380	440	600	610
Iron	1400	110	0.1	1.6	1.2	0.5	0.2
Magnesium	720	87	300	160	95	95	130
Manganese	190	---	<0.1	3.5	2.7	1.1	0.2
Potassium	100	27	12	35	26	17	32
Sodium	770	270	530	530	910	280	1200
Strontium	6.7	---	2.6	7.7	6.6	5.6	8.4
Gross Alpha[f]	6.9 E4 (<1)	2.7 E4 (2.7)	<3.7 E0	7.6 E1 (24)	3.9 E1 (56)	1.7 E1 (64)	3.6 E1 (67)
Gross Beta[f]	1.9 E5 (<1)	1.2 E5 (1.2)	1.0 E2 (34)	3.5 E4 (<1)	5.8 E2 (7)	<3.4 E1	<3.4 E1
Tritium	5.1 E9 (<1)	1.3 E8 (<1)	4.9 E6 (<1)	6.7 E8 (<1)	3.7 E7 (<1)	1.5 E5 (<1)	1.7 E4 (<1)
^{90}Sr[g]	1.5 E5 (10)	3.0 E4 (10)	3.9 E1 (20)	1.9 E4 (10)	2.3 E2 (10)	1.8 E1 (10)	3.5 E1 (22)
^{238}Pu[g]	2.6 E4 (10)	1.3 E5 (10)	2.5 E1 (10)	6.8 E1 (10)	1.6 E2 (10)	2.2 E1 (10)	4.9 E0 (18)
^{239,240}Pu[g]	2.4 E3 (10)	3.5 E3 (10)	3.4 E-1(100)	1.0 E0 (10)	1.7 E0 (34)	8.9 E-1(50)	2.5 E-1(100)

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[a] Measurement given in mg/L, unless otherwise noted.
[b] Sampled July, 1977.
[c] Laboratory measurement.
[d] In-line measurement not made.
[e] Determined by: colorimetric procedure/ion-chromatography.
[f] Radiochemical unit = pCi/L. Number in ( ) = ±2σ% counting uncertainty.
[g] Analyses performed by LFE Laboratories, Richmond, California.

Table 2.13

Compounds Identified in Experimental Interceptor Trenches at Maxey Flats, Kentucky, Disposal Site

Experimental Trench	Concentration (mg/L)
Interceptor	
Acid fraction:	
none	
Basic fraction:	
none	
Neutral fraction:	
tetrahydrofuran	N.Q.[a]
DOC	10
Interceptor 4E	
Acid fraction:	
none	
Basic fraction:	
tetrahydrofuran	N.Q.
Neutral fraction:	
2-butanone	N.Q.
tetrahydrofuran	N.Q.
cyclohexanone	N.Q.
DOC	30
Interceptor 3W	
Acid fraction:	
ethylene glycol-diTMS	N.Q.
(ethylene glycol) n-diTMS	N.Q.
dioctyl adipate	3.4
di-isooctyl pthalate	N.Q.
Basic fraction:	
p-dioxane	N.Q.
Neutral fraction:	
p-dioxane	N.Q.
DOC	15
Interceptor 2E (anaerobic)	
Acid fraction:	
phenol	0.06
C_8 acid TMS	N.Q.
2-ethylhexanoic acid	0.44
Basic fraction:	
p-dioxane	N.Q.
Neutral fraction:	
tetrahydrofuran	N.Q.
p-dioxane	N.Q.
cyclohexanone	N.Q.
DOC	110
Interceptor 2E	
Acid fraction:	
phenol	0.6
C_8 acid TMS	N.Q.
2-ethylhexanoic acid	0.48
Basic fraction:	
p-dioxane	N.Q.
Neutral fraction:	
2-butanone	N.Q.
tetrahydrofuran	N.Q.
p-dioxane	N.Q.
cyclohexanone	N.Q.
DOC	120

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[a] N.Q.-not quantified.

Table 2.14

Concentration of Carbon in Water Samples Taken From the Experimental Interceptor Trenches and Well UB1-A, Maxey Flats, Kentucky, Disposal Site, October-November 1979

Sampling Location	Total Carbon (mg/L)	Inorganic Carbon (mg/L)	Organic Carbon (mg/L)
Well UB1-A	20	15	5
Interceptor 2E (anaerobic)[a]	180	70	110
Interceptor 2E	190	70	120
Interceptor 3W	140	120	20
Interceptor 4E	80	50	30
Interceptor 5	100	90	10

[a] Sampled using the anaerobic collection procedure.

2.3 Analyses of Waters Collected From the Barnwell, South Carolina, Disposal Site - May 1980

This sampling trip was the second to the Barnwell disposal facility. The first sampling was performed in March 1979. Results from these earlier samples are included with the more recent data for comparison purposes. In addition to the trench water samples, approximately 20 liters of water were collected from an observation well on the site (monitoring well 6). The depth of the well is approximately 200 feet below the surface. This water is presumably typical of the local groundwater and is to be used in laboratory experiments. "Undisturbed" cores of sediment were obtained from the floor of a disposal trench under construction. Approximately 3 feet of cored material was obtained to be used in the laboratory flow-through column experiments.

2.3.1 Field Measurements

Trench waters were collected by means of anaerobic sampling procedures developed for this purpose. A complete description of these procedures has been reported previously.(1) The trenches sampled were limited to those in which a sufficient quantity of water had accumulated to allow sampling. Efforts were made to collect water from the same trenches sampled on the first trip, but not all of these trenches could be resampled due to the absence of water accumulations. In-line measurements of temperature, specific conductance, dissolved oxygen, Eh and pH were performed.

Field measurements are given in Table 2.15, and the locations of the trenches sampled during the May 1980 sampling trip, as well as the March 1979 trip are shown in Figure 2.3. In comparison to the field measurements taken at the Maxey Flats (Table 2.1) and West Valley disposal sites, (Table 5.19 in Reference 1), the waters sampled at Barnwell have a higher redox potential, indicating more chemically oxidized waters. This is not unexpected because water is not continually present in the trenches at Barnwell, as opposed to other eastern United States sites where anoxic regimes develop in the stagnant trench water accumulations.

Hydraulic conductivities of the Barnwell unconsolidated sediments are in the order of 10^{-5} cm/s,(9) while those of the Maxey Flats shale and West Valley till are in the order of 10^{-7}-10^{-9} cm/s.(10,11)

Table 2.15

Field Measurements of Water Samples Collected at the Barnwell, South Carolina, Disposal Site

Sampling Location	Date	Temperature (°C)	Specific Conductance (μmho/cm)[a]	Oxygen (mg/L)	Eh (mV,NHE)[b]	pH
Burial Trenches:						
3D1	3/79	13.0	210	0.1	225	5.8
5D2	3/79	19.0	600	0.8	148	6.6
6D1	3/79	19.5	370	1.3	358	5.9
	5/80	15.3	260	4.2	350	6.1[c]
8D2	3/79	19.0	1400	1.5	308[d]	6.6[c]
8D3	5/80	16.0	2600	0.25	130	7.4
13D4	5/80	17.0	30	4.3	390	7.6[c]
18D5	5/80	12.8	42	3.0	330	7.0[c]
25/21D1	3/79	18.5	550	1.0	538	5.9
	5/80	13.3	190	0.15	160	6.2[c]

[a] Specific conductance expressed as μmho/cm at 25°C.

[b] Field measurements of Eh are reported relative to the Normal Hydrogen Electrode (NHE).

[c] Due to instrumentation problems pH measurements were not obtained in the field. The listed values were obtained after filtration of samples at BNL.

[d] Redox potential (Eh) calculated using an assumed water temperature of 19 °C.

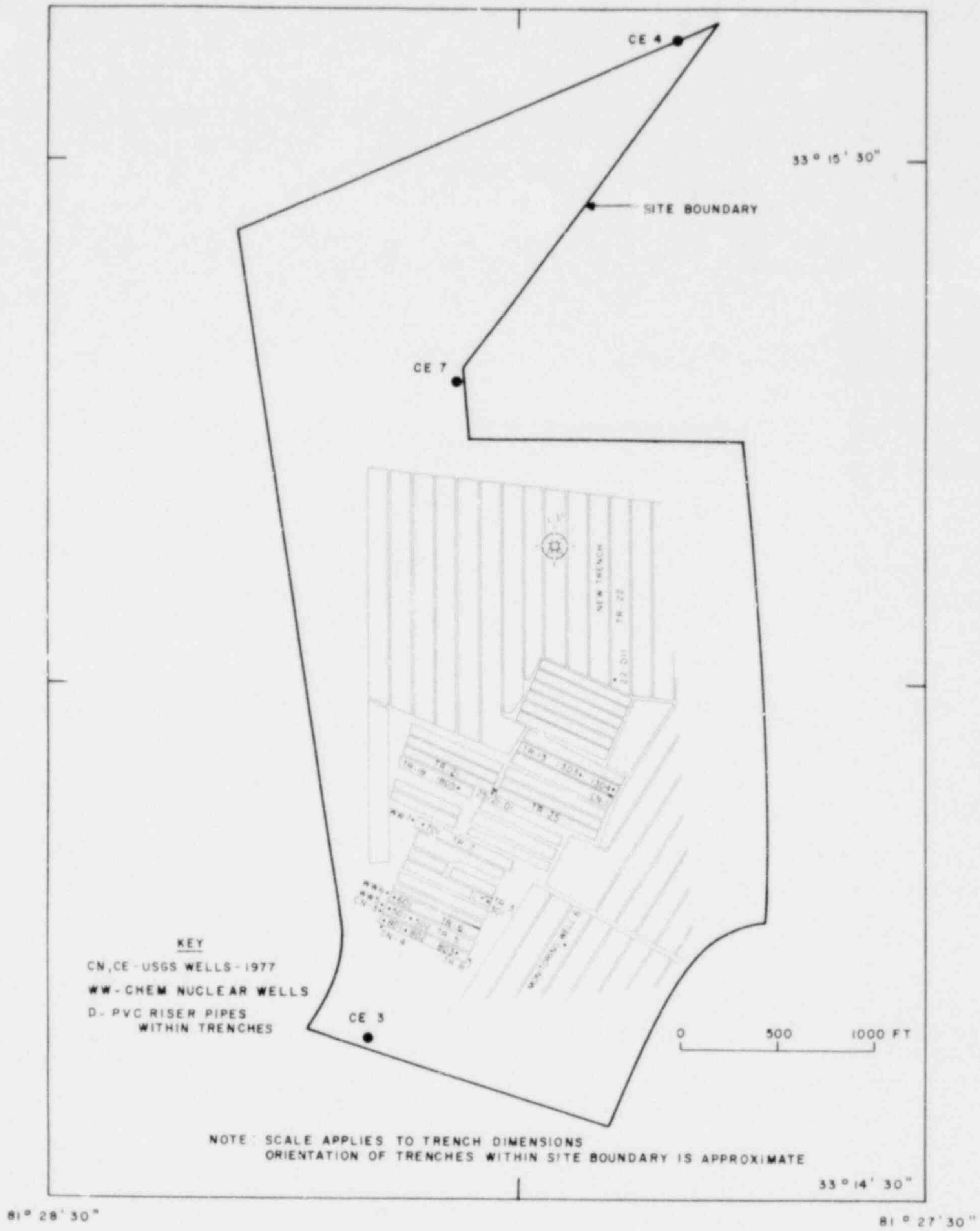

Figure 2.3 Locator map of the Barnwell, South Carolina, disposal facility.

2.3.2 Radiochemical Analyses

Results of the radiochemical analyses are presented in Table 2.16. Gross alpha and beta activities are low in the Barnwell samples, particularly when contrasted against results for the Maxey Flats (Table 2.2) and West Valley (Table 5.30 in Reference 1) trench water data. Tritium concentrations are high compared to the gross alpha and beta activity levels but still generally orders of magnitude lower than those observed in the other two disposal sites. Low activity levels are found in the Barnwell samples because trench waters do not accumulate and remain in the trenches for long periods compared to other sites sampled. This in turn is a reflection of the relatively more permeable sediments.

2.3.3 Inorganic Analyses

Results of cation and anion analyses of the waters collected at Barnwell are presented in Tables 2.17-2.18. Analyses of the well water (monitoring well 6, Figure 2.3) are included for comparison against the trench water results. Presumably, the well sample is more representative of the local groundwaters.

In comparison with the well water, the trenches have a different chemical composition, reflective of their interaction with the buried wastes. The trench waters are higher than the well waters in alkalinity, Total CO_2 (C_T) (C_T = the sum of aqueous carbon dioxide, carbonate and bicarbonate species), DOC, chloride, and ammonia, while generally lower in sulfate content. These changes are a function of bacterial action on organic material in the wastes. During bacterial degradation of organic matter, carbon dioxide and ammonia are produced which raises the pore water alkalinity, C_T and ammonia content. When bacterial processes deplete the pore water dissolved oxygen content, nitrate and sulphate are successively used as oxygen sources by the bacteria as they continue to degrade the organic material in the trench waters. Carbon dioxide and ammonia are produced during the nitrate and sulfate reduction phases, also resulting in continually increasing alkalinity, C_T and ammonia levels as the reactions continue. Relative to the well waters, trenches 3, 5, 6, 8, and 25/21 show the chemistry expected based on these processes; namely, high alkalinity, total CO_2 (C_T) and ammonia along with low sulphate and nitrate concentrations.

The alkalinity is a useful scaling parameter to indicate the extent of bacterial degradation in the waters. Higher alkalinity indicates relatively increased bacterial action. The increases may be due to higher organic matter contents and/or a longer time period during which the bacterial processes have been active. In comparison to the trench water compositions at Maxey Flats and West Valley, the Barnwell waters are much less "anoxic", in that the alkalinity and ammonia levels are lower, although qualitatively the water chemistry is similar. Here again, the relative differences are due to the fact that water accumulations do not persist in the trenches in Barnwell, as opposed to the situation in Maxey Flats and West Valley.

Table 2.16

Concentration of Dissolved Radionuclides in Water Samples
Taken From the Barnwell, South Carolina, Disposal Site,[a]
[pCi/L ($\pm 2\sigma$ %)][b]

Radionuclide	Date	Trench 3D1	Trench 5D2	Trench 6D1	Trench 8D2
Gross alpha	3/79	<14	<14	1.6 E1 (65)	<9
	5/80	----[c]	----	1.5 E1 (67)	----
Gross beta	3/79	<28	4.1 E 2 (8.3)	<28	7.9 E 2 (6.6)
	5/80	----	----	<36	----
Tritium	3/79	1.2 E4 (6.5)	9.9 E 6 (<1)	5.7 E5 (<1)	4.8 E 8 (<1)
	5/80	----	----	6.1 E5 (13)	----
^{60}Co	3/79	N.D.[d]	1.3 E 2 (18)	N.D.	2.6 E 1 (69)
	5/80	----	----	N.D.	----
^{134}Cs	3/79	N.D.	N.D.	N.D.	N.D.
	5/80	----	----	N.D.	----
^{137}Cs	3/79	N.D.	1.6 E 2 (14)	N.D.	N.D.
	5/80	----	----	N.D.	----
^{238}Pu[e]	3/79	f	1.4 E 0 (56)	f	1.9 E 0 (40)
	5/80	----	----	g	----
^{239,240}Pu[e]	3/79	f	1.9 E-1 (200)	f	4.6 E-1 (110)
	3/80	----	----	g	----
^{90}Sr[e]	3/79	f	4.2 E 1 (10)	f	3.7 E 1 (18)
	3/80	----	----	g	----

[a] Samples were filtered through a 0.45 μm Millipore filter.
[b] Number in ( ) = $\pm 2\sigma$% counting uncertainty.
[c] ----Not sampled on this date.
[d] N.D. = not detected.

An additional analysis was performed on this most recent set of trench water samples; namely, measurement of bicarbonate ion concentration. Bicarbonate concentrations are frequently derived from the pH and titration alkalinity measurements. However the complex titration curves, observed for some disposal trench waters,(1) preclude bicarbonate calculation based only on pH and alkalinity values. Other analytical determinations are required for these complex waters. The carbon dioxide sensing probe was selected for this measurement because it determines the total carbonate content (C_T), which is equal to the sum of aqueous carbon dioxide, bicarbonate and carbonate ions. Combined with pH, and measurements using titration alkalinity values as an independent check, the bicarbonate ion concentration can be determined. The procedure was tested on this recent set of trench waters from Barnwell. A detailed explanation of these calculations is given in Appendix B. When the

Table 2.16, Continued

Concentration of Dissolved Radionuclides in Water Samples
Taken From Barnwell, South Carolina, Disposal Site,[a]
[pCi/L (±2 σ%)][b]

Radionuclide	Date	Trench 8D3	Trench 13D4	Trench 18D5	Trench 25/21D1
Gross alpha	3/79	----[c]	----	----	<14
	5/80	<11	8.8 E 0 (100)	<8.5	1.0 E 1 (90)
Gross beta	3/79	----	----	----	1.0 E 2 (27)
	5/80	9.6 E2 (4.8)	<36	<36	<36
Tritium	3/79	----	----	----	3.7 E 5 (<1)
	5/80	7.8 E8 (<1)	<730	<710	2.2 E 5 (8.3)
^{50}Co	3/79	----	----	----	N.D.
	5/80	3.7 E2 (9.4)	N.D.	N.D.	N.D.
^{134}Cs	3/79	----	----	----	N.D.
	5/80	3.4 E1 (24)	N.D.	N.D.	N.D.
^{137}Cs	3/79	----	----	----	N.D.
	5/80	5.1 E2 (7.4)	N.D.	N.D.	N.D.
^{238}Pu[e]	3/79	----	----	----	4.6 E 0 (18)
	5/80	[g]	[g]	[g]	[g]
^{239,240}Pu[e]	3/79	----	----	----	1.9 E -1 (200)
	3/80	[g]	----	----	[g]
^{90}Sr[e]	3/79	----	----	----	9.3 E 0 (78)
	3/80	[g]	[g]	[g]	[g]

---

[e] Analyses performed by LFE Laboratories, Richmond, California.
[f] Analysis not performed.
[g] Analysis in progress.

reliable bicarbonate concentrations are used in calculations of the anion-cation totals, a satisfactory balance is obtained for trenches 6, 25/21, and the well 6. The discrepancy for trench 8 may be due to the presence of organic species (see Table 2.19) and more complex composition which may be causing errors in other analyses that are not apparent. Trench 13 and 18 have such small concentrations of inorganic species that the magnitude of the analytical errors preclude accurate calculations of the anion-cation balances.

In summary, trench water compositions at Barnwell, range from essentially groundwaters (trenches 3, 13, 18) to waste waters similar in composition (trench 8D2-May 1980) to those in Maxey Flats and West Valley. The water quality reflects the interaction of groundwaters with the buried wastes and the effects of bacterial degradation of organic waste components.

Table 2.17

Concentrations of Dissolved Nonmetals in Water Samples Taken From Barnwell, South Carolina, Disposal Site (Concentrations in mg/L)

Dissolved Component	Date	Disposal Trenches 3D1	5D2	6D1	8D2	8D3	13D4	18D5	25/21D1	Well 6
Total Alkalinity[a]	3/79	100	200	40	600	---[b]	---	---	80	---
(as $CaCO_3$)	5/80	---	---	86	---	1340	46	30	104	61
Total CO_2[a,c]	3/79	d	d	d	d	---	---	---	d	---
(as $CaCO_3$)	5/80a	---	---	330	---	1700	54	38	370	81
Bicarbonate[e]	5/80	---	---	70	---	1120	d	d	75	48
Hardness (Mg+Ca)	3/79	20	81	44	160	---	---	---	66	---
(as $CaCO_3$)	5/80	---	---	61.2	---	450	6.1	10	47.7	15
Inorganic Carbon	3/79	24	f	11	130	---	---	---	38	---
	5/80	---	---	8	---	258	<2	2	17	6
DOC	3/79	7	f	2	170	---	---	---	12	---
	5/80	---	---	7	---	203	83	5	6	6
Chloride-color[g]	3/79	7	10	90	85	---	---	---	42	---
	5/80	---	---	13.3	---	46.6	3	3	12.1	3
Nitrogen-N	3/79	d	d	d	d	---	---	---	d	---
(NH_3-probe)	5/80	---	---	3.7	---	200	<1	<1	4.1	<1
Nitrogen-N	3/79	0.3	f	1.4	59	---	---	---	25	---
(NH_4^+-color)	5/80	---	---	3.89	---	205	<2	<2	34.6	<2
Nitrogen-N	3/79	<0.05	<0.05	<0.05	<0.05	---	---	---	0.05	---
(NO_2^--color)	5/80	---	---	0.11	---	<0.05	<0.05	<0.05	<0.05	<0.05
Nitrogen-N	3/79	<0.04	<0.1	23	8.0	---	---	---	15	---
(NO_2^-+NO_3^-color)	5/80	---	---	4.21	---	<0.1	0.1	0.29	<0.1	<0.1
Phosphate	3/79	<0.5	<0.5	<0.5	<0.5	---	---	---	<0.5	---
	5/80	---	---	<1	---	<1	<1	<1	<1	<1
Silica	3/79	4.3	7.6	5.8	6.0	---	---	---	5.0	---
	5/80	---	---	7.28	---	4.49	1.10	2.34	7.20	<1
Sulfate-color	3/79	<5	7	18	34	---	---	---	56	---
(anaerobic)	5/80	---	---	44.5	---	7.1	<5	<5	<5	17.2
pH[a]	3/79	6.50	7.00	6.20	6.65	---	---	---	6.10	---
	5/80	---	---	6.08	---	7.20	8.5	7.00	6.21	7.54
Total Anions	3/79[h]	2.3	4.4	4	16	---	---	---	5.7	---
(meq/L)	5/80[i]	---	---	2.6	---	20.0	d	d	1.81	1.2

---

[a] Measurements were made immediately after anaerobic filtrations.
[b] ---No sample was collected.
[c] Probe method-see Appendix A.
[d] Measurement was not made.
[e] Bicarbonate calculated from titration and probe measurements - Appendix B.
[f] Insufficient sample.
[g] Colorimetric method determines bromide and iodide as chloride.
[h] Total alkalinity results were used for total anions calculations.
[i] Bicarbonate results were used for total anions calculations.

Table 2.18

Concentrations of Dissolved Metals in Water Samples Taken From Barnwell, South Carolina, Disposal Site (Concentrations in mg/L)

Metal	Date	Disposal Trenches								Well
		3D1	5D2	6D1	8D2	8D3	13D4	18D5	25/21D1	6
Barium	3/79	<1	<1	<1	<1	---[a]	---	---	<1	---
	5/80	---	---	0.6	---	0.5	<0.5	<0.5	<0.5	<0.5
Calcium	3/79	4.0	3.2	16	34	---	---	---	21	---
	5/80	---	---	14.0	---	82.4	1.2	2.1	9.5	3.6
Cesium	3/79	<0.1	<0.1	<0.1	<0.1	---	---	---	<0.1	---
	5/80	---	---	<0.5	--	<0.5	<0.5	<0.5	<0.5	<0.5
Iron[b]	3/79	0.15	1.5	0.4	1.2	---	---	---	0.2	---
	5/80	---	---	<1	---	24.0	<1	<1	6.1	<1
Iron[c]	3/79	d	d	d	d	---	---	---	d	---
	5/80	---	---	<0.1	---	23.0	<0.1	<0.1	6.2	<0.1
Fe^{+2}/Fe^{+3}	3/79	d	d	d	d	---	---	---	d	---
	5/80	---	---	d	---	>100	d	d	30	d
Lithium	3/79	<0.1	<0.1	<0.1	<0.1	---	---	---	<0.1	---
	5/80	---	---	<0.2	---	<0.2	<0.2	<0.2	<0.2	<0.2
Magnesium	3/79	2.5	3.3	1.0	18	---	---	---	3.3	---
	5/80	---	---	1.43	---	40.3	0.48	0.66	3.20	0.15
Maganese	3/79	0.24	0.34	0.45	0.72	---	---	---	0.32	---
	5/80	---	---	0.70	---	0.88	<0.1	<0.1	0.62	<0.1
Potassium	3/79	1.0	4.6	1.4	12	---	---	---	3.5	---
	5/80	---	---	2.95	---	18.1	1.3	0.03	1.15	12.2
Sodium	3/79	2.3	20	29	87	---	---	---	37	---
	5/80	---	---	28	---	120	0.50	1.1	10.7	15.1
Strontium	3/79	<0.1	<0.1	<0.1	<0.1	---	---	---	<0.1	---
	5/80	---	---	<0.5	---	0.5	<0.5	<0.5	<0.5	<0.5
Total Cations[e] (meq/L)	3/79	0.55	2.9	2.3	12	---	---	---	4.8	---
	5/80	---	---	2.4	---	28.6	0.15	0.26	1.73	1.15

[a] ---No sample was collected.

[b] Atomic absorption method.

[c] Colorimetric method.

[d] No measurement was made.

[e] Total meq/L for metals plus nitrogen from NH_4^+ analyses.

Table 2.19

Concentration of Carbon in Water Samples Taken From the Barnwell, South Carolina, Disposal Site

Sampling Location	Date	Total Carbon (mg/L)	Inorganic Carbon (mg/L)	Organic Carbon (mg/L)
Trench 3D1	3/79	31	24	7
Trench 6D1	3/79	13	11	2
	5/80	15	8	7
Trench 8D2	3/79	300	130	170
Trench 8D3	5/80	460	260	200
Trench 13 D4	5/80	83	<2	83
Trench 18D5	5/80	7	2	5
Trench 25/21D1	3/79	50	38	12
	5/80	23	18	5

2.3.4 Carbon Analyses

Aliquots of the trench waters were analyzed by means of a Beckmen Total Carbon Analyzer. Total and inorganic carbon are measured; the organic carbon is equal to the difference between these numbers. Results for the trench waters are presented in Table 2.19. Multiply sampled trenches gave similar results for both samplings. Highest levels were found in trench 8 for both sampling dates. In comparison with the Maxey Flats (Table 2.9) and West Valley (Table 5.22, in Reference 1) results, the Barnwell data are quite low. Here again, the data reflects the relative residence time of the trench waters in Barnwell vs the other two sites.

2.4 Trench Water Source Term Studies-Summary and Recommendations

The routine sampling and analysis of disposal trench waters has been in progress since 1976. During this period, the Maxey Flats, Kentucky, disposal site has been sampled four times; the West Valley and Barnwell facilities twice; and the Sheffield, Illinois, site once. Procedures have been developed for the collection, storage, and analyses of these trench waters as described in previous reports. The objectives of this effort were to (1) characterize the nature of the trench water systems at various sites, (2) determine radionuclide and other chemical species concentrations in the trench waters, (3) to determine the temporal variation in species concentrations and, (4) identify viable bacteria types. Data from these efforts can be used in modeling studies of the hydrologic flow regimes in and around the disposal sites, as well as geochemical investigations concerning radionuclide retention.

2.4.1 Trench Water Composition and Stability

The following conclusions are based on the analytical results obtained during the four year sampling period:

- Trench waters from the Maxey Flats and West Valley, disposal sites have strongly anoxic water chemistries developed from the bacterial decomposition of organic components in the waste. Interaction of groundwaters with other waste components further complicates the trench water chemistry. These waters are anaerobic, with high titration alkalinities, chemically reducing (negative redox potential) and dominated by the processes of denitrification and sulfate reduction. High dissolved iron concentrations develop in some of the waters due to corrosion of the metal disposal drums.

- Exposure of strongly anoxic trench waters to oxygen initiates a series of irreversible changes in the water chemistry; namely, precipitation of iron oxyhydroxides, decrease in alkalinity, pH and Eh changes, which in turn affect other chemical components. Analyses of trench waters after air exposure are not representative of in situ chemistry. However, these changes would be expected to take place when trench waters move away from the immediate trench vicinity. Alterations in water chemistry will affect radionuclide retention and migration through processes such as redox state changes, precipitation, and coprecipitation.

- Relative to samples from Maxey Flats and West Valley, trench waters collected from the Barnwell, South Carolina, disposal site are much closer to natural groundwaters than organic laden waste waters. The redox potential is oxidizing; DOC, alkalinities, and waste derived components such as chloride and iron are lower than those found in the anoxic trench waters. However, the trench waters do show the effects of bacterial decomposition processes in that alkalinities are higher and sulphate concentrations lower than local groundwater concentrations. Water from trench 8 most closely resembles the anoxic trench waters.

- Tritium was the most abundant radionuclide found in all the trench waters. Chemically bound in water molecules, it has the greatest migration potential of any radionuclide.

- ^{90}Sr, ^{238,239,240}Pu and ^{137}Cs were found as dissolved species in the majority of trench waters. However, radionuclide concentrations in the Barnwell, South Carolina, samples are exceedingly small and often undetectable.

- No overall systematic changes in water chemistry are detectable for the multiply-sampled disposal trenches at the three sites studied. Longer term evolution in the trench chemistry may be taking place, but is not detectable over the brief sampling interval used in this study. Changes in some radionuclide and inorganic component concentrations were observed in several trenches. These changes may be due to trench water pump-outs or random breaking of drums and other buried containers.

- Numerous organic compounds were identified in methylene chloride extracts of trench waters. Some of these compounds can act as chelating agents for radionuclides, thereby enhancing their migration potential. However, radionuclides may enter the trench environment already complexed. The amounts of water soluble chelating agents (such as EDTA) in the trench waters should be determined, and the fate of such radionculide complexes should be addressed.

- The presence of radionuclides above background levels in wells UB1 and UB1-A at Maxey Flats, together with organic compounds that are also found in nearby trenches, indicates migration of radionuclides between the wells and trench water leachates. A multi-disciplined effort is being carried out to assess the extent of this migration.

2.4.2 Trench Water Analyses - Recommendations

Results of the inorganic, organic, and radiochemical analyses performed over the four-year sampling interval did not detect any systematic variation in trench water chemistry. Trench water chemistry is controlled by a complex combination of bacterial degradation processes and interactions with the wastes. It is unlikely that continued routine sampling and analysis of the disposal trenches will further clarify the water chemistry to a degree sufficient to justify the effort involved, either in terms of understanding the chemical regimes or detecting longer term evolution of the trench water compositions. Sufficient data have been collected to characterize the trench waters with respect to source term input for modeling studies. It is recommend that:

1. Routine sampling and analyses of trench waters from the various disposal sites should be discontinued. Further sampling should be restricted to that necessary to obtain samples for directed efforts.

2. Additional efforts to understand the water chemical regime should focus on the changes resulting from migration (oxidation and precipitation reactions), as well as the effects of water chemistry on sorption processes, and sulfide precipitation in anoxic systems.

Future efforts concerning water chemistry will focus on the concerns mentioned above. Additional sampling trips to the disposal sites will be for the purpose of obtaining samples to be used in more directed laboratory studies (see section 6), or to participate in efforts such as that involving the experimental interceptor trenches at Maxey Flats.

3. SORPTION OF RADIONUCLIDES FROM SOLUTION

(R. Pietrzak, K. Czyscinski, and C. Anderson)

3.1 Introduction

Sorption capacity measurements of the geomedia at the various disposal sites are an integral part of the source term characterizations of each disposal site. General scoping studies have been performed, along with studies to compare the relative sorption behavior of "oxic"[a] versus anoxic water-sediment systems. Results of these experiments have also been reported previously.(1) All of these studies were performed by a batch technique using site-specific materials and under simulated in situ conditions. Simulating these conditions requires that the anoxic nature of the trench waters be preserved for the duration of the experiments. This in turn requires that oxygen must be excluded during all sample preparation procedures and subsequent manipulations. Apparatus and procedures used in previous experiments were only partially successful in maintaining the anoxic character of the trench waters. The work described here reports the results obtained using an improved experimental design. These new sorption experiments are designed to obtain quantitative measurements of the geomedia sorption capacity under simulated site-specific conditions, rather than to study the relative sorption in "oxic" versus "anoxic" waters. Materials from the Maxey Flats, Kentucky, and West Valley, New York, disposal sites were used in the experiments.

Additional sorption studies were initiated during the past year in several other areas of concern. A study is in progress to monitor the sorption behavior as a function of time for material from the Barnwell, South Carolina, disposal site. This was initiated as part of the source term characterization of this site. Early results are presented here. Experiments to gauge the effect of small amounts of organic chelating agents on the sorption capacities of site-specific material, as well as typical soil-forming minerals, were also performed in the past year.

3.2 Batch Sorption Experiments - Anoxic Water Systems (Maxey Flats, Kentucky, and West Valley, New York) - Oxic Water System (Barnwell, South Carolina)

3.2.1 Materials and Experimental Procedures

3.2.1.1 Water Samples

Water samples used for the determination of radionuclide sorption (K_d) were collected at disposal sites using an anaerobic collection procedure described in a previous report.(1) To preserve the low oxygen and

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[a] "Oxic" is defined here as trench waters that have been exposed to air and the ferric oxyhydroxide precipitate removed. The term K_d is also used here to denote the measured sorption capacity, however, no implications concerning the thermodynamic correctness of this number are intended. Simply defined, the sorption coefficient (K_d) is the ratio of activity in the solid phase to that in the liquid phase for the solid-liquid system studied.

reducing Eh conditions, these waters were stored in glass bottles with a nitrogen atmosphere at approximately 4 °C. These water samples are referred to in this report as "anoxic" trench waters. A list of the water samples used in the sorption experiments is given in Table 3.1. Analyses of the inorganic components of these waters are presented in another section of this report and in other reports (see Table 3.1).

3.2.1.2 Solid Phases

Samples of the geomedia representative of the trench material were supplied by the United States Geological Survey. Unweathered till was obtained from the West Valley, New York, disposal site; unweathered shale from Maxey Flats; and unconsolidated silty sands from Barnwell. More complete decriptions are given in Table 3.2. The samples were characterized in terms of parameters though to influence sorption behavior, such as particle size distribution and cation exchange properties. Characterization representative data for materials are given in Table 3.3. Methods used have been described previously.(1)

3.2.1.3 Procedures for Handling Anoxic Waters

A detailed description of the improved experimental apparatus design and sample preparation procedures for working with anoxic waters, is given in Appendix C. Briefly, the procedure is as follows. Spiked trench waters are prepared by evaporating tracer solutions to dryness, converting them to chloride salts by evaporation with hydrochloric acid, and dissolving the dry salts in trench water.

The spiked trench water is added to rock chips in Teflon containers. Containers without rock chips are used for control solutions. All sample handling procedures involving anoxic waters are performed under inert atmospheres. The sealed containers are tumbled on a ball mill which disaggregates the solids and equilibrates the two phases. The samples are periodically counted by gamma-ray spectroscopy to monitor the progress of the experiments. Radionuclide activity in solution is counted while shielding the solid phase from the Ge(Li) detector.

At the conclusion of an experiment, a final measurement is made on an aliquot of liquid phase. The final steps are to: (1) centrifuge the samples; (2) filter the liquid through a 0.2 μm filter; and (3) count an acidified aliquot of the liquid phase to determine the amount of radionuclide in solution without inteference from radionuclide activity on the soil. The amount of radionuclide initially in solution is determined from the control samples.

Table 3.1

Trench Waters Used in Sorption Experiments

Sample No.	Disposal Site	Trench No.	Collection Date	Analytical Data
WV-40	West Valley, NY	2-1A	11/77	Ref. 1
MF-187	Maxey Flats, KY	27	10/79-11/79	This report section 2.2.6
MF-193	Maxey Flats, KY	Interceptor Trench 2	10/79-11/79	This report section 2.2.8
BN-17	Barnwell, SC	6D1	5/80	This report section 2.3.3

Table 3.2

Geomedia Samples Used in Sorption Experiments

Material	Disposal Site	Site Location	Collection Date
Till (Lavery Till)	West Valley, NY	Drill core section Trench 2-east end Test Hole A2 at 34.8 to 35.1 feet	1975
Shale (Nancy Shale)	Maxey Flats, KY	Bulk rock sample Trench 46 at approx. 20 feet	1977
Silty Sand (Hawthorne Formation)	Barnwell, SC	Drill core section approx. 30 ft depth	1978

Table 3.3

Characterization Date for Geomedia Samples Used in Sorption Experiments

Parameter	West Valley Till	Maxey Flats Shale	Barnwell Silty Sand
Particle size distribution sand: silt: clay-wt.% bulk samples (av.)	5:40:55	10:45:45	75:10:15
Surface area[a]-m^2/g	22.6	25.7	0.3-13
Cation exchage capacity[b] meq/100 g	7.4	10.9	6.0
Organic carbon-wt.%	1.7	0.8	0.03
Extractable iron-wt.%	0.35	0.15	0.2-0.3
Carbonate content-wt.%	14.2	0.0	0.0
<u>Mineralogy</u> (M) major component (m) minor component (Tr) trace amounts	quartz (M) illite (M) calcite (M) dolomite (M) feldspars (m) kaolinite (M) mixed layer clays (m) goethite (Tr)	quartz (M) illite (M) feldspar (M) kaolinite (M) chlorite (m) goethite (Tr)	quartz (M) mica (m) feldspar (m) kaolinite (m) goethite (Tr) hematite (Tr)

[a] Surface area data obtained using Ethyleneglycol Monoethyl Ether (EGME).
[b] Sodium used as indexing ion.

3.2.2 Maxey Flats and West Valley, Sorption Experiment Results

Only preliminary results for sorption experiments using anoxic trench waters are discussed below because these experiments are still in progress.

3.2.2.1 West Valley Sorption Experiment

Samples prepared from a West Valley trench water (2-1A) and the till maintained a low Eh in the double containers, Table 3.4. The Eh differed from the original value, but was still in the reducing region relative to an air-exposed sample of the same water. Sorption coefficients are given in Table 3.5 for an equilibration period of approximately seven days for the anoxic experiment and 19 days for the oxic experiment.

3.2.2.2 Maxey Flats, Sorption Experiment

Preliminary results indicate that the time required to approach steady-state conditions appears to be quite long. Figures 3.1, 3.4, and 3.5 show the activities remaining in solution for samples which were tumbled for five months. Concentrations of ^{85}Sr, ^{134}Cs, ^{137}Cs, and ^{60}Co decrease with time without an apparent approach to steady state conditions. The ^{85}Sr, ^{137}Cs, and ^{60}Co results for two samples show identical behavior indicating that the results are reproducible (Figures 3.2, 3.3, and 3.6). The expected decrease in activity due to radioactive decay is insufficient to account for the decrease.

A sample from another set of Maxey Flats samples spiked with ^{152}Eu shows adsorption but no significant time dependency for a contact time of approximately 2-1/2 months (Figure 3.7).

Compared to the sorption studies reported previously,(1) these recent experiments illustrate that the sorption processes in anoxic water systems are slower relative to those in "oxic" systems, where steady-state conditions are reached more rapidly. The changes in activity observed could be responses to changing water chemistry in the liquid phases rather than kinetically slow sorption process. These experiments will be continued for longer contact times before final measurements are made. Only the final measurements on the liquid phases will indicate if the anoxic character of the water has been preserved for the duration of the experiment.

3.2.3 Barnwell Sorption Study Results

Preliminary results for the Barnwell trench water system are reported as part of the source term characterization work for this site. The results also provide an interesting comparison with the West Valley and Maxey Flats data because the trench waters at Barnwell are chemically much more oxidized water regimes.

No significant decrease in the concentration of ^{241}Am and ^{85}Sr were observed after two months of tumbling (Figures 3.8 and 3.9). Slight decreases in the ^{134}Cs and ^{137}Cs concentrations in solution were observed (Figures 3.10 and 3.11). However, a relatively large increase in ^{60}Co

Table 3.4

pH and Eh of West Valley, New York, Trench 2-1A,
Anoxic Water - Before and After Sorption Experiment

Sample	pH		Eh(mV)[a]	
	Before	After	Before	After
1	7.74	8.16	-83	-68
2	7.74	8.02	-83	+82
3	7.74	7.99	-83	+160
Oxic[b]	----	8.28	----	+406

[a] Eh(mV) is the potential for a platinum electrode relative to a normal hydrogen reference electrode at 25°C.

[b] Anoxic water (West Valley Trench 2-1A) was exposed to air and filtered to remove ferric oxyhydroxide.

Table 3.5

Sorption Coefficients for
West Valley, Trench 2-1A Water and Till

	Sorption Coefficient (mL/g)	
	Oxic[a]	Anoxic[b]
^{134}Cs	55 ± 4	252 ± 1
^{137}Cs	55 ± 4	252 ± 2
^{60}Co	<1	<1
tumbling time	19 days	7 days

[a] Oxic - Trench water exposed to air, filtered to remove ferric oxyhydroxide, and used to prepare sorption samples without use of an inert atmosphere.

[b] Anoxic - Sample preserved in low oxygen environment.

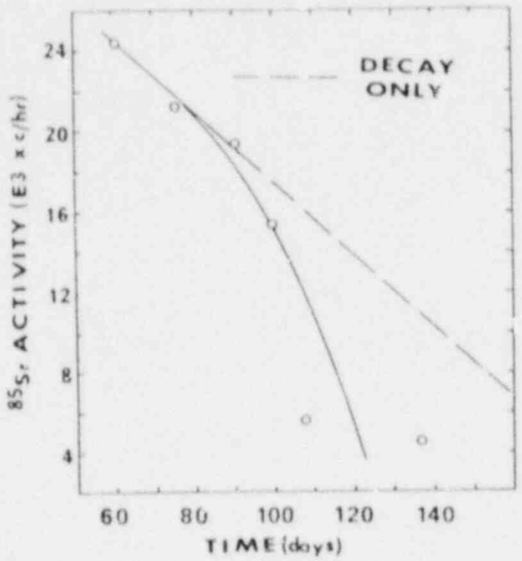


Figure 3.1 ^{85}Sr activity remaining in Maxey Flats, Trench 27 anoxic water vs tumbling period with shale. First sample (187-16) ^{85}Sr $t_{1/2}$ = 65 days.

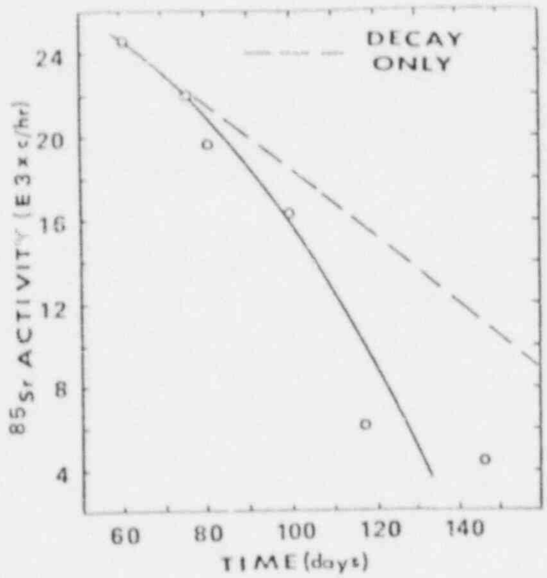


Figure 3.2 ^{85}Sr activity remaining in Maxey Flats, Trench 27 anoxic water vs tumbling period with shale. Second sample (187-17) ^{85}Sr $t_{1/2}$ = 65 days.

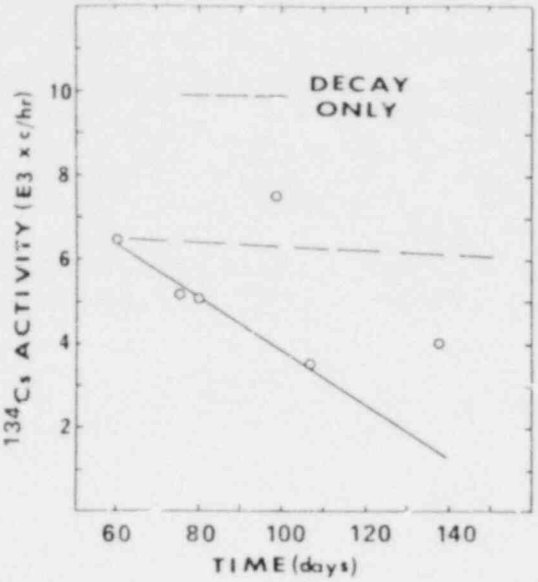


Figure 3.3 ^{134}Cs activity remaining in Maxey Flats, Trench 27 anoxic water vs tumbling period with shale. First sample (187-16) ^{134}Cs $t_{1/2}$ = 2.05 years.

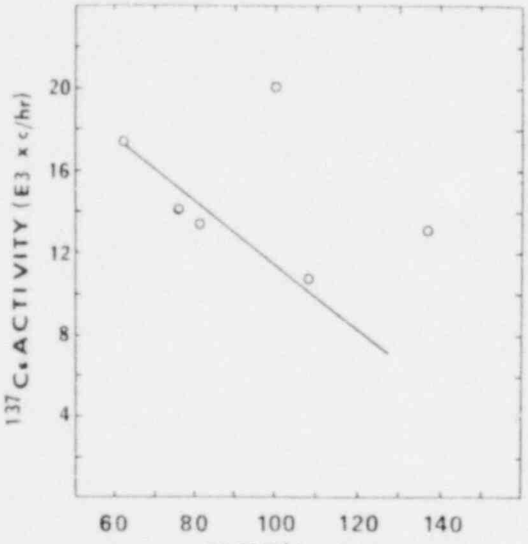


Figure 3.4 ^{137}Cs activity remaining in Maxey Flats, Trench 27 anoxic water vs tumbling period with shale. First sample (187-16) ^{137}Cs $t_{1/2}$ = 30 years.

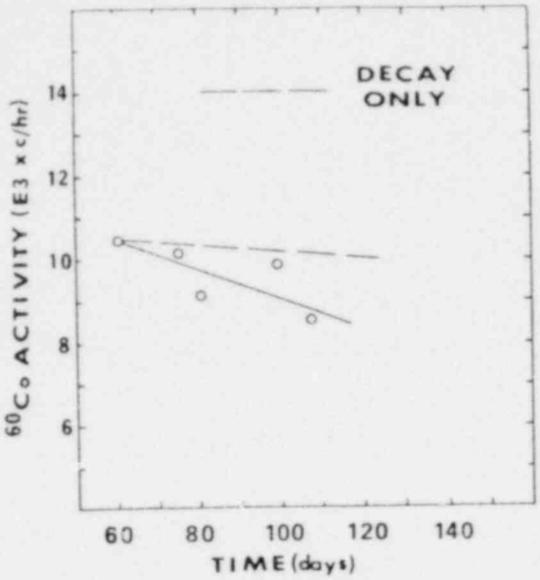


Figure 3.5 ^{60}Co activity remaining in Maxey Flats, Trench 27 anoxic water vs tumbling period with shale. First sample (187-16) ^{60}Co $t_{1/2}$ = 5.26 years.

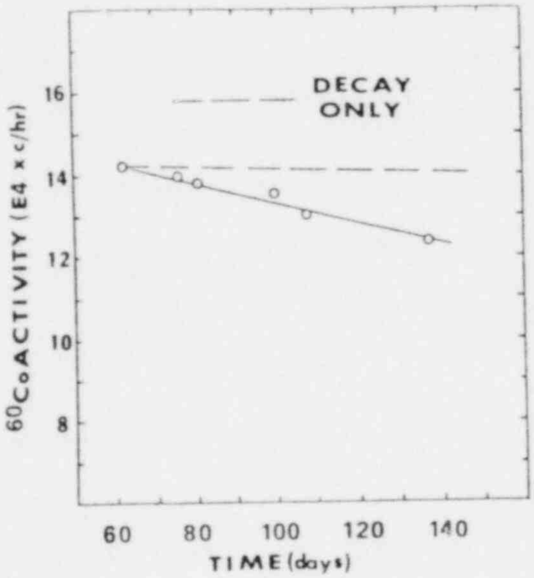


Figure 3.6 ^{60}Co activity remaining in Maxey Flats, Trench 27 anoxic water vs tumbling period with shale. Second sample (187-17) ^{60}Co $t_{1/2}$ = 5.26 years.

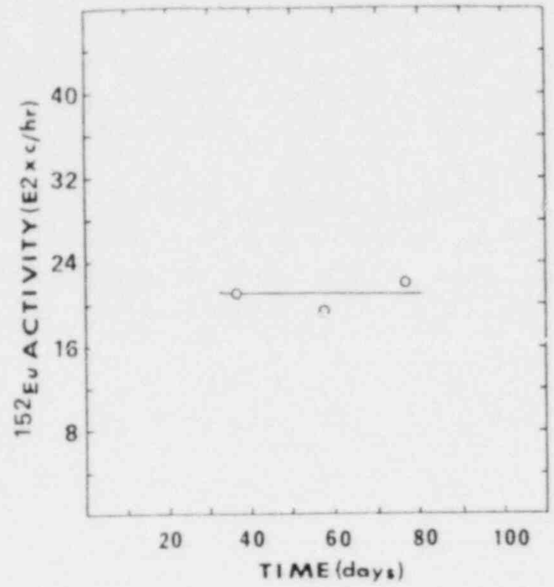


Figure 3.7 ^{152}Eu activity remaining in Maxey Flats, Trench 27 anoxic water vs tumbling period with shale. ^{152}Eu $t_{1/2}$ = 12.2 years.

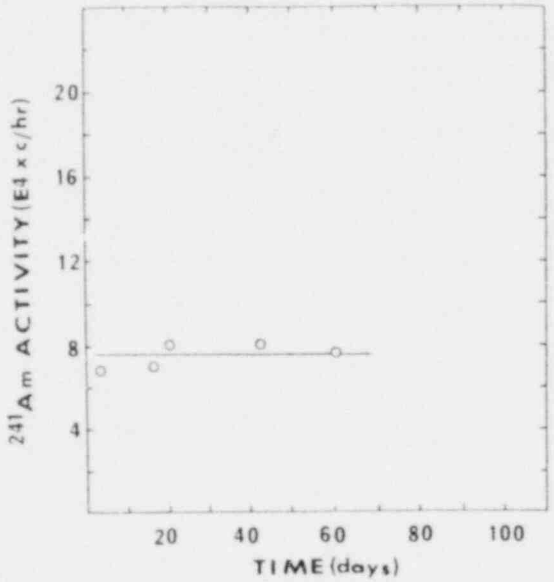


Figure 3.8 ^{241}Am activity remaining in Barnwell, Trench 6D1 oxic water vs tumbling period with Barnwell sediment (Sample 17-23) ^{241}Am $t_{1/2}$ = 458 years.

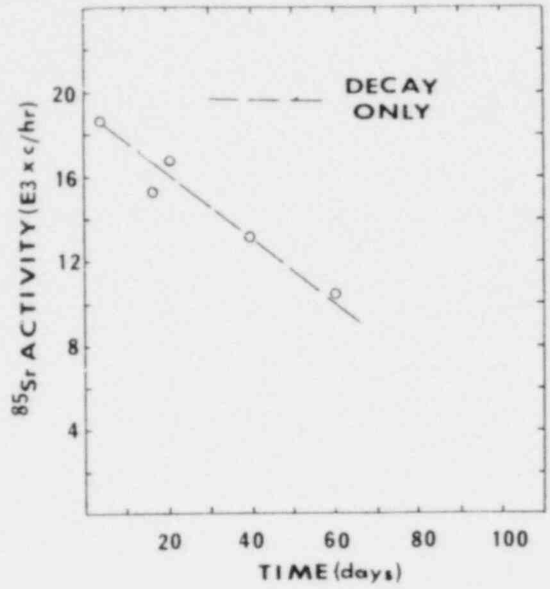


Figure 3.9 ^{85}Sr activity remaining in Barnwell, Trench 6D1 oxic water vs tumbling period with Barnwell sediment (Sample 17-23). ^{85}Sr $t_{1/2}$ ≈ 65 days.

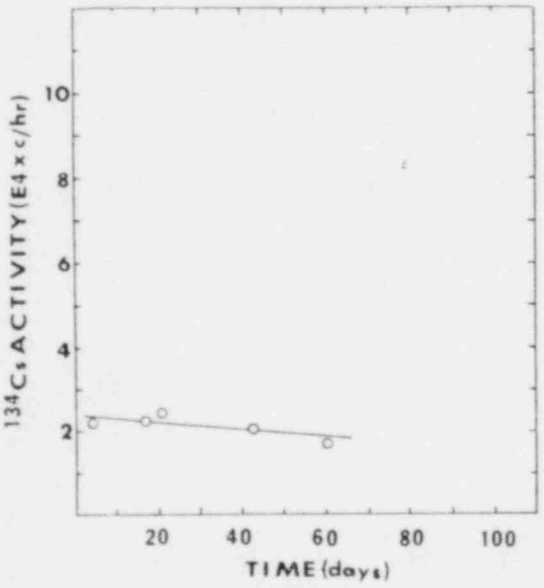


Figure 3.10 ^{134}Cs activity remaining in Barnwell, Trench 6D1 oxic water vs tumbling period with Barnwell sediment (Sample 17-23). ^{134}Cs 1/2 = 2.05 years.

concentration was observed (Figure 3.12) which is anomalous compared to the other results. These experiments will also be continued and the systems examined in more detail in the coming year.

3.3 Effect of Organic Substances on Radionuclide Sorption Coefficients

3.3.1 Introduction

Radionuclide mobilization appears to be enhanced by organic complexing agents buried in the disposal trenches. It has been reported that EDTA causes ^{60}Co to migrate from intermediate level trenches at the Oak Ridge National Laboratory burial grounds.(12)

Experimentally measured batch K_d results given in this report illustrate the decreasing sorption for ^{241}Am, ^{85}Sr, and ^{60}Co when organic substances are added to the soil-water systems. Several reference minerals were used for comparison with the site specific soil material.

3.3.2 Materials and Experimental Procedures

3.3.2.1 Materials

Detailed descriptions of the materials used in these experiments have been described previously.(3)

Water

Water from well UB1-A was collected at the Maxey Flats, Kentucky, disposal site in May 1978. Analytical data for this water was given in an earlier report.(1) The water was filtered through 0.45 μm membrane filter prior to sample preparation.

The solid phases used in these experiments consisted of shale from the Maxey Flats disposal sites (see Table 3.3 for detailed description) and various reference samples of soil forming minerals; namely, vermiculite, montmorillonite, kaolinite, illite, and limonite. More detailed description of the materials have been reported previously.(3)

3.3.2.2 Organic Complexing Agents

Five organic complexing agents were used in the experiments. They were added to the well water to give concentrations of 2, 10, and 100 mg/L. Organic compound free water-shale mixtures were used for comparison. The complexing agents were:

EDTA - Ethylenediaminetetraacetic acid tetrasodium salt dihydrate

Oxalic acid

THF - Tetrahydrofuran, HP grade with 0.1 percent hydroquinone

TBP - Tributyl-n-phosphate

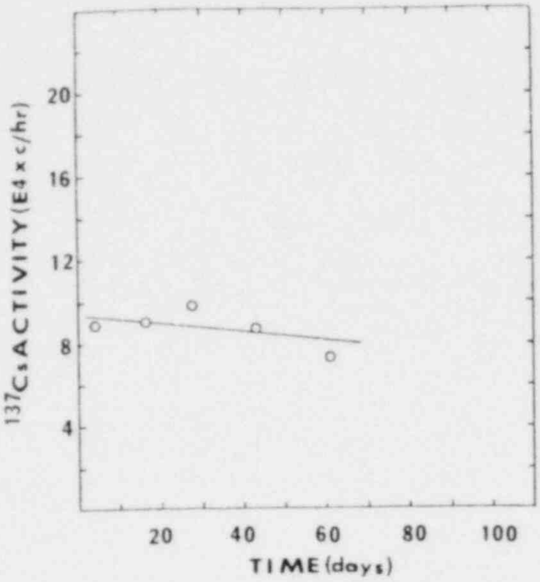


Figure 3.11 ^{137}Cs activity remaining in Barnwell, Trench 6D1 oxic water vs tumbling period with Barnwell sediment (Sample 17-23). ^{137}Cs $t_{1/2}$ = 30.0 years.

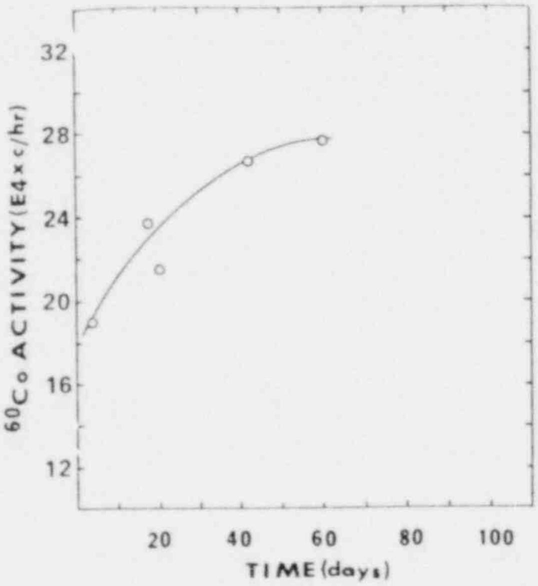


Figure 3.12 ^{60}Co activity remaining in Barnwell, Trench 6D1 oxic water vs tumbling period with Barnwell sediment (Sample 17-23). ^{60}Co $t_{1/2}$ = 5.26 years.

MIBK - Methyl iso-butyl ketone.

Blank - deionized water

Reaction Containers

Polystyrene test tubes, 16 x 125 mm

Tracer Solutions

Mixed tracer solution - a carrier-free solution containing approximately one mCi/mL of commercially obtained ^{85}Sr, $^{134,137}Cs$, and ^{60}Co in 0.5 M HCl was used to spike the well water. A 0.02 mL aliquot of tracer solution was used per 100 mL of well water.

^{241}Am tracer solution - a carrier-free solution containing approximately one mCi/mL of commercially obtained ^{241}Am in 8 M HNO_3 was used to spike the well water. A 0.02 mL aliquot of tracer solution was used per 100 mL of well water.

3.3.2.3 Experimental Procedures

The mixed tracer and ^{241}Am tracer solutions (0.02 mL each) were added to 120-mL glass septum bottles and evaporated to dryness by heating with an infrared lamp. Concentrated hydrochloric acid (0.1 mL) was then added to convert the nitrate salts to chlorides. Care was taken to wet the inner surfaces before the acid solution was evaporated again.

The well water was filtered through a 0.45 μm membrane filter and 100 mL added to the radionuclide tracers in the septum bottles. Stock organic solution was added to the spiked water, in volumes sufficient to produce separate solutions containing approximately 2, 10, and 100 mg/L of organic substance in the spiked well water.

Approximately 0.75 g of solid material and 15 mL of spiked well water were put into polystyrene test tubes. Duplicate samples were prepared, along with a test tube containing only the spiked well water which was used to determine the initial activity of the radionuclides. The tubes were sealed and vibrated in an ultrasonic bath for 30 minutes to disaggregate the solids.

The tubes were then tumbled for 250 hours to equilibrate the solutions with the solids. After tumbling, the test tubes were centrifuged (five minutes at 2000 rpm) to separate the solid and liquid phases, and the solutions filtered (0.45 μm membrane filter) to remove suspended clay size particles. A 10-mL aliquot was pipetted into a 20-mL polyethylene bottle containing 1.0 mL of 8 M HNO_3, and the radionuclides were determined by gamma-ray spectroscopy using a Ge(Li) detector.

3.3.3 Results and Discussion

Results indicate that organic complexing agents exert different effects for specific radionuclides (Table 3.6). All the organics decreased the

Table 3.6

Effect of Organic Substances on Radionuclide Sorption Coefficients
(Water and Shale Collected at the Maxey Flats, Kentucky, Disposal Site)

Isotope	Conc. (mg/L)	K_d(mL/g)[a] Oxalic Acid	TBP[b]	THF	MIBK	EDTA
^{241}Am	0	1.2 ± 1.5 E6	1.2 ± 1.5 E6	1.2 ± 1.5 E6	1.2 ± 1.5 E6	1.2 ± 1.5 E6
	2	1.6 E5	----	----	8.0 ± 3.0 E4	3.0 ± 4.0 E5
	10	2.9 ± 1.5 E5	----	1.9 ± 1.0 E5	----	3.0 ± 2.0 E4
	100	----	8.3 E4	----	1.6 E5	3.0 ± 3.0 E3
^{85}Sr	0	3.9 ± 0.2 E0	3.9 ± 0.2 E0	3.9 ± 0.2 E0	3.9 ± 0.2 E0	3.9 ± 0.2 E0
	2	2.2 ± 0.1 E0	----	----	3.1 ± 0.3 E0	5.2 ± 0.0 E0
	10	1.2 E0	----	1.6 ± 1.0 E0	4.4 ± 0.4 E0	2.4 ± 1.3 E0
	100	4.1 ± 0.2 E0	2.1 ± 0.1 E0	3.2 ± 1.4 E0	2.4 ± 0.3 E0	1.7 E0
^{134}Cs	0	5.2 ± 0.3 E3	5.2 ± 0.3 E3	5.2 ± 0.3 E3	5.2 ± 0.3 E3	5.2 ± 0.3 E3
	2	4.8 ± 0.7 E3	----	----	5.2 ± 0.7 E3	5.5 ± 0.9 E3
	10	4.5 ± 0.1 E3	----	5.1 ± 0.4 E3	----	5.1 ± 0.6 E3
	100	4.9 ± 0.1 E3	4.9 ± 0.2 E3	5.3 ± 0.6 E3	5.8 ± 0.5 E3	4.7 ± 1.4 E3
^{137}Cs	0	5.3 ± 0.2 E3	5.3 ± 0.2 E3	5.3 ± 0.2 E3	5.3 ± 0.2 E3	5.3 ± 0.2 E3
	2	4.4 ± 0.3 E3	----	----	5.1 ± 0.1 E3	5.4 ± 0.2 E3
	10	4.3 ± 0.1 E3	----	5.0 ± 0.2 E3	----	4.6 ± 0.3 E3
	100	5.3 ± 0.1 E3	5.0 ± 0.1 E3	5.3 ± 0.1 E3	4.6 ± 0.3 E3	4.7 ± 0.1 E3
^{60}Co	0	4.1 ± 0.7 E2	4.1 ± 0.7 E2	4.1 ± 0.7 E2	4.1 ± 0.7 E2	4.1 ± 0.7 E2
	2	4.7 E2	----	----	3.4 ± 0.1 E2	1.9 ± 0.1 E2
	10	5.7 ± 0.4 E2	----	4.2 ± 0.2 E2	----	2.2 ± 0.2 E1
	100	3.1 ± 0.1 E2	5.0 ± 2.0 E2	4.3 ± 0.4 E2	4.8 ± 0.1 E2	1.5 ± 0.9 E0

Water: Well UB1-A collected at the Maxey Flats, Kentucky, disposal site, May 1978.
Shale: Nancy Shale, Maxey Flats, Kentucky, disposal site, trench 46 at 20 foot depth.
TBP: Tributyl phosphate.
THF: Tetrahydrofuran.
MIBK: Methyl-isobutyl ketone.
EDTA: Ethylenediaminetetraacetic acid tetrasodium salt dihydrate.
Reaction containers: Polystyrene test tubes.
Solution/soil ratio: 20 mL/g.
Equilibration time : 250 hours.

[a] K_d is reported as an average ± one standard deviation of observed results on a 10-mL aliquot of the liquid phase K_d ± s.d. = $\bar{a} \times 10^b \pm c \times 10^b = a \pm c$ Eb.

[b] A saturated solution.

^{241}Am sorption. EDTA produced the most drastic change. These results are not surprising since laboratory studies have shown that complexing agents increase americium mobility in soils.

Strontium and cobalt showed little decrease in K_d, except in the EDTA system. A decrease of an order to magnitude was observed for ^{60}Co in the EDTA system. Migration of cobalt away from waste disposal pits at Oak Ridge(11) has been attributed to increased mobility due to EDTA complexing.

Complexing by EDTA appears to be a potentially important mechanism for increased mobility of some radionuclides in the systems investigated. In the disposal trenches, EDTA is likely to be present because it is frequently used in commercially prepared decontaminating solutions.

Cesium sorption appears unaffected by the added organics. Alkali metals show relatively little affinity toward forming complexes,(13-16) and the cesium results are consistent with this pattern.

Clay minerals, particularly the expandable 2:1 layer silicates, exhibit the ability to adsorb organic molecules.(17) A preliminary study was performed to determine the effect of EDTA on retention of radionuclides by various commonly encountered soil forming minerals. Samples of the major classes of clay minerals were used along with limonite, a common iron bearing soil component. Distribution coefficients were measured with and without the addition of EDTA to the well water-mineral system. Results of this study are presented in Table 3.7. When the organic complexing agent, EDTA, was added to the trench water, the observed K_d generally decreased for all the minerals, with the notable exception of the montmorillonite (nontronite) clay. An increase in K_d was actually observed for americium in the montmorillonite system. Adsorption of organic molecules (particularly polar molecules) by montmorillonite type clays is well known.(17) The practical application of these results is that montmorillonite clays in the soil around a disposal trench would tend to counteract the increased migration potential of organo-radionuclide complexes. Montmorillonite type clays could also be used as disposal trench linings to enhance the retention capacity of the geologic media. Additional studies of this type would be necessary to determine which members of the montmorillonite family of clay minerals are most effective in this regard. These results can be used in formulating siting criteria, based on the mineralogy of the geological media at a potential burial site, and improving burial procedures, such as the use of trench lining materials. Both areas are of direct concern in NRC licensing functions.

Table 3.7

Effect of EDTA on Radionuclide Sorption Coefficients
(Water Collected at the Maxey Flats, Kentucky, Disposal Site, and Soil Forming Minerals)

Isotope	EDTA (mg/L)	K_d(mL/g)[a]					
		Shale	Montmorillonite (Nontronite)	Kaolinite	Illite	Limonite	Vermiculite
^{241}Am	0	2.2 E6	5.6 ± 0.4 E1	1 E 7	8.3 ± 3.8 E 4	1 E 7	6.0 ± 0.3 E2
	100	3.3 ± 3.4 E3	8.4 ± 0.1 E1	7.0 ± 0.4 E 0	4.4 ± 0.6 E 2	1.2 ± 0.7 E 3	9.1 ± 0.9 E1
^{85}Sr	0	3.9 ± 0.2 E0	1.8 ± 0.2 E1	1.3 E 0	3.9 ± 0.4 E 0	1.1 ± 0.1 E 1	9.0 ± 2.0 E0
	100	1.7 E0	1.9 ± 0.1 E1	4.0 E-1	3.0 ± 2.0 E 0	8.1 ± 0.2 E 0	2.6 ± 0.8 E0
^{134}Cs	0	5.2 ± 0.3 E3	1.7 ± 0.2 E2	1.1 ± 0.1 E 1	4.6 ± 0.7 E 3	1.3 ± 0.1 E 3	1.1 ± 0.1 E3
	100	4.7 ± 1.4 E3	1.4 ± 0.1 E2	1.0 ± 0.1 E 1	4.4 ± 1.3 E 3	1.2 ± 0.1 E 3	1.0 ± 0.1 E3
^{137}Cs	0	5.3 ± 0.2 E3	1.6 ± 0.2 E2	1.1 ± 0.1 E 1	4.6 ± 0.3 E 3	1.3 ± 0.1 E 3	1.1 ± 0.1 E3
	100	4.7 ± 1.4 E3	1.4 ± 0.1 E2	1.1 ± 0.1 E 1	4.9 ± 0.2 E 3	1.2 ± 0.1 E 3	9.8 ± 0.3 E2
^{60}Co	0	4.1 ± 0.7 E2	9.7 ± 0.5 E0	2.0 ± 0.1 E 1	6.8 ± 1.9 E 2	2.8 ± 0.6 E 2	3.2 ± 0.1 E2
	100	1.5 ± 0.9 E0	1.1 ± 0.1 E1	2 E-1	5.0 ± 7.0 E-1	2.0 ± 2.0 E-1	1 E0

Water: Well UB1-A collected at the Maxey Flats, Kentucky, disposal site, May 1978.
Shale: Nancy Shale, Maxey Flats, Kentucky, disposal site, trench 46, at 20 foot depth.
Equilibration time: 250 hours.
Solution/Soil ratio: 20 mL/g.
Reaction container: Polystyrene test tube.
[a] K_d is reported as an average ± one standard deviation of observed results on a 10-mL aliquot of the liquid phase.
$K_d \pm \text{s.d.} = a \times 10^b \pm c \times 10^b = a \pm c\ \text{E}b$.

3.4 Flow-Through Column Sorption Experiments

3.4.1 Introduction

Laboratory determinations of sorption coefficients use either a dynamic or a static experimental design. The "batch" test is the most commonly used static test, involving solid and liquid phase interactions in a closed system. The K_d determinations reported in this project to date have been of this type. Flow-through columns are the most commonly used dynamic test. Flow-through column tests are being undertaken to compare results from batch tests with those obtained from column tests using comparable materials and experimental conditions. These results will be compared with results from analyses of trench core material recovered from the disposal sites. Future batch and column tests will be performed so that the results can be closely compared for the purpose of formulating a detailed testing procedure for testing the sorption capacity of potential disposal site geomedia.

3.4.2 Materials

Sediments from the Barnwell, South Carolina, disposal facility were selected for the column experiments for several reasons: (1) the relatively high permeability of the silty-sands allows manageable experimental flow rates and breakthrough times, (2) trench cores are available for comparison with laboratory experiments and, (3) trench waters are available for use in batch and column experiments. "Undisturbed" core material for use in the experiments was obtained from J. Cahill of the U.S. Geological Survey. The sediments were characterized in terms of sedimentary parameters thought to influence sorptive behavior using techniques described previously.(1) The appropriate data are listed in Table 3.3. The sediments are silty-sand and sand composed primarily of quartz with minor amounts of mica and feldspars. The fine fraction is composed of kaolinite with minor amounts of hematite and goethitic materials. Sandy sediments were selected for the experiments because, (1) the trench cores are composed of these materials and, (2) experiments can be performed without a great deal of difficulty. A more detailed description of the materials and the column apparatus has been given previously.(18)

3.4.3 Flow-Through Column Apparatus

The "undisturbed" core material was trimmed to uniform cylindrical columns (approximately 4 x 7.5 cm) for the experiments. A duplicate column was made from repacked powdered material for comparison with the intact core. The apparatus for the column is shown schematically in Figure 3.13.

Components of the design are shown in Figure 3.13 and function as follows: The sediment column (G) is saturated with water from the main reservoir (A) by use of the bypass line (I). After the column is saturated, the water is redirected through the hydraulic head resevoir (D). This device maintains a constant pressure head by means of a float (E)-microswitch (C) combination, which opens a solenoid valve (B) allowing water to flow from the main reservoir into the head resevoir. As water drains through the column (G), a

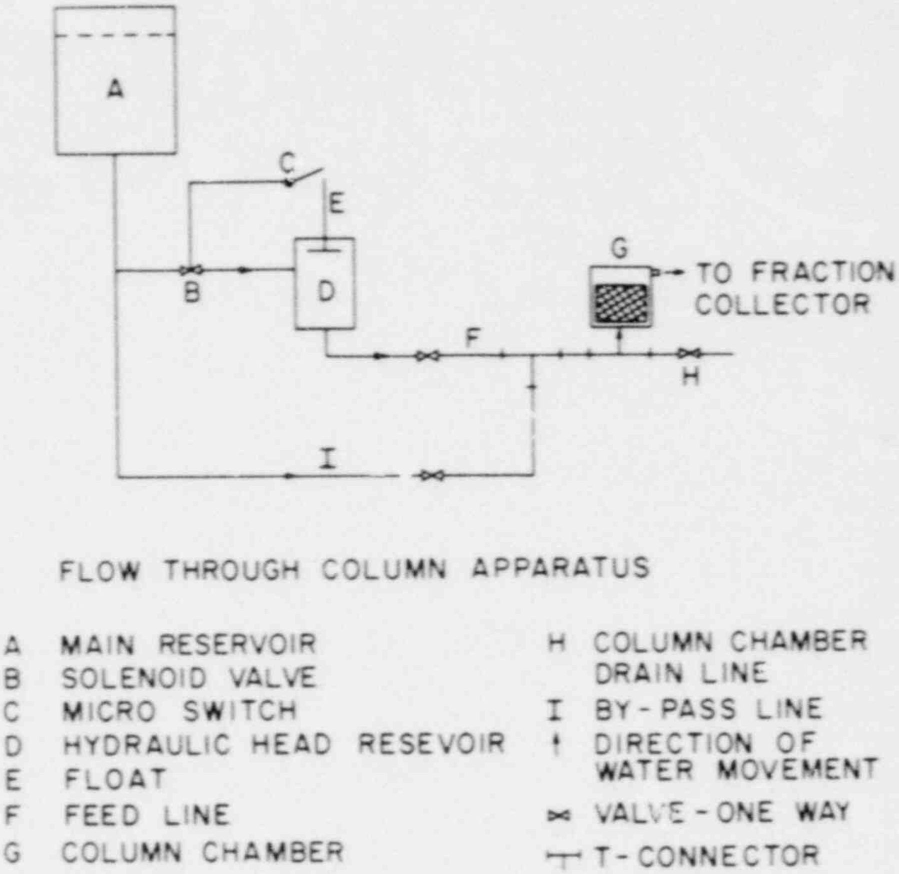


Figure 3.13 Schematic diagram of flow-through column apparatus.

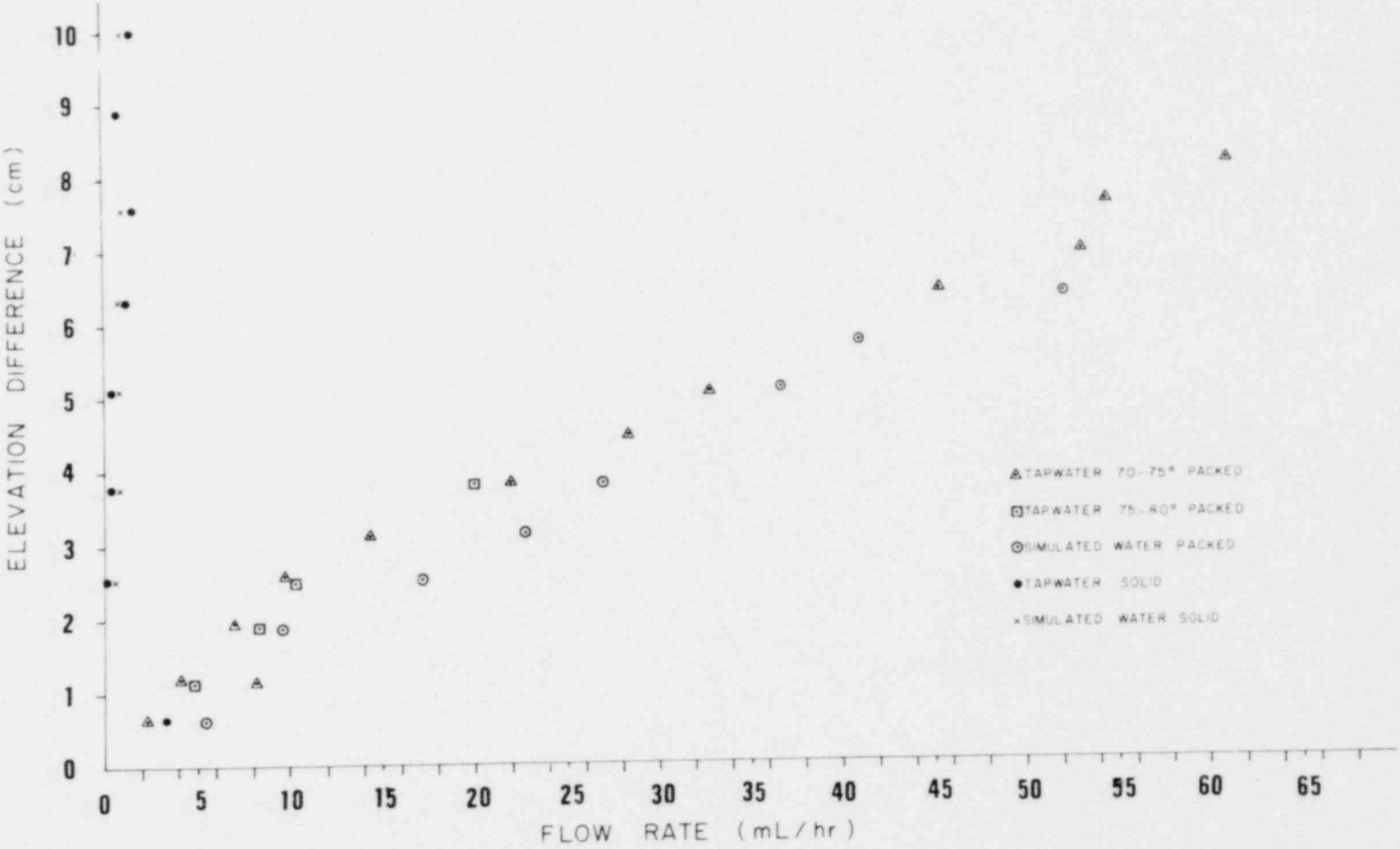


Figure 3.15 Flow rates for intact and repacked sediment columns. Temperatures are in degrees Fahrenheit.

4. TRENCH CORE ANALYSES

(J. Clinton, B. Nine, J. Smith, R. Pietrzak, K. Czyscinski, S. Garber, and A. Weiss)

4.1 Introduction

An integral part of the present program is the analysis of cores recovered from some of the commerical disposal facilities. Analyses of these cores in terms of their radionuclide content serves several purposes: (1) to supply data for site-specific modeling studies, (2) determine mineral-radionuclide associations and, (3) compare results of laboratory K_d studies against the field situation. The general analytical plan has been described previously.(1) A flow chart of the core analysis scheme is shown in Figure 4.1.

Tritium analysis is the first step in the scheme after the core material is sectioned. This report presents results of tritium distillations for cores taken from a pump-out lagoon at the West Valley, New York, disposal facility, and cores taken from beneath the disposal trenches at the Barnwell, South Carolina, disposal site. Preliminary results for semi-quantitative analyses of ^{60}Co as a function of depth in one of the Barnwell trench cores are also included here.

4.2 Tritium Content of Water in Soil Cores Collected at the West Valley, New York, and Barnwell, South Carolina, Disposal Sites

Detailed description of the apparatus, core material, and procedures used are given elsewhere.(18) Only a relatively brief discussion will be repeated here.

4.2.1 West Valley, New York - Lagoon Cores

In 1975, a holding lagoon was excavated at the West Valley, New York, disposal site to receive water pumped out of the burial trenches. The lagoon is located 40 feet west of trench 14, has sloping walls, and is approximately 40 feet wide, 100 feet long, and 10 feet deep (Figure 4.2). The lagoon has been used to hold trench water from at least three previous pumpouts-fall of 1975, summer and fall of 1976, and fall of 1977. The lagoon has not been used since this time. The trench water in the lagoon was periodically stirred by means of an electric motor.

Two core samples were collected from the lagoon (by D. Prudic, U.S. Geological Survey) in December 1978. The samples were obtained from the center of the lagoon, approximately one foot apart. The sampling procedure was as follows: an aluminum tube covered with a plastic bag was driven into the lagoon floor thus keeping water from entering the inside of the tube. A two inch thin-walled steel tube was driven about 18 inches below the lagoon floor. After retrieving the sample tube, the outside was cleaned and the ends capped for shipping. Two cores were collected and brought to BNL where they were subdivided in the laboratory by cutting through the steel tubing with a hacksaw. Using a sharpened brass tube, a "clean" cylinder of material was

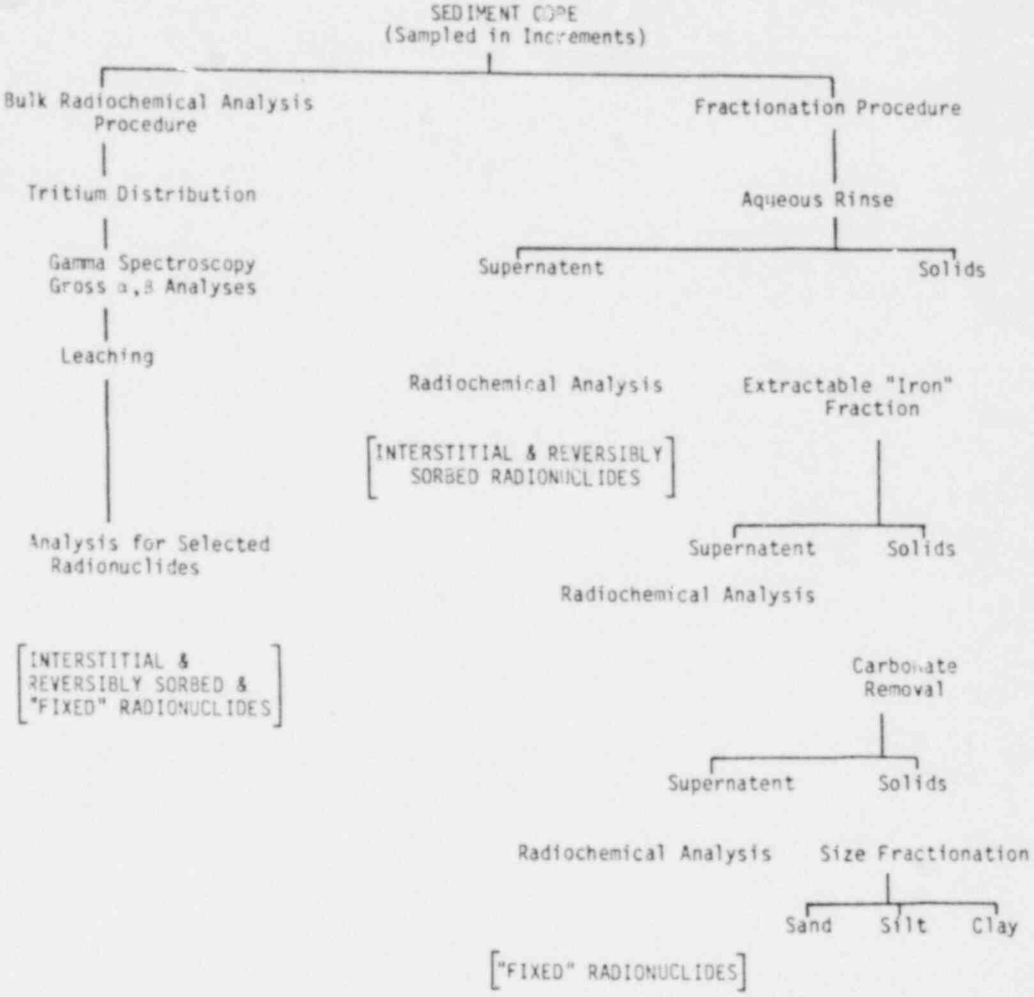


Figure 4.1 Flow chart outline for core analysis.

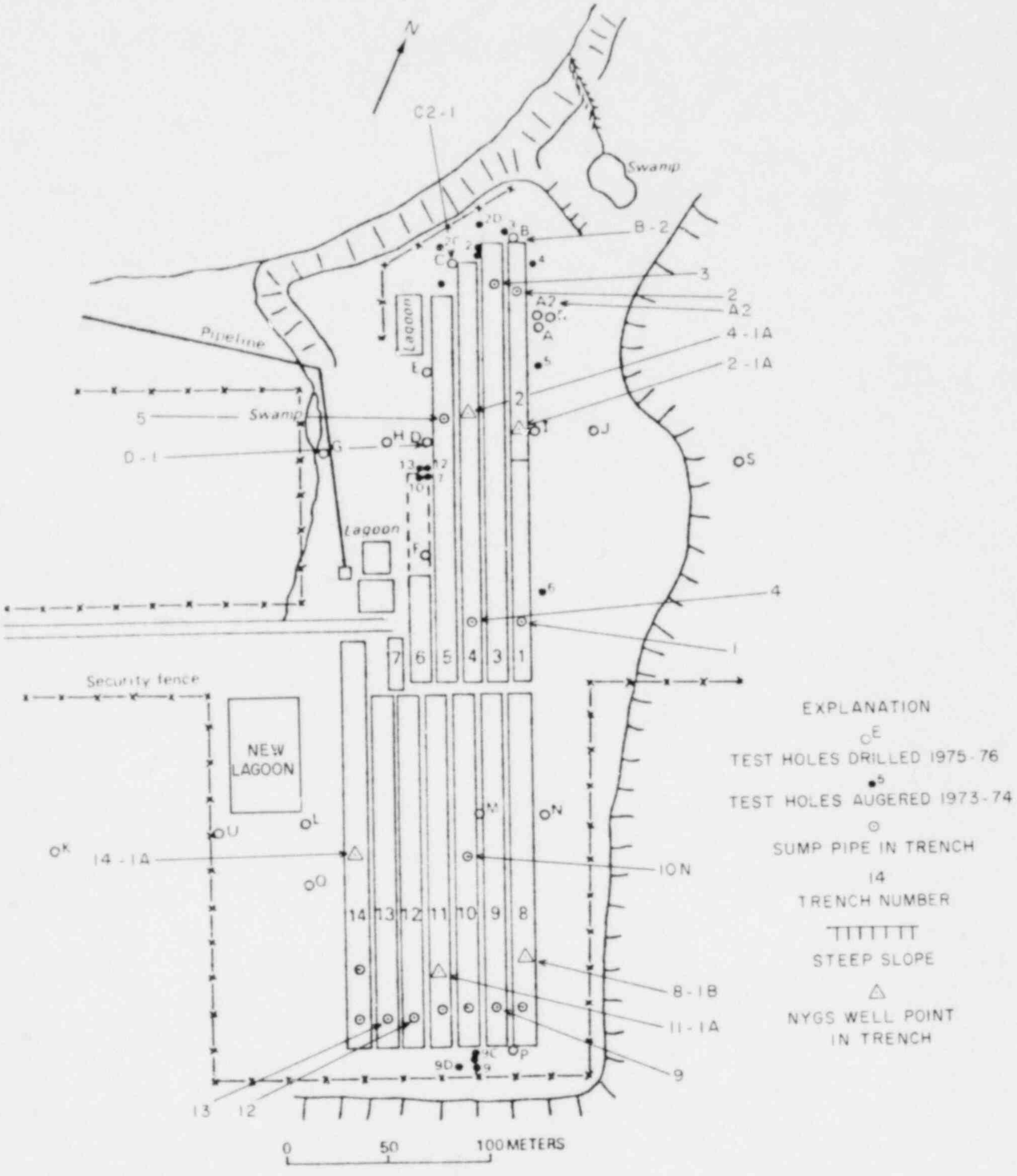


Figure 4.2 Locator map of the West Valley, NY, disposal facility showing the location of the pump-out lagoon sampled.

bored out of the center of each core section. The remaining sediment (the annular portion) was kept in the lengths of metal tubing which were in turn stored in sealed glass jars.

4.2.2 Barnwell, South Carolina - Trench Cores:

Four cores were collected by J. Cahill of the U.S. Geological Survey in 1979. The cores were taken from beneath disposal trenches by drilling through the top of the selected trenches. The locations where cores were taken are shown in Figure 4.3.

The material was sectioned and alternate lengths of the cored sediment were sent to BNL for analysis. These lengths were packed in PVC tubing, with paper packing at each end to prevent moisture loss and sealed with duct tape at each end. Prior to futher sectioning for analysis, the core sections were stored in a refrigerator as a further precaution against moisture loss.

4.2.3 Equipment and Procedures

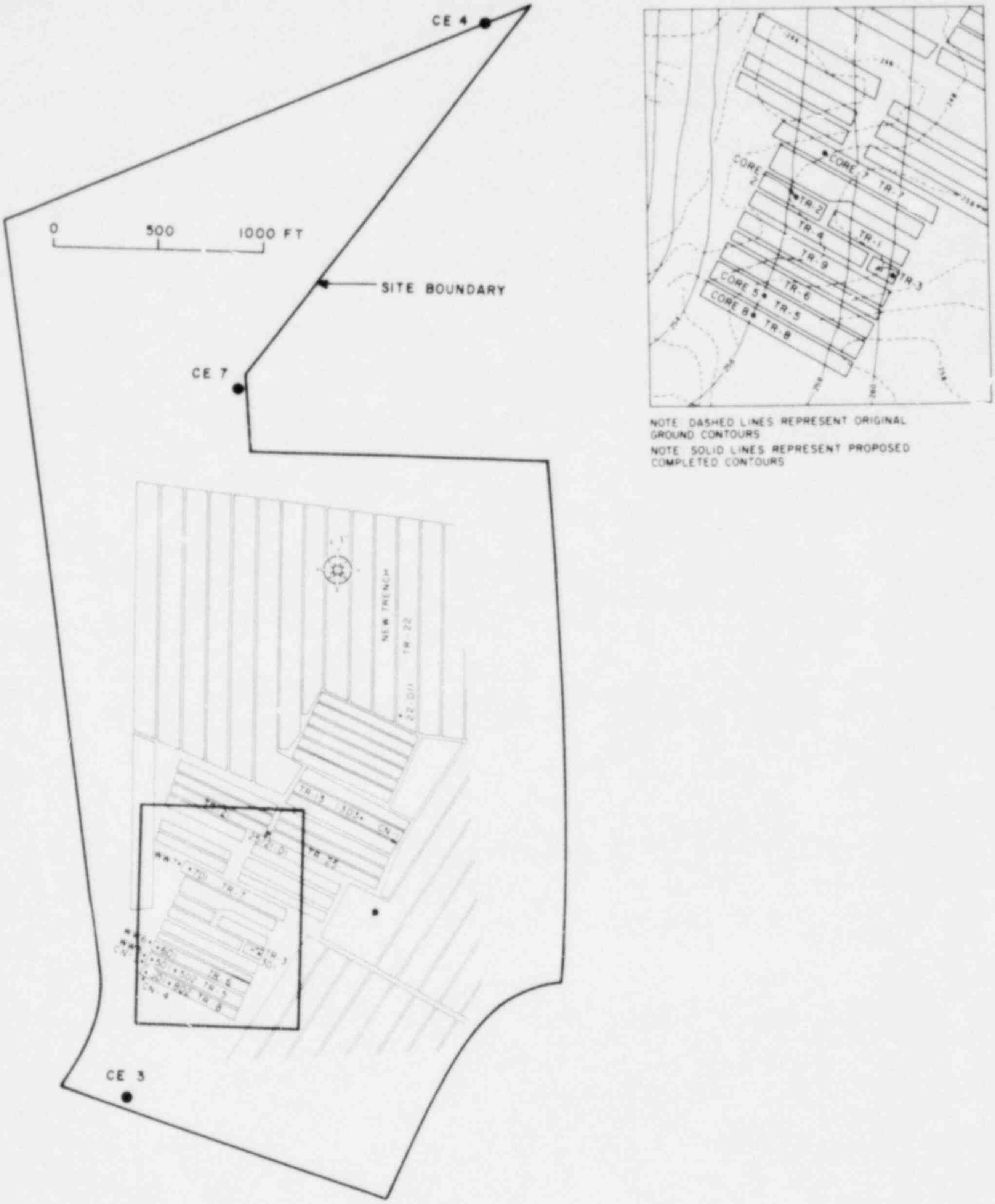
A vacuum distillation apparatus was constructed from glass pipe and is shown in Figure 4.4.

The soil core sections were subdivided into small cylinders approximately 2.5 cm in diameter by 5 cm in length. The exterior of the core was removed to minimize any possible cross contamination that may have occurred during the sampling operation. The cylinders were kept in preweighed glass weighing bottles equipped with a ground glass lid. Before distillation, the lid was removed and the bottle containing the core section placed in the glassware assembly.

Water was distilled from the core samples by vacuum distillation and collected in a trap cooled with liquid nitrogen. The cores were heated (two hours) in an oven at 180°C to completely dry the soil core sections. An aliquot of the distillate was pipetted into a glass liquid scintillation vial containing 10 mL of scintillation cocktail and shaken to form a solution.

Deionized water was distilled to prepare blanks. Tritium calibration standards were prepared by addition of small volumes (0.02 mL) of tritiated water to a blank.

The standards and samples were cooled and dark-adapted for at least one hour prior to counting (50 minutes) in a liquid scintillation counter. To calculate the tritium activity, the counts in a tritium window (which excludes higher energy beta particles) were corrected for background counts, counting time, counting efficiency, and sample volume.



NOTE: DASHED LINES REPRESENT ORIGINAL GROUND CONTOURS

NOTE: SOLID LINES REPRESENT PROPOSED COMPLETED CONTOURS

Figure 4.3 Locator map of the Barnwell, South Carolina, disposal facility.

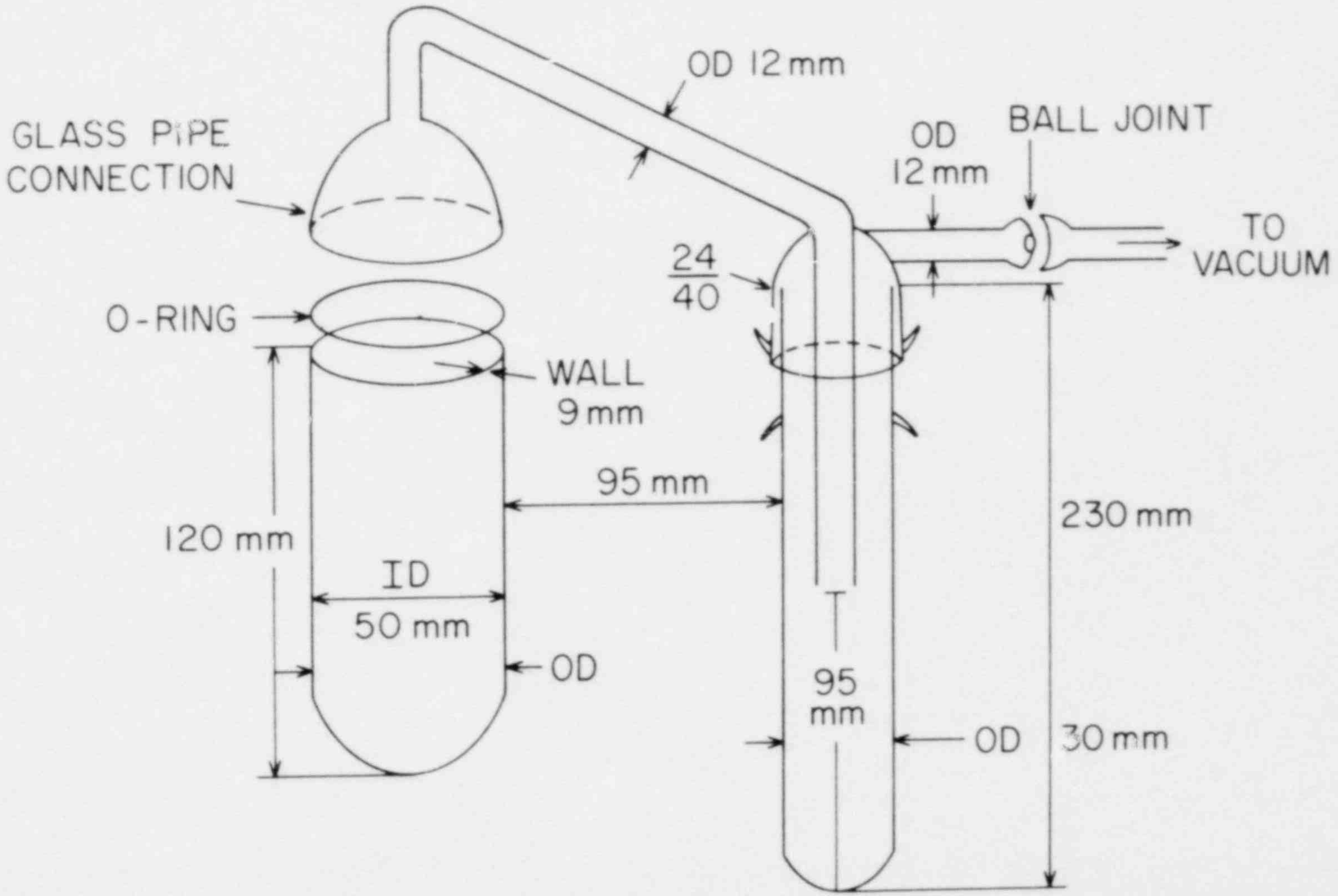


Figure 4.4 Glassware assembly for tritium distillation.

4.2.4 Results and Discussion

West Valley Lagoon Cores

The tritium activity vs depth for the the two cores is shown in Figure 4.5. Tritium activity in the cores decreased from the lagoon floor downward into the clay bed. The scatter in the data may reflect some experimental problems that occurred during the distillation process. Linear regression of the data shows poor correlation ($r = 0.3$) with a degree of certainty of greater than 80%. A curved (dashed) line shows a better correspondence with the data; however, this distribution suggests that the tritiated water moves downward from the lagoon floor into the clay bed by a diffusion mechanism. Considering the very low hydraulic conductivities of sediments at West Valley (10^{-7} to 10^{-9} cm/s)(11) the diffusion mechanism appears reasonable.

Barnwell Trench Cores

In Figure 4.6, the data for all four cores are presented. The data points are grouped for each segment of packaged core material. The tritium distributions below the trenches show an immediate drop to the lowest levels at approximately ten meters, followed by an increase in tritium levels at lower depths. This profile may represent either, (1) the intersection of two water flow paths beneath the trenches or, (2) two slugs of water moving downward through the unsaturated sediments. The first explanation appears unlikely in that a change in sediment character would be expected at approximately ten meters for this explanation to be correct. However, the cores are uniform in texture throughout their lengths (coarse sands), and no significant changes in bulk density occur at ten meters depth. No correlation is apparent between tritium levels and either bulk density or moisture content.(4) The second explanation appears more likely. Rainfall in the southeastern United States varies during the year, with the heaviest rainfalls in the earlier months. Consequently, water accumulates in the trenches via groundwater infiltration only when the rainfall is relatively heavy. Because the hydraulic conductivity of these sediments is low (in the order of 10^{-5} cm/s), accumulated water stays in the trenches long enough to develop high tritium contents before percolating through the surrounding sediments. Presumably, the deeper tritium maxima represent trench waters that developed high tritium contents during an earlier period of water accumulation in the trench, and subsequently migrated to this lower depth. Based on a hydraulic conductivity of 10^{-5} cm/s, water will migrate approximately three meters in a one year period under saturated flow conditions and less under unsaturated flow conditions. The distance between the tritium maximum in trench 8 core and the lower maximum in trench 2 core is approximately three meters, a distance roughly equal to one years migration distance, if the two maxima represent yearly high water accumulations. For trench 5 and 7, the distance between high tritium levels are approximately three and two meters respectively. Both distances are within the expected range based on hydraulic conductivity measurements.

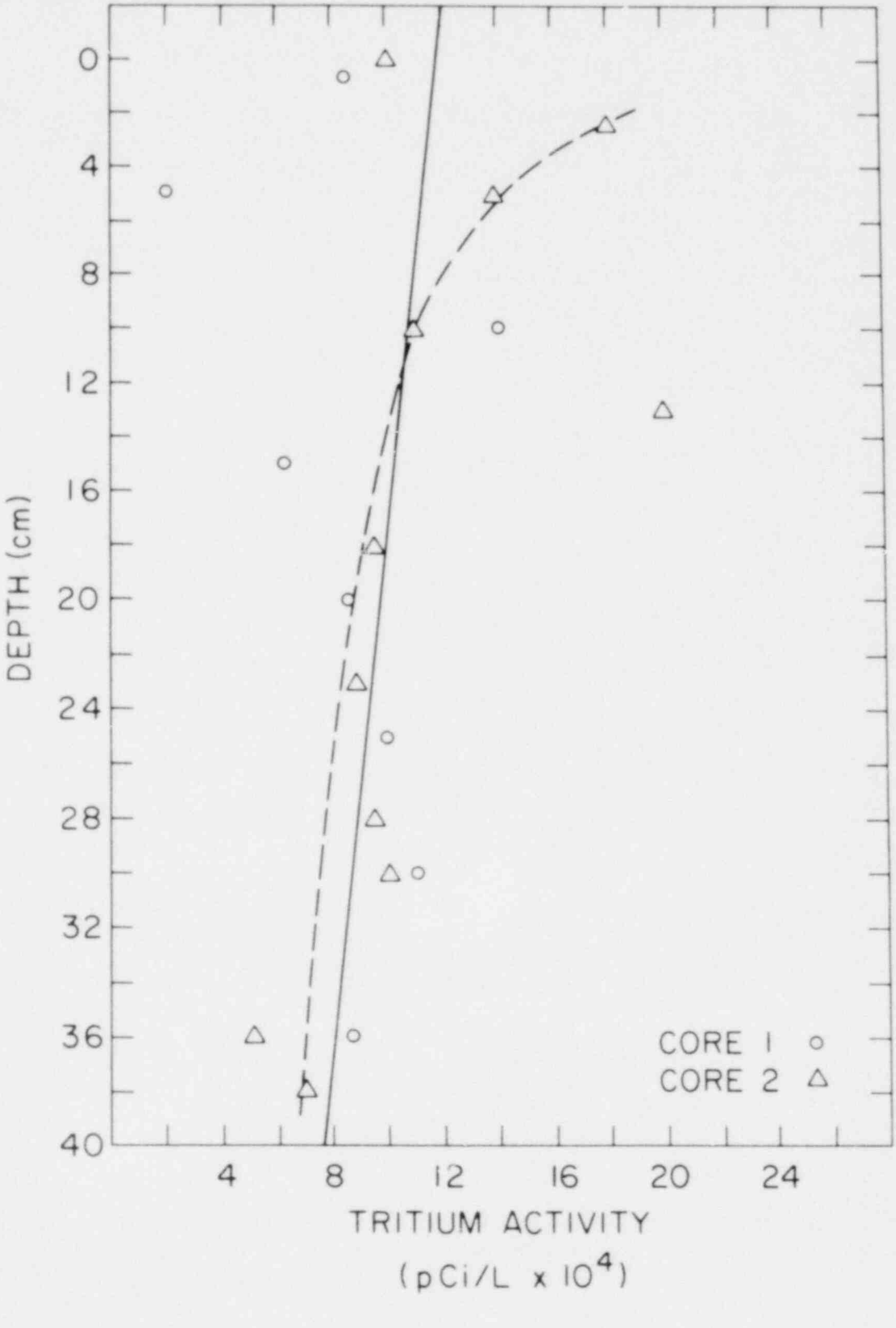


Figure 4.5 Tritium activity vs depth - West Valley lagoon cores.

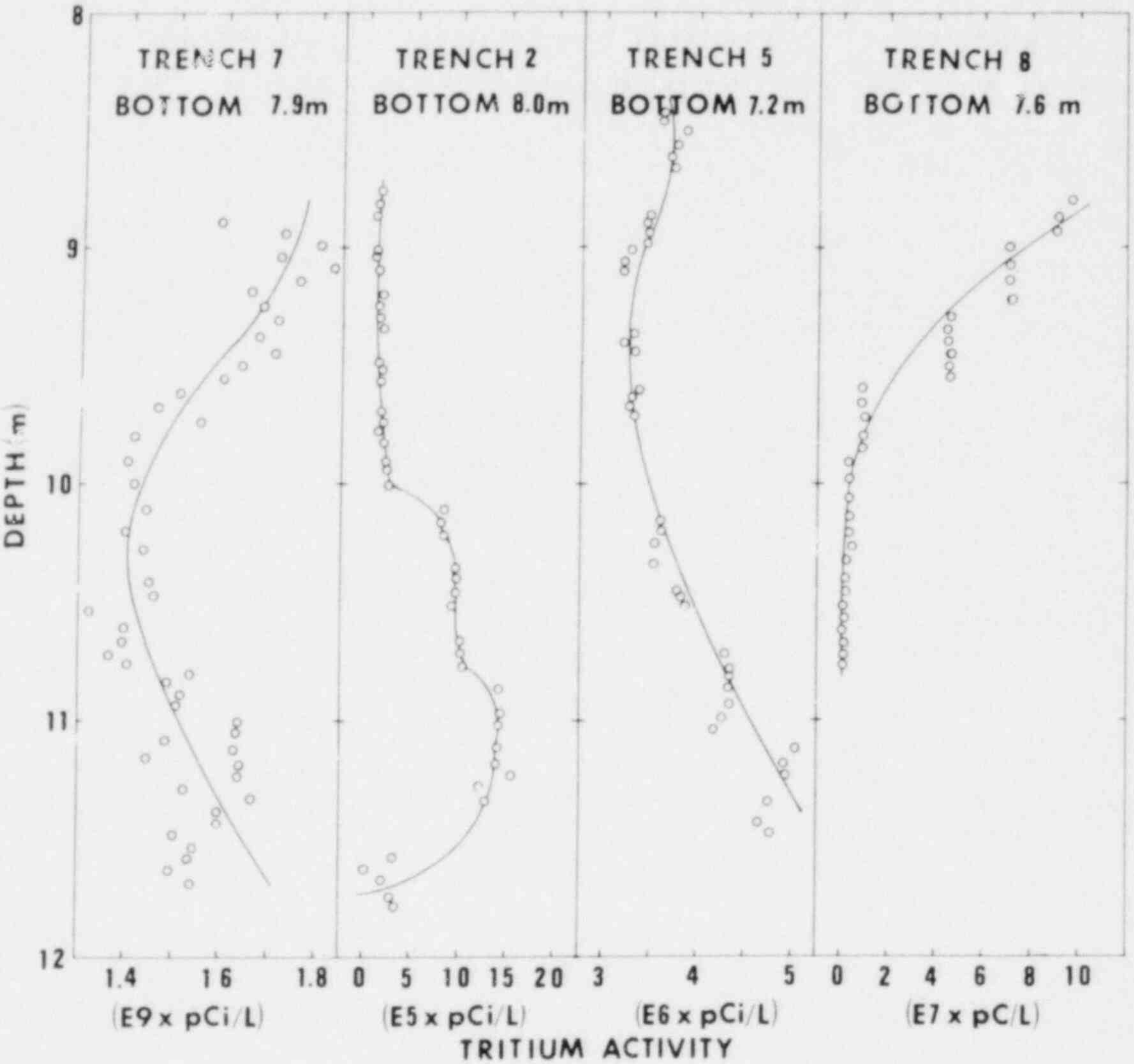


Figure 4.6 Tritium activity vs depth - Barnwell, South Carolina, disposal trench cores.

4.3 Gamma-Ray Spectroscopic Analyses of the Barnwell Trench Cores

Preliminary results of a semi-quantitative analysis of the Barnwell trench 2 core are presented here.

4.3.1 Procedures

Qualitative analyses by gamma-ray spectroscopy (Ge(Li) detector) were performed on the packed core sections as received (section 4.2.2) to obtain estimates of the activity in each section and to identify the major gamma emitters present. These qualitative scans showed ^{60}Co to be the only significant gamma emitter in the core from trench 2 which was the only sample that contained activity levels detectable without additional sample preparation. After the core sections were subdivided into cylindrical plugs and the tritium distillations performed (section 4.2), the cylindrical plugs contained in glass weighing bottles were counted again for a more accurate analysis.

Standards were prepared containing aqueous solutions with varying concentrations of ^{60}Co. The standards were counted in glass bottles of the same size as those containing the cylindrical core material, so that counting geometries were similar. For the analysis to have at least semi-quantitative validity, an assumption is required here in that the gamma ray self-absorption in the aqueous standards must be similar to that in the sediment samples. For the weaker ^{60}Co gamma energy (1.173 MeV), gamma-ray attenuation coefficients for water and silicon are 0.0706 and 0.0635 respectively, for photon energies of 1 MeV.(19) The coefficient for silicon is used because the Barnwell sediments are largely quartz (SiO_2). The error due to variation in matrix composition is equal to the logarithm of the difference in the self-absorption coefficients. For this case, the error in the analyses due to matrix differences is approximately ten percent. A ten percent error due to matrix composition is sufficiently low to regard the analytical results as valid at the semi-quantitative level.

4.3.2 Results

Preliminary results of the ^{60}Co analyses are given in Table 4.1 for dried core sections. Cobalt is detectable all the way down the core, but reach background levels at the bottom of the core.

Gamma-ray energies belonging to the uranium series were also identified in all the samples but were apparently due to the natural background. The remainder of the core is presently being analyzed, and the complete results will be published in the near future. The initial qualitative scans of the packaged core sections indicated that only trench core 2 contained significant activity. More detailed counting will be performed by procedures described above to determine ^{60}Co levels on the remaining three cores.

Table 4.1

Relative Distribution of ^{60}Co Activity in Barnwell, Trench Core #2

Depth (m)	Mean Activity		Relative Activity[a]	
	(pCi/g)	(pCi/cm^3)	by weight	by volume
8.76 - 8.81	491.75	1147.23	1.0000	1.0000
8.81 - 8.86	420.64	966.51	0.8554	0.8425
8.86 - 8.92	410.07	922.48	0.8339	0.8041
9.02 - 9.04	114.58	277.69	0.2330	0.2421
9.04 - 9.09	36.00	84.41	0.0732	0.0736
9.09 - 9.14	17.71	41.38	0.0360	0.0361
9.20 - 9.25	1.791	4.45	0.0036	0.0039
9.25 - 9.30	2.38	5.34	0.0048	0.0046
9.30 - 9.35				
9.45 - 9.49	1.33	3.05	0.0027	0.0027
9.49 - 9.52	1.96	3.93	0.0040	0.0034
9.52 - 9.56				
9.56 - 9.60	3.418	8.782	0.0070	0.0077
9.70 - 9.74				
9.74 - 9.78	4.25	10.52	0.0086	0.0092
9.78 - 9.83	5.63	14.45	0.0114	0.0126
9.83 - 9.91				
9.91 - 9.94				
9.94 - 10.01	2.49	6.80	0.0051	0.0059
10.01 - 10.03	4.53	---	0.0092	---
10.11 - 10.16	11.35	25.61	0.0231	0.0223
10.16 - 10.22	12.03	30.51	0.0245	0.0266
10.22 - 10.29	12.39	28.20	0.0252	0.0246
10.36 - 10.41	4.134	7.786	0.0084	0.0068
10.41 - 10.46	3.260	7.954	0.0066	0.0069
10.46 - 10.52	2.127	3.877	0.0043	0.0034
10.52 - 10.67	0.861	1.437	0.0018	0.0013
10.67 - 10.72				
10.72 - 10.77				
10.77 - 10.82				
10.92 - 10.97				
10.97 - 11.02	0.1070	0.1926	0.0002	0.0002
11.02 - 11.12	0.1539	0.3327	0.0003	0.0003
11.12 - 11.18	0.1389	0.2685	0.0003	0.0002
11.18 - 11.23				
11.23 - 11.28				
11.28 - 11.34	0.0884	0.1196	0.0002	0.0001
11.34 - 11.40				
11.59 - 11.67	0.2589	0.5028	0.0005	0.0004
11.67 - 11.74	0.0677	0.1056	0.0001	0.0001
11.74 - 11.79	N.S.[b]	N.S.	N.S.	N.S.
11.79 - 11.84	N.S.	N.S.	N.S.	N.S.

[a] Activity expressed relative to the activity of the uppermost segment in the core.

[b] N.S. = no significant activity detected

5. ORGANO-RADIONUCLIDE COMPLEXES IN TRENCH WATER
(M. Kinsley, B. Nine, A. Weiss, K. Czyscinski)

5.1 Introduction

Migration of radionuclides through the geomedia can be considerably enhanced if the nuclides are bound with complexing agents. Complexed radionuclides are less apt to be sorbed on the solid phases (see 3.3) and are able to migrate at the same velocity as the groundwater with little effective retention by the soil components. Such enhanced migration has been observed, and attributed to EDTA complexing in the groundwaters.(12) Decontamination agents contain large amounts of complexing agents and these wastes are typically disposed of by shallow land burial. In light of this common practice, a significant portion of the radionuclides put into the commercial burial facilities may be in a complexed form when buried. In the past year, a series of gel-filtration chromatography experiments were performed using trench waters in an effort to detect the existence of organo-radionuclide complexes.

5.2 Methodology

Gel filtration chromatography is a method of separating molecules based on their molecular weights. The chromatographic columns are filled with one of three beadforms; cross-linked gels Sephadex G10, G15, and G25 were used, each of a different porosity. When a sample is put into the column, molecules whose sizes are too large to enter into the gel are "excluded" and remain in the void volume (V_0) between the beads where they are eluted rapidly. The exclusion limit is defined as the molecular weight (size) of the smallest molecule which is incapable of penetrating the pores of the gel matrix. Void volumes are empirically determined by fractionating solutions of Blue Dextran 2000. Molecules small enough to enter the gel matrix are eluted in decreasing order of their molecular size, the smallest molecules being eluted last. The fractionation range and behavior of the gel columns are determined largely by the gel porosity, but also affected by sample volume, bed length, temperature, eluant flow rate and molecular configuration of the material moving through the gels. If experimental variables such as temperature, flow rate, column length, etc., are held constant, eluant volumes collected as a function of time will contain species of different size ranges.

5.3 Procedures

Detailed descriptions of the experimental design, equipment, and calibration procedures are presented elsewhere;(3,18) only a brief description is presented here.

The experimental procedure is straightforward. A small volume of solution, either of known or unknown composition, is put into the column and washed through with a carrier solution (eluant). Fixed volumes of the eluant are collected from the bottom of the columns as a function of time and analyzed for gamma activity and dissolved organic carbon (DOC).

To calibrate the columns, solutions containing known species are passed through and the eluant fractions analyzed for the presence of the known components. Such a calibration is shown in Figure 5.1. Separate samples containing Blue Dextran 2000 (to determine the exclusion limit-V_0), CsCl-(^{137}CsCl labeled inorganic), and an EDTA solution containing ^{60}Co and ^{137}Cs were passed through the column. Detailed gamma spectrometric and DOC analyses on the eluant fractions of the EDTA solution showed that the ^{60}Co gamma-ray activity is associated with high DOC, while the ^{137}Cs activity corresponds to the location where the ^{137}CsCl solution was eluted. This indicates that cobalt formed an EDTA complex while cesium did not.

5.4 Trench Water Fractionations

The trench waters selected for these experiments came from trench 8 at the West Valley disposal facility.(1) Maintaining the anoxic character of these waters during the gel-filtration experiments would have required an extremely complicated experimental design and very difficult sample handling procedures. In order to produce results in a reasonable time frame, the trench waters used were exposed to air and then filtered before they were used in the experiments. Cesium was the only gamma-ray emitter in the air-exposed samples used in the experiments. Results from a fractionation are shown in Figure 5.2, along with the calibration position of V_0 and inorganic CsCl. Gamma-ray spectrometric and DOC analyses of the trench water eluant fractions showed that the gamma activity overlapped both the DOC and inorganic CsCl peaks. This suggests that cesium in the trench water is associated with some type of organic material.

Because the total gamma activity in the trench waters is low, fractionations were also performed with spiked (250% and 3500% increase in ^{137}Cs) trench water samples. Figure 5.3 shows the results of one of these fractionations (for a 250% increase in Cs activity). A distribution similar to that in Figure 5.2 was found. Again, the cesium appears to overlap a portion of the organic component in the trench water. A similar distribution was observed for the more strongly spiked trench water sample.

In another series of fractionations, trench water was spiked with ^{60}Co and ^{137}Cs to determine whether cobalt would associate with the trench water organic components. A longer column (100 cm vs 40 cm) was used to give better resolution of the eluted species. Results are shown in Figure 5.4. Better resolution of the organic fraction was obtained with the longer colu. Once again, the cesium and cobalt are partly associated with a portion of the trench water organic components.

5.5 Discussion

Results of these experiments suggest that cobalt and cesium may be associated with organic components in the trench waters. Based on the position of the EDTA peak in Figure 5.1, it appears that the organic material in the trench water is not EDTA. This is not unreasonable because alkali earth elements such as cesium, show a lesser tendency to form complexes(16) in general, (as well as with EDTA), compared to alkaline earths such as calcium or

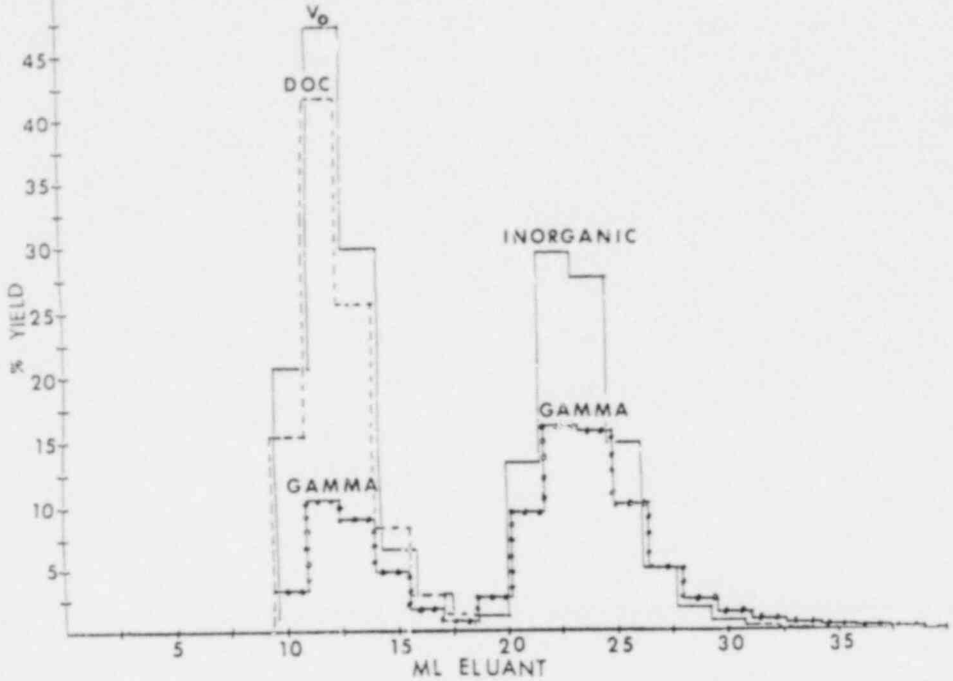


Figure 5.1 Fractionations of Blue Dextran (Vo), ^{137}CsCl (inorganic), and ^{60}Co-^{137}Ca-EDTA (DOC and gamma) using Sephadex G10 gel (40-cm column).

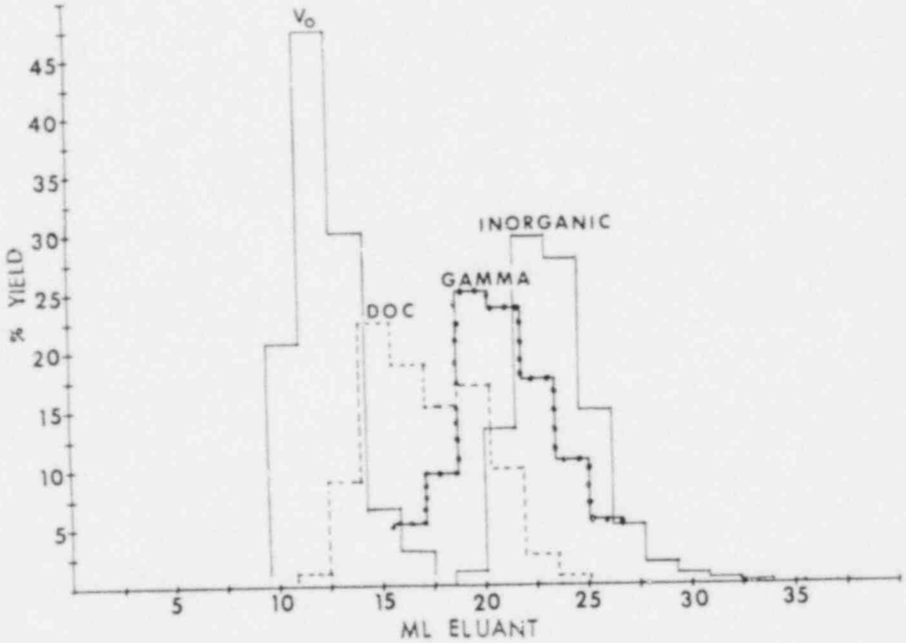


Figure 5.2 Fractionations of Blue Dextran (Vo), ^{137}CsCl (inorganic), and West Valley trench water (DOC and gamma) using Sephadex G10 gel (40-cm column).

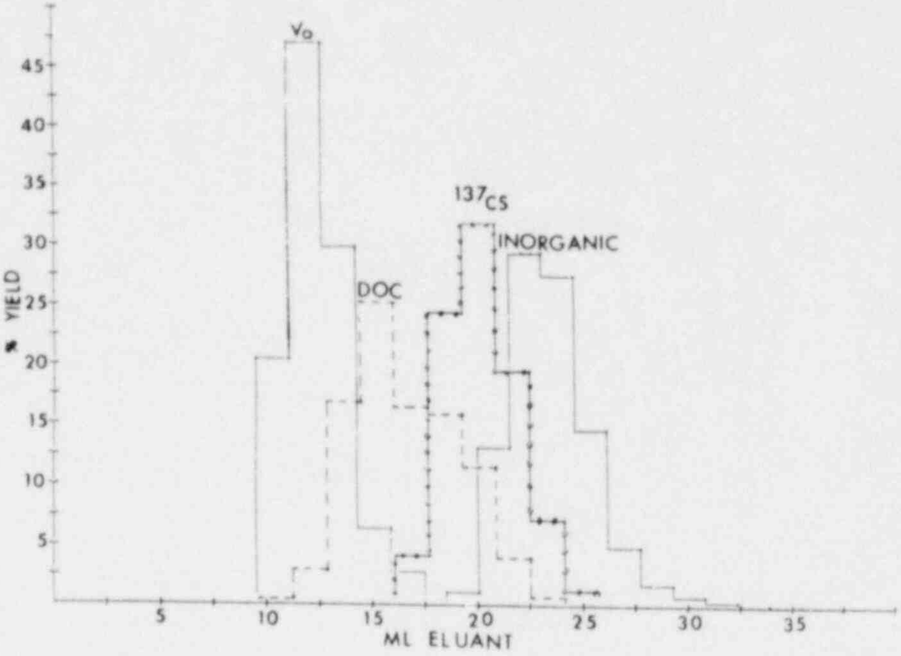


Figure 5.3 Fractionations of Blue Dextran (Vo), ^{137}CsCl (inorganic), and spiked (250% increase in ^{137}Cs) West Valley trench water (DOC and ^{137}Cs) using Sephadex G10 gel (40 cm column).

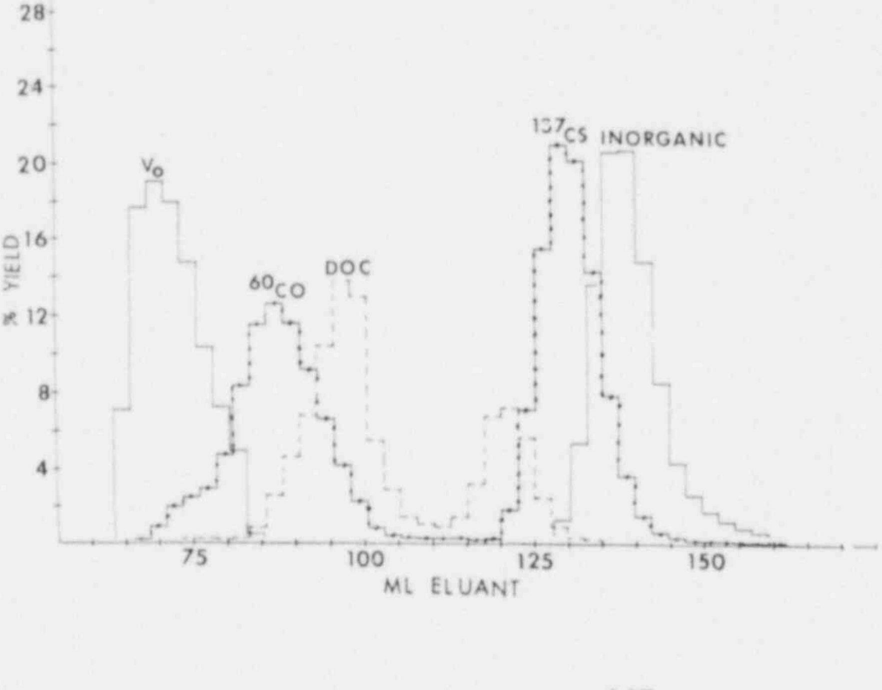


Figure 5.4 Fractionations of Blue Dextran, ^{137}CsCl, and West Valley trench sample, using Sephadex G10 gel-column B (100 cm column).

metals such as iron and cobalt. Based on the gel filtration experiments alone, it is difficult to form more substantial conclusions about the existence of organo-radionuclide complexes in the waters studied for the following reasons.

1. The experiments indicate that some of the cesium and organic material move through the column at the same velocity. The fact that a particular portion of column eluant contains both organic material and gamma activity does not, a priori, establish the existence of an organo-radionuclide complex. For example, the cesium may be associated with small inorganic compounds such as layer silicates or fine colloidal particles. In this event, the cesium-organic association is purely circumstantial. Additional procedures are required to demonstrate the existence of actual complexing.

2. Because a spike was added to the trench waters to obtain adequate counting rates, the possibility exists that the observed results may be due in part to the spike, and not reflect the trench water chemistry. The similarity between Figures 5.2 and 5.3 suggests that the spike has not altered the water chemistry, but this possibility cannot be completely eliminated.

3. In experiments with $^{60}CoCl_2$, all the cobalt in this ionic form was retained on the columns, and required and EDTA solution for removal. This indicates that the columns show a significant component of ion exchange behavior. The columns are designed to separate components based on size alone, but when ion exchange component reactions occur, an unequivical interpretation of the results is not possible.

4. Because the waters used in the experiments were oxidized samples rather than the anoxic chemical regimes present in the trench waters <u>in situ</u>, the results observed may be controlled by the chemical regime of the oxidized water and not representative of the anoxic systems. This possibility cannot be discounted because air exposure does produce drastic changes in the trench water chemistry. The only way to determrine if this is the case would be to repeat the experiments and maintain the anoxic character of the water. As mentioned previously, this would involve a large increase in experimental difficulty. In the light of other complicating factors mentioned above, the additional effort required to repeat these experiments under anaerobic conditions would not be justified by the results to be obtained.

5.6 Future Direction

Continuing gel filtration experiments with other trench waters does not appear to be the most productive course, for the reasons mentioned previously. The low activities in the trench waters makes the use of spiked samples almost unavoidable. In addition, the tenuous radionuclide-organic associations can not be more firmly established without a considerably expanded effort. Two avenues of research appear to be more productive.

One approach involves obtaining concentration measurements of free and bound chelating agents which can be combined with analyses of major and minor cations to produce speciation models using the tabulated complex stability constants.(16) These calculations can indicate the approximate extent of complexing in specific waters, which can then be compared with experimental data from experiments such as those described here.

Another approach is to simulate the anoxic trench water environment in a controlled laboratory experiment in which an organo-radionuclide complex is introduced. The stability of this complex can then be monitored with time. Results of such an experiment would indicate if the radionuclide will remain in a complexed form in this geochemical environment. Such experiments have been performed by workers interested in plant nutrition.(20) Previous experiments on radionuclide-organic complexes have centered on the stability of the complexing agent.(21,22) However, the persistence of the radionuclide in a complexed form is the point of interest, rather than the persistence of the complexing agent. The emphasis in these previous stability studies appears misplaced. Experiments in which the radionuclide-complex stability is measured directly rather than inferred from the stability of the complexing agent would be more appropriate. These types of stability experiments will be performed in the coming year.

6. WORK IN PROGRESS AND FUTURE DIRECTION

6.1 Program Goals and Structure

During the early stages of this investigation, the objective of the project was simply to gather descriptive data concerning disposal trench water compositions. This information was to be used as source term data for input into modeling efforts. Routine sampling and analysis of disposal trench waters appear to have generated sufficient information to characterize the geochemical regimes at the disposal sites studied. At this point, emphasis should be directed towards evaluating the role of water chemistry and sorption processes on the retention and migration of radionuclides in the geochemical environments typified by the anoxic trench waters from Maxey Flats and West Valley, as well as the relatively more oxidized waters at Barnwell. This approach serves two purposes; (1) by understanding the functions of existing sites, appropriate remedial actions can be initiated to modify the geochemical environment to improve radionuclide retention where needed and; (2) when effective retention mechanisms are identified in the existing sites, these geochemical mineral-radionuclide associations can be used as siting criteria for the selection of future disposal sites. Both of these objectives are important to NRC concerns, in terms of regulating the operation of existing sites and licensing new disposal sites. A brief description of the work in progress and to be initiated, in the areas of sorption studies, trench core analysis and trench water chemistry is presented here, along with applications of the information to the goals mentioned above.

6.2 Sorption Experiments

The goal of laboratory sorption experiments is to predict the radionuclide retention ability of the geomedia under a particular set of site-specific conditions. To achieve this, batch and/or column testing procedures are required which are flexible enough to accommodate a range of experimental conditions. Also, the correlation between batch and column tests must be known so that the proper techniques can be selected and the results properly evaluated for a particular field situation.

The experimental work to be performed in the coming year will be closely interrelated with the trench core analyses and water chemistry efforts. Water chemistry will be examined after, as well as before the experiments, since it has been shown to affect the observed sorption. The solid phases will be examined at the conclusion of the experiments to determine mineral-radionculide associations responsible for the observed sorption. Predictions based on laboratory experiments can be critically evaluated only by comparison with the field situation. Most of the effort will focus on the Barnwell site for several reasons; namely, (1) trench cores are available for comparison with laboratory studies, (2) the relatively oxidized geochemical environment presents less experimental difficulties and, (3) manageable flow rates can be achieved in column experiments because the sediments are relatively permeable compared to the West Valley till and Maxey Flats shale.

The sorption experiments planned or in progress for the next year include the following:

(1) Batch experiments using the improved anaerobic procedures will be continued for the anoxic water systems (section 3). At the conclusion of the sorption experiment, the water and solid phases will be analyzed to determine mineral-radionuclide associations responsible for the observed results.

(2) Batch experiments with Barnwell sediments will continue (section 3). These experiments will focus on (1) characterizing the sorption properties of the more oxidized geochemical environment and (2) comparison of batch results with column testing.

(3) A continuous "loop" experiment(23) using Barnwell sediments has been initiated for the purpose of evaluating the results obtained with those of batch tests (#2 above) and single-pass column experiments (#4 below).

(4) Single pass column experiments (see section 3) will be continued using trench water and a mixture of radionuclides similar to those used in batch experiments. Results of these experiments will be compared to the results of 2 and 3 above. The solid phase will be analyzed to determine the mineral-radionuclide associations responsible for the observed sorption. Autoradiography will be employed for these studies.

These laboratory efforts will focus on one objective - to determine the relationship between batch and column testing. The aim here is not to develop a series of rigid testing procedures, but guidelines for testing by batch and/or column techniques. The need for general guidelines is a direct NRC concern because methods of testing the sorption capacity of potential disposal site geomedia will undoubtedly be part of the liscensing process. This program presents a unique opportunity to achieve these goals for two reasons; (1) site-specific data and materials are available, as well as a developed expertise for handling these materials and (2) the results of trench core analyses can be compared with the laboratory results. The critical test of laboratory work is the comparison against the field situation.

6.3 Trench Core Analyses

The cores collected from beneath several of the disposal trenches at Barnwell provide key input to the three part study. Relationships developed as a result of laboratory work can be compared to the field situation based on a careful analysis of the trench cores.

A schematic analytical plan is shown in Figure 4.1, as well as in relation to the mineral content (right side of Figure 4.1). The mineral fractionation analyses are particularly important for comparison with the mineral-radionuclide associations observed in laboratory sorption experiments. Work has been initiated in this area and some results reported here as follows:

(1) Tritium analyses are completed and analyses of gamma emitters are in progress for the bulk sediment analysis scheme (left side of Figure 4.1).

(2) The mineral fractionation procedure is being tested on spiked samples of reference soil forming minerals before the scheme is applied to the trench cores.

Results of these experiments will be useful in terms of site selection criteria, evaluating the existing disposal site and testing the results and conclusions of laboratory experiments. These applications are as follows:

(1) Mineral-radionuclide associations found will make useful site selection criteria for potential disposal sites. For example, if analyses of the Barnwell cores show that iron-bearing minerals such as goethite or hematite are associated with specific radionuclides, the presence of these minerals in the geomedia of a potential burial site would be beneficial in terms of its retention ability. Such minerals could be added to burial trenches during filling to improve the retention capacity.

(2) Depth distribution of radionuclides will supply needed information to evaluate the efficiency of the burial trenches at Barnwell.

Mineral-radionuclide associations observed in the field cores can be compared against those observed in laboratory experiments. Retention predictions based on laboratory results can also be compared against what is observed in the cores. The critical test of laboratory work is comparison against the field situation.

6.4 Water Chemistry

The coming year's effort in water chemistry will be directed into three areas; (1) examining the stability of organo-radionuclide complexes as a function of the trench water redox (Eh) environment, (2) supplying input to sorption experiments and, (3) evaluating the role of iron sulfide and iron oxyhydroxide precipitates in contributing to the total retention capacity of chemically reducing trench water systems.

The first of these areas has been discussed in section 5 and will not be elaborated upon further. Previous sorption experiments have shown that differences in water chemistry appear to control the observed sorption. Future sorption experiments will monitor selected chemical components before and after the experiments. These measurements are needed to draw valid conclusions from the results of different testing techniques and to determine whether differing results are due to variations in experimental techniques or to changes in the aqueous phase composition.

One particularly useful water chemistry study involves exposing anoxic trench waters to air and monitoring the pH changes. Sorption test conditions frequently include a wide range of pH. If the buffered trench waters do not undergo significant pH changes during exposure to oxygen, there would be no useful purpose in requiring a wide range of pH in general testing guidelines for sorption measurements. Results of such a study are directly related to the goal described in section 6.2.

The total retention capacity of a particular trench geochemical environment is the sum of all the mechanisms which can prevent radionuclide migration from the immediate trench vicinity. Sorption processes (based mainly on K_d studies) have been largely credited as the total retention mechanism. However, this is not entirely correct, particularly for the anoxic, chemically reducing, geochemical environments typified by Maxey Falts and West Valley. From information collected in this program, two other mechanisms appear to have an effect on radionuclide retention; (1) precipitation of iron monosulfides (FeS) in the anoxic trench environment and (2) precipitation of iron oxyhydroxides as trench waters migrate away from the immediate trench vicinity and mix with more oxidized groundwaters. Field measurements have shown the presence of free sulfide ion in solution and black particulate matter in the Maxey Flats trench waters.(4) Active sulphate reducing bacteria have also been identifed in trench waters.(1) Exposure of iron bearing trench waters to air results in the precipitation of ferric oxyhydroxide and causes drastic changes in the water chemistry. Coprecipitation of radionuclides during both sulfide and hydroxide precipitations is expected. In fact, the ferric oxyhydroxide precipitation reaction is a well known water purification technique. Both mechanisms act as in situ scavenging mechanisms and should increase the total retention capacity of the anoxic, chemically reducing geochemical environments. This is an important point to be kept in mind when considering these environments for future disposal sites. Results of sorption studies involving these systems (section 3 and section 7 in Reference 1) showed that anoxic water regimes exhibited lower sorption capacities relative to more oxidized systems. This observation taken alone would argue against the selection of a similar environment for a future disposal site. However, the retention in such a situation would be the sum of that due to sorption processes and coprecipitation reactions. To date, no quantitative data are available from this program or other studies to evaluate the relative importance of these reactions. However, they should play major roles based on general chemical principles.

Laboratory experiments planned to obtain some quantitative information about co-precipitation of radionuclides are as follows:

(1) Samples of anoxic trench waters will be exposed to air to precipitate the ferric oxyhydroxides. Changes in water chemistry will be monitored and the radionuclide content of the water will be determined before and after the precipitations.

(2) To measure co-precipitation on iron monosulfide, a more elaborate experimental design is required. Trench water must be maintained in an anoxic condition in a reaction vessel into which sulfide ion and ferrous iron are introduced in a controlled manner. The amount of dissolved radionculides can be monitored during the precipitation process.

Results of these studies will supply information necessary to characterize the behavior of the chemically reducing environments and quantify the effects of in situ scavenging mechanisms on radionuclide retention. These efforts are consistent with the program direction and goals in that the information is an integral part of characterizations of particular sites, as well as being important in evaluating the effects of specific environmental conditions on radionuclide retention. This latter aspect is particularly important for formulating site selection criteria.

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APPENDIX A

PROBE METHOD FOR CARBON DIOXIDE

A.1 Summary

Carbon dioxide dissolves in water to form dilute weak carbonic acid solutions consisting of aqueous carbon dioxide, bicarbonate (HCO_3^-), and carbonate ($CO_3^=$) species. The distribution of various species is a function of the solution pH. In solutions with pH less than 5, almost all the carbon dioxide exists as dissolved gas. In this method, a buffer solution is used to adjust the pH of the sample to 4.8-5.2, and thereby converts all the bicarbonate and carbonate to dissolved carbon dioxide. The carbon dioxide electrode is then used to measure the total amount of dissolved carbon dioxide in the solution.

The electrode contains a gas permeable membrane through which carbon dioxide diffuses from the sample solution to the internal filling solution. An equilibrium is reached between the partial pressure of carbon dioxide in the sample solution and the carbon dioxide in the internal filling solution. The partial pressure is proportional to the concentration of carbon dioxide in the sample.

In the probe method, standards and samples are adjusted to a pH range where the HCO_3^- and $CO_3^=$ species are converted to aqueous CO_2. The probe measurements then represent the sum of the carbonate, bicarbonate, and aqueous CO_2 contents of the original samples (C_T). Using the disassociation constants for aqueous CO_2 and the original pH of the solutions before adjustment, the concentrations of HCO_3^- and $CO_3^=$ in the original solutions can be calculated.

A.2 Interferences

Volatile weak acids are potential electrode interferences. Acetic acid, formic acid, nitrogen dioxide, sulfur dioxide, and hydrogen sulfide interfere significantly with the electrode measurements.

A.3 Sampling and Storage

Waters should be analyzed as soon as possible after filtration. When it is necessary to store samples prior to analysis, they should completely fill tightly-capped glass bottles. Also, reduced temperatures prevent carbon dioxide escape, and replacement of air with nitrogen prevents dissolution of carbon dioxide from the air.

An alternate storage procedure to prevent the loss of carbon dioxide from the samples is to adjust the pH to 8-9 with 10 M NaOH. The alkaline samples must then be acidified with the buffer solution just before making measurements.

The NaOH solution usually contains carbonate as a contaminant and should not be added to samples containing less than 200 mg/L as $CaCO_3$. These samples should completely fill the bottle and be capped tightly to prevent carbon dioxide escape.

A.4 Equipment

Probe - Orion CO_2 electrode model 95-02
Meter - Orion model 407A or Orion Model 701 meter
Beakers and pipets
Magnetic stirrer and stirring bars
Thermometer

A.5 Reagents

Stock Standard Solution - 1000 mg $CaCO_3$/L.
Dissolve 167.9 mg dried reagent-grade $NaHCO_3$ in deionized water and dilute to volume in a 200 mL volumetric flask.

Working Standard Solution - 100 mg $CaCO_3$/L
Pipet 10.0 mL of the 1000 mg $CaCO_3$/L solution into a 100-mL volumetric flask and dilute to volume with deionized water.

Carbon Dioxide Buffer Solution
Dissolve 294 g sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) in about 800 mL deionized water. Acidify to pH 4.5 with concentrated HCl (approximately 100 mL). Dilute to volume in a 1000 mL volumetric flash. Transfer to a polyethylene bottle.

Storage Solution - 0.1 M NaCl
Dissolve 0.58 g reagent grade NaCl in 100 mL deionized water.

Internal Filling Solution
Orion Cat. No. 95-02-02.

A.6 Procedure

1. Assemble the electrode according to the manufacturer's instructions.(1)

2. Check the electrode slope daily. The procedure depends upon the meter used and is detailed in Reference 1.

3. Calibrate the system (Ref. 1) using standards made from the 100 mg $CaCO_3$/L standard before measuring samples, and check the calibration every hour when running a series of samples.

4. Ten mL of the buffer solution are added to 100 mL of the calibration standards and samples just before measuring with the electrode.

5. Samples and standards should be measured at the same temperature. A temperature difference of 1°C results in a measurement error of 2%.

6. Highly basic, acidic, or buffered samples should be adjusted to pH 4.8-5.2 with 10 M NaOH or concentrated HCl before the buffer solution is added.

7. Read the concentration of samples directly from the meter or a calibration curve.

Water moves across the membrane as water vapor, changes the concentration of the internal filling solution, and causes electrode drift. Water vapor is not a problem if the total level of dissolved species in the sample solution (osmotic strength) is approximately equal to that in the internal filling solution and the temperature of the electrode and sample are the same. The buffer solution adjusts the total level of dissolved species to 0.4 M. If the total level of dissolved species is greater than 1 M after addition of the buffer, the sample should be diluted before measurement.

Samples with high carbon dioxide concentrations (above 2000 mg/L as $CaCO_3$) should be diluted before measurement because the partial pressures in these solutions are greater than the normal atmospheric partial pressure of carbon dioxide, resulting in a loss of carbon dioxide to the air.

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APPENDIX B

DETERMINATION OF BICARBONATE - CARBONATE CONCENTRATIONS IN DISPOSAL TRENCH WATERS - TITRATION ALKALINITY AND CO_2 PROBE METHODS

One of the most important components in natural waters is the carbonate content, controlled by the equilibria between the species H_2CO_3 (CO_2aq.), HCO_3^-, $CO_3^=$, and H^+. In many natural waters, these equilibria control the pH, buffering capacity, and concentrations of other major and minor cations. Consequently, analytical determinations of the carbonate species are necessary for a complete analysis of the water chemistry. Without this information, water quality analysis in terms of the complete system is not possible, and thus the usefulness of the analytical data severly limited. Also, the first test for internal consistency of any water analyses data is the anion-cation balance. In most natural waters HCO_3^- + $CO_3^=$ contribute significantly to the anion content.

B.1 CO_2-$CO_3^=$ Equilibria in Natural Waters

Relationships between the various species are shown in Figure B.1. The relative distribution diagram (Figure B.1) is for a water of fixed C_T and P_{CO_2}, (C_T = [CO_2aq.] + [HCO_3^-] + [$CO_3^=$], and P_{CO_2} is the partial pressure of carbon dioxide).

For nonmarine surface waters where CO_2-$CO_3^=$ is the only protolysis system, the carbonate species can be determined from the pH and titration alkalinity (T.A.) as defined below:

$$\text{Titration alkalinity} = [HCO_3^-] + 2[CO_3^=] + [OH^-] - [H^+] \tag{B.1}$$

Where the CO_2-$CO_3^=$ system is the only significant buffering component, the titration alkalinity is essentially equivalent to the carbonate alkalinity (C.A. = [HCO_3^-] + 2[$CO_3^=$]).(2) Where other components are present, the carbonate alkalinity (C.A.) is only a part of the titration alkalinity, as described below.

In naturally occurring stagnant waters (particularly anoxic systems), other processes such as sulfate reduction and ammonia generation contribute to the titratable components of the water. For such waters, the definition of titration alkalinity must be extended to include ammonia, phosphate, silica, and sulfide species as follows:

$$\begin{aligned} T.A. = {} & [HCO_3^-] + 2[CO_3^=] + [OH^-] - [H^+] + [NH_3] \\ & + [HS^-] + [H_2PO_4^-] + [H_2SO_4^-] \end{aligned} \tag{B.2}$$

(only the first dissociation products are included for simplicity). For waters where P_{CO_2} is known, or at least constant, the concentrations of the carbonate species can be extracted from the titration alkalinity if the

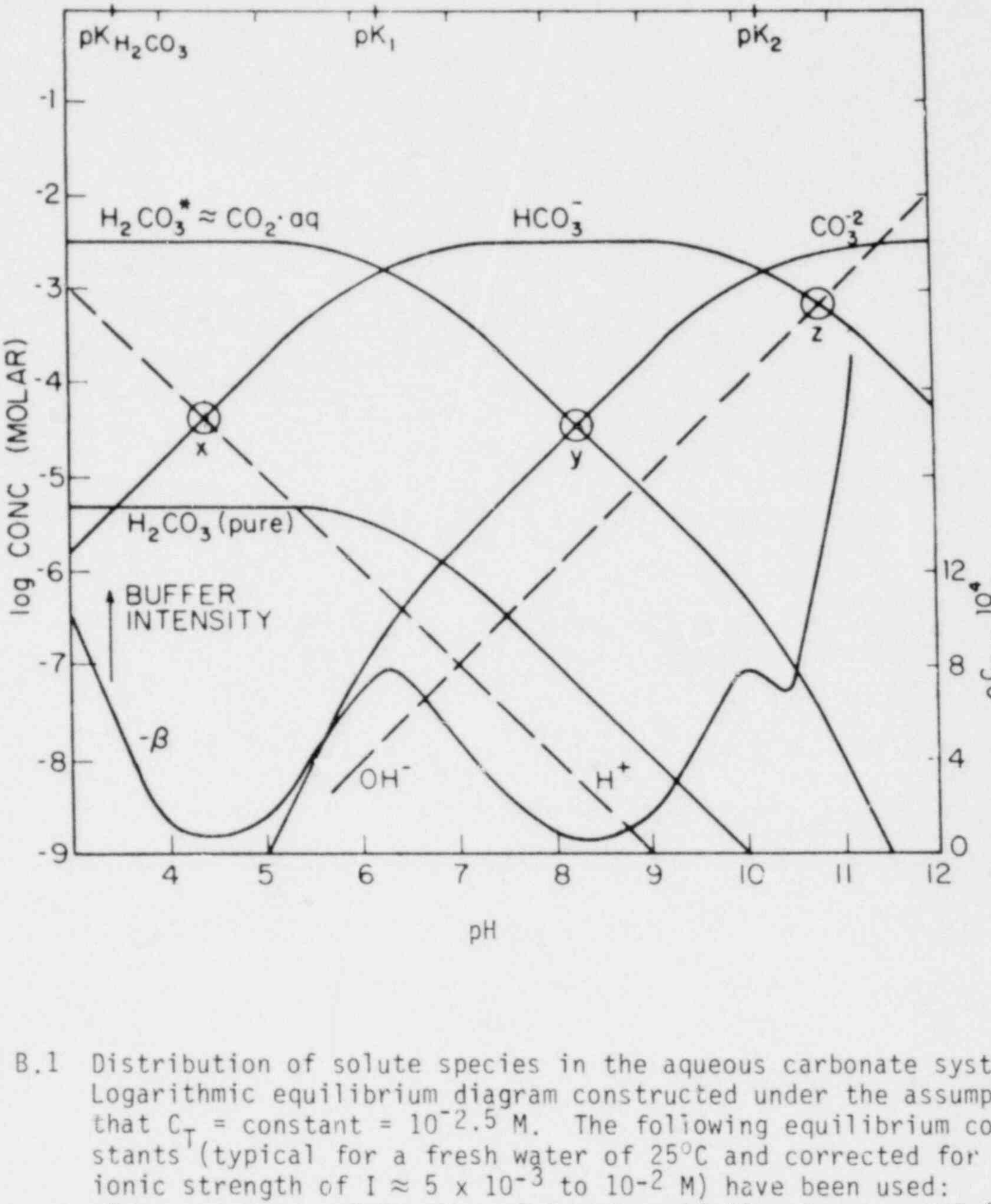

Figure B.1 Distribution of solute species in the aqueous carbonate system. Logarithmic equilibrium diagram constructed under the assumption that C_T = constant = $10^{-2.5}$ M. The following equilibrium constants (typical for a fresh water of 25°C and corrected for an ionic strength of $I \approx 5 \times 10^{-3}$ to 10^{-2} M) have been used: pK(hydration) = -2.8, pK_1 = 6.3, pK_2 = 10.25. Because $[CO_2(aq)] >> [H_2CO_3]$, $[CO_2aq] \approx [H_2CO_3^*]$. Pure H_2CO_3 has a pK value (where $[H_2CO_3] = [HCO_3^-]$) of $pK_{H_2CO_3}$ = 3.5. The equivalence points corresponding to pure solutions (C_T-molar) of $H_2CO_3^*$, $NaHCO_3$ and Na_2CO_3 are a function of pH. Taken from Stumm and Morgan (B1).

concentrations of the additional species (NH_3, $H_2PO_4^-$, HS^- and $H_3SiO_4^-$) are known at the pH of the water.(1)

B.2 Titration Alkalinity in Disposal Trench Waters

Determinations of the carbonate species in the disposal trench waters are complicated by two additional considerations beyond those mentioned previously. First, additional components derived from the waste can contribute to the tiration alkalinity. For example, anions from weak organic acids, such as acetate ion or organic amines, can contribute to the titration alkalinity. Once again, Eq. (B.2) must be extended to include these components:

$$T.A. = [HCO_3^-] + 2[CO_3^=] + [OH^-] - [H^+] + [NH_3] + [HS^-] + [H_2PO_4^-] + [H_3SiO_4^-] + [\text{titratable waste derived components}] \qquad B.3$$

The irregular shapes of the titration curves for Maxey Flats and West Valley waters reported previously(1) indicate the presence of such waste derived components.

This new component is particularly difficult to evaluate since the waste derived material varies qualitatively and quantitatively in each water sampled. Defining it would require an exhaustive analytical effort for each sample which is impractical.

A second consideration in waste waters and soil solutions is the P_{CO_2}, which builds up to relatively high levels in such closed systems. The CO_2 is produced by bacterial action but cannot escape from the closed trench waters, consequently, the P_{CO_2} in the water increases which in turn causes shifts in the various equilibria shown in Figure B.1. When the trench waters are removed from the closed environment, changes in the P_{CO_2} begin, with consequent changes in the pH, H_2CO_3 and carbonate alkalinity. Until a new equilibrium P_{CO_2} is established, the water system is dynamic and analytical results represent only transitory states.

For the anoxic waste waters therefore, analytical determinations of the aqueous carbonate species cannot be readily obtained from the titration alkalinity alone, as described in a previous report.(1) The titration alkalinity must be interpreted as simply an indication of the acid neutralizing capacity (alternately-the buffer capacity) of the waste water. An alternate analytical procedure is required to determine the actual $HCO_3^- + CO_3^=$ contents of the waters, which are in turn used in the anion-cation balance calculations and water quality evaluations.

The determination of C_T with the CO_2 probe (Appendix A) permits an alternate means of deriving bicarbonate concentrations independent of the titration alkalinity measurement. For a static, relatively uncomplicated system, bicarbonate concentrations calculated from probe and titration measurements should agree.

In an effort to develop a procedure for analytically determining bicarbonate concentrations in disposal trench waters, measurements of titration alkalinity and C_T were performed on the disposal trench water samples collected from the Barnwell, South Carolina, site (May 1980-see section 2.3). The Barnwell waters are comparatively clean, in that the waste derived component of the titration alkalinity (Eq. B.3) should be insignificant in most of the samples. Therefore, bicarbonate concentrations derived from probe and titration results should agree. These samples afford a good opportunity to test one method against the other.

B.3 Determinations of Bicarbonate in Barnwell Trench Water Samples - Titration Alkalinity vs CO_2 Probe Method

In the normal sequence of sample handling and analysis procedure used for trench water analyses,(1) titration alkalinities are measured immediately after anaerobic filtration. At this point in the sequence, measurements of C_T are also performed with the CO_2 probe along with the usual titration measurement. Calculations of bicarbonate concentrations from probe and titration measurements can be compared in this manner. Bicarbonate concentrations calculated from these measurements are listed in Table B.1. Measurements made on the samples immediately after filtration are listed under the headings "anaerobic" in Table B.1. Comparison of the bicarbonate concentrations calculated from the titration and probe measurements are in disagreement for all the trench waters, as well as the well water (trench samples 13D4 and 18D5 are omited because of the small content of dissolved components). The disagreement for the well water sample is particularly disturbing in that the well sample should be a simple groundwater without the complications described above (section B.2). When these measurements were made, the trench waters may have been dynamic systems responding the changes in temperature and P_{CO_2}, which would explain the discrepencies observed.

Table B.1

Barnwell, South Carolina, Disposal Trench and Well Waters - CO_2 Probe and Titration Alkalinity Data and Calculations

Dissolved Component	Method	6D1		8D3		25-21D1		Well	
		Anaerobic	Aerobic	Anaerobic	Aerobic	Anaerobic	Aerobic	Anaerobic	Aerobic
C_T(mg/L as $CaCO_3$)	P[a]	330	76	1700	1630	375	125	81	84
Titration Alkalinity	T.A.[b]	1.70	1.10	26.8	18.4	2.08	1.20	1.20	0.78
(meq/L)	P	1.10	1.00	14.9	16.6	1.50	1.20	0.76	0.77
HCO_3^-	T.A.[b]	100	70	1630	1120	127	75	74	48
(mg/L)	P[c]	67	61	900	970	91	76	46	47
pH		6.08	7.65	7.20	8.75	6.21	8.25	7.54	7.35
Anions/cations	T.A.	1.2	1.1	1.0	0.70	1.54	1.0	1.6	1.0
	P	1.0	1.0	0.6	0.6	1.2	1.0	1.0	1.0

[a] P = carbon dioxide probe.
[b] T.A. = Titration alkalinity.
[c] Titration alkalinity calculated from probe measurements of C_T.

To test this explanation, samples of the filtered trench and well waters were left standing for a period of time, after which the titration and probe measurements were repeated. Results of these analyses, and bicarbonate concentrations calculated from them, are listed under the "aerobic" headings in Table B.1. Agreement between bicarbonate concentrations calculated from probe and titration measurements is excellent for the well water and trench 25-21D1, good for trench 6D1 and only fair for trench 8D3. Use of the "aerobic" values for bicarbonate concentrations in the anion/cation balances yielded greatly improved results compared to the poor agreement based on "anaerobic" values for bicarbonate. Using the "aerobic" bicarbonate numbers, satisfactory balances are obtained for all of the waters except 8D3. It should be noted that trench 8D3 sample most closely resembles the more complex trench waters from Maxey Flats (section 2.3).

Good agreement between the two methods for the equilibrated waters indicates that the waters are dynamic systems immediately after the anaerobic filtration process. Waters should be left to equilibrate before titration and probe measurements are taken for reliable determination of bicarbonate concentrations. Titration curves for these samples are shown in Figures B.2-B.5, for measurements immediately after the filtration step (designated "anaerobic" in the figures) and after the waters were left standing (designated "equilibrium" in the figures).

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1. W. Stumm and J. J. Morgan, Aquatic Chemistry, pp. 118-159, Wiley-Interscience, Inc., New York 1970.[1]

2. G. Skirrow, "The Dissolved Gases - Carbon Dioxide," in Chemical Oceanography, J. P. Riley and G. Skirrow, Eds. (Academic Press, Inc., New York, 1965), Chap. 7, pp. 227-322,.[1]

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[1] Available in public technical libraries.

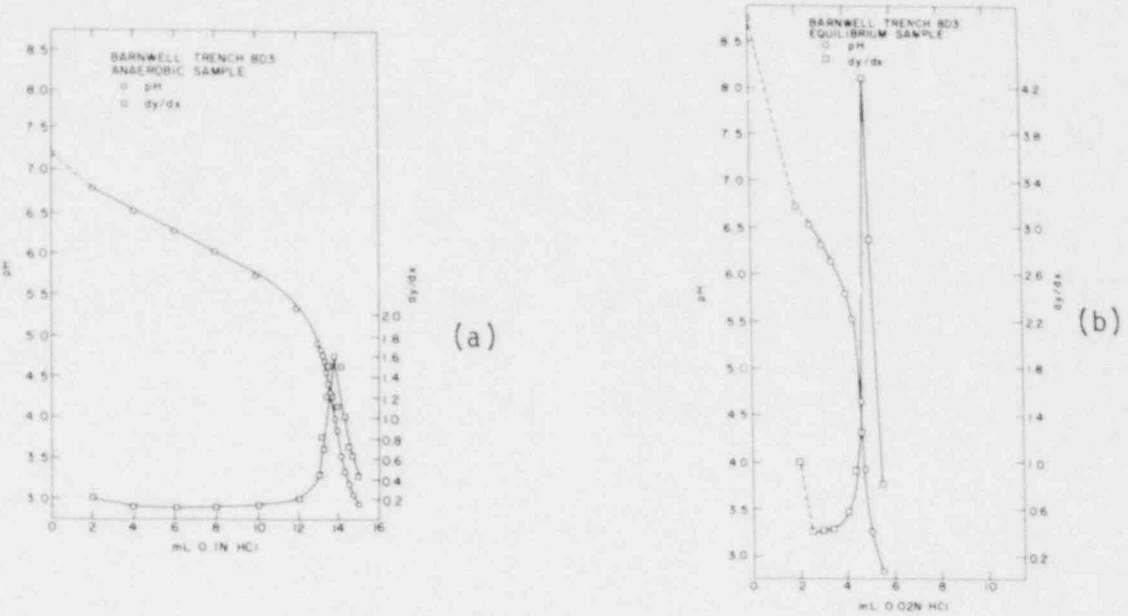

Figure B.2 Titration alkalinity curve and first derivative (dy/dx) - Barnwell disposal trench water sample 8D3, (a) filtration (anaerobic) and, (b) after standing (equilibrium).

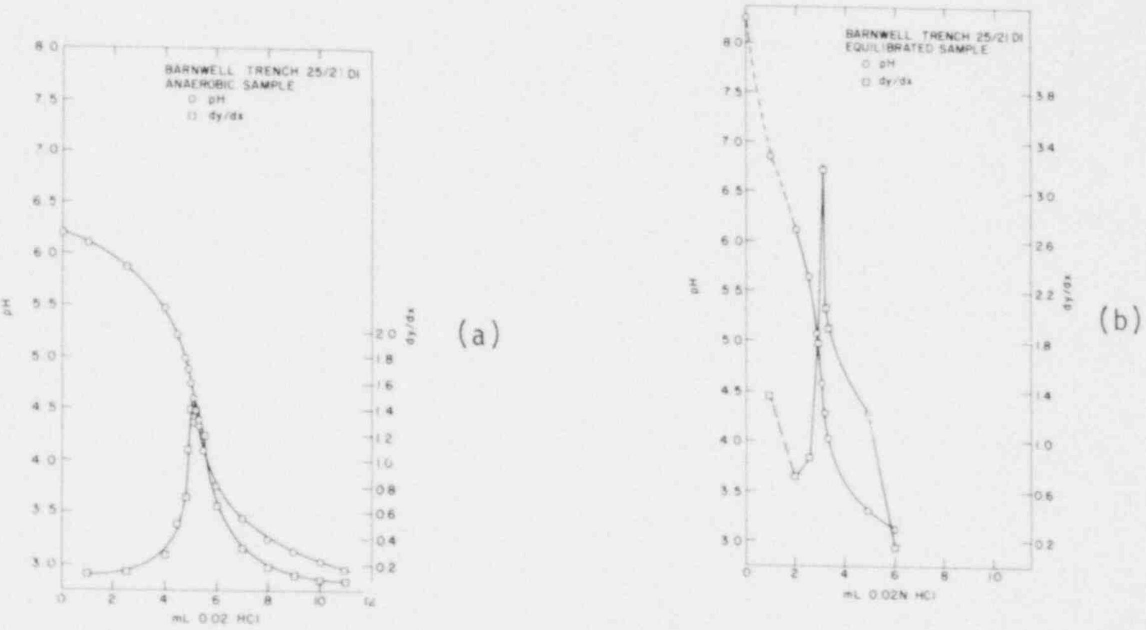

Figure B.3 Titration alkalinity curve and first derivative (dy/dx) - Barnwell disposal trench water sample 25/21 D1, (a) after filtration (anaerobic) and, (b) after standing (equilibrium).

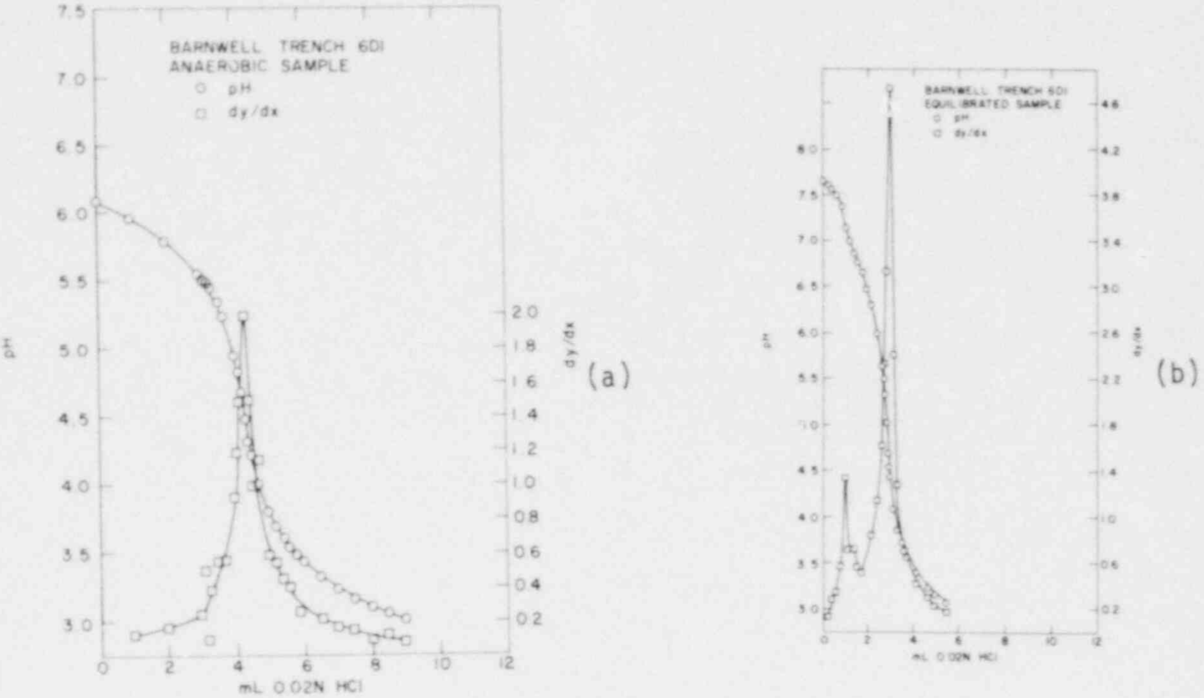

Figure B.4 Titration alkalinity curve and first derivative (dy/dx) - Barnwell disposal trench water sample 6D1, (a) after filtration (anaerobic) and, (b) after standing (equilibrium).

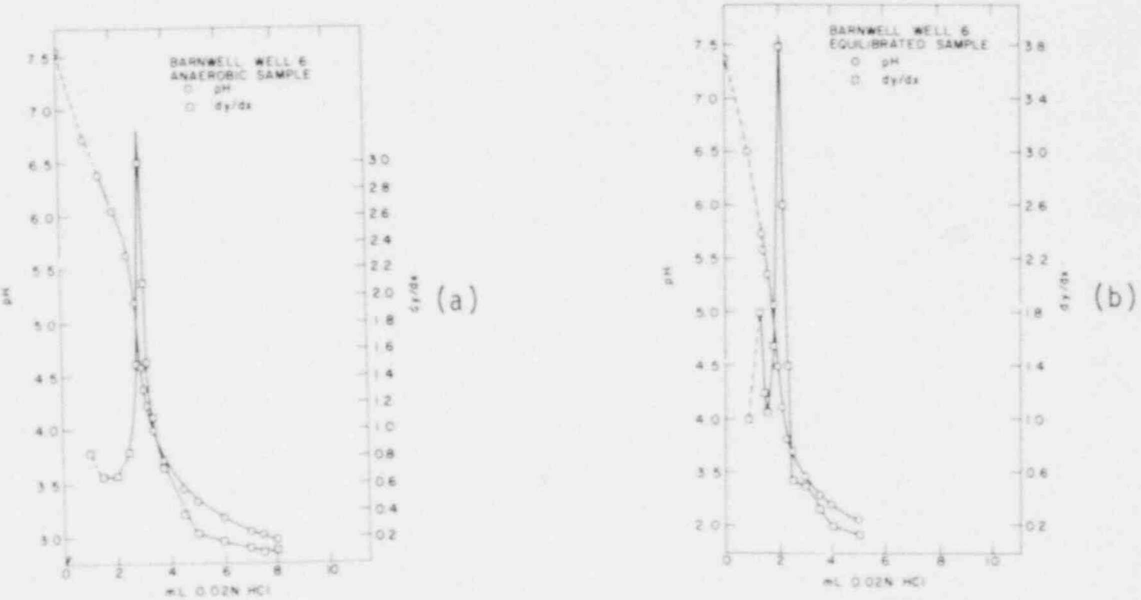

Figure B.5 Titration alkalinity curve and first derivative (dy/dx) - Barnwell well water sample (Well 6), (a) after filtration anaerobic) and, (b) after standing (equilibrium).

APPENDIX C

PREPARATION PROCEDURE - SORPTION EXPERIMENTS USING ANOXIC WATERS

C.1 Introduction

Performing laboratory sorption studies to simulate *in situ* conditions requires that the anaerobic condition of the aqueous-solid system be maintained during the course of the experiment.

This procedure describes an experimental design which will protect the integrity of the trench water used in the experiments. Trench waters are frequently anoxic water systems which have low dissolved oxygen and Eh values and appreciable concentrations of ferrous ion in solution. Air exposure of an anoxic trench water results in the co-precipitation of radionuclides on ferric oxyhydroxide formed by the oxidation of ferrous ion. To prevent this precipitation, the anoxic character of the trench waters must be preserved.

C.2 Sample Containers and Tumbling Chamber

The adsorption of trace radionuclides on the walls of samples containers is best avoided by the use of Teflon. TFE Teflon was used to fabricate containers. Teflon faced septa with aluminum caps were used to seal the containers. However, oxygen very rapidly passed through even relatively thick TFE Teflon container walls. To preserve the anoxic waters, a Lucite outer container was fabricated to enclose the Teflon containers. The double container is shown in Figure C.1.

Since long equilibration periods were anticipated, tumbling chambers were constructed through which nitrogen could be passed to provide additional protection to the samples. These are shown in Figure C.2.

C.3 Sample Preparation Procedure

C.3.1 Preparation of Spiked Trench Waters

Chloride salts of the radionuclides ^{241}Am, ^{85}Sr, ^{134}Cs, ^{137}Cs, ^{59}Fe, ^{60}Co, and ^{152}Eu were prepared in glass septum bottles (120 mL), by evaporation of their carrier acid solutions (20 μL of 1 mCi/mL) under an IR lamp.

The glass containers were then sealed with butyl rubber septa and aluminum caps. The bottles were flushed with ultra-high purity argon (O_2 < 1 ppm) overnight, shown schematically in Figure C.3.

Clear, but unfiltered anoxic trench water was transfered via an argon flushed manifold to the argon filled glass septum bottles containing radionuclide salts. See Figure C.4.

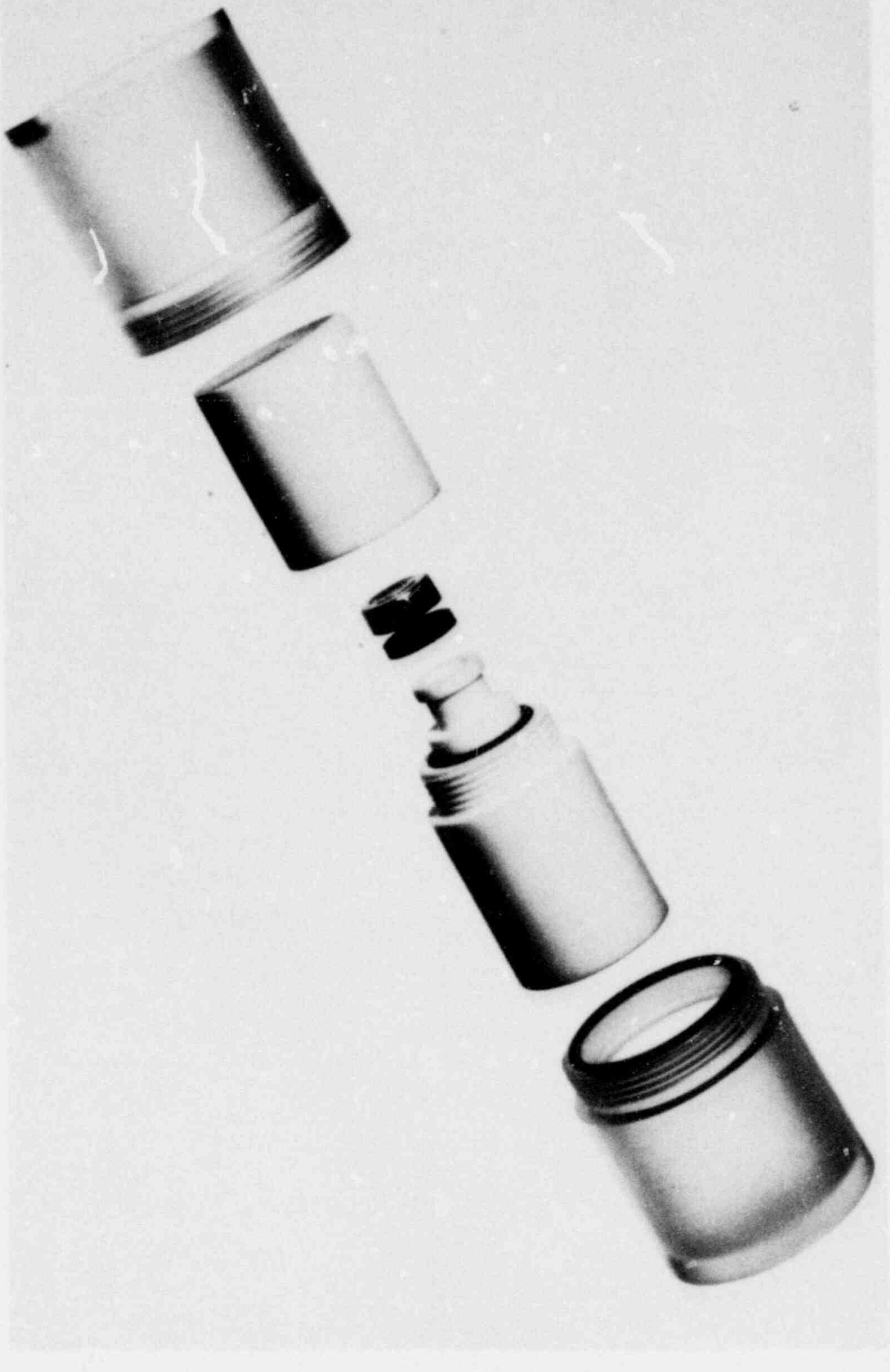

Figure C.1 Teflon container and outer polystyrene enclosure.

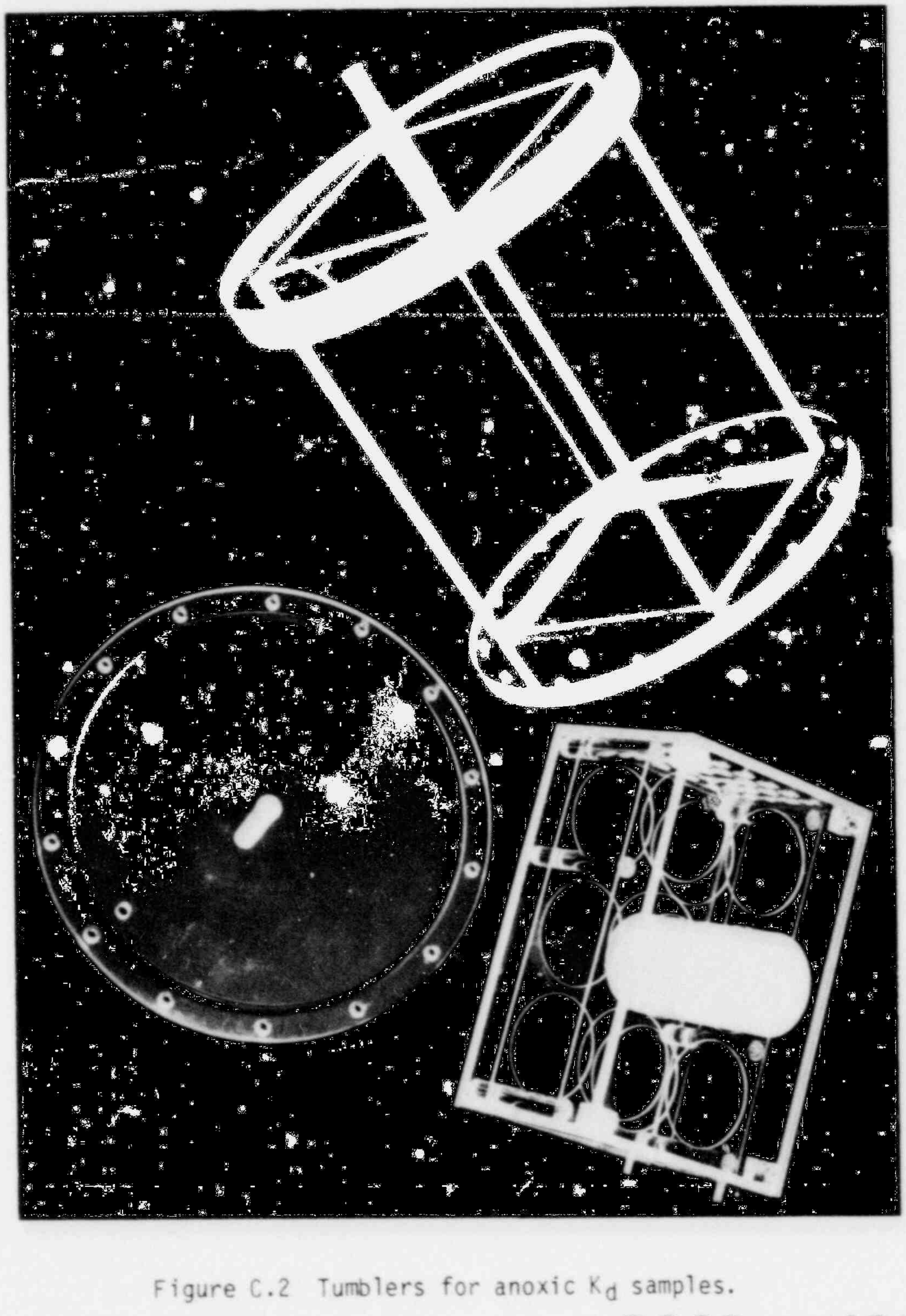

Figure C.2 Tumblers for anoxic K_d samples.

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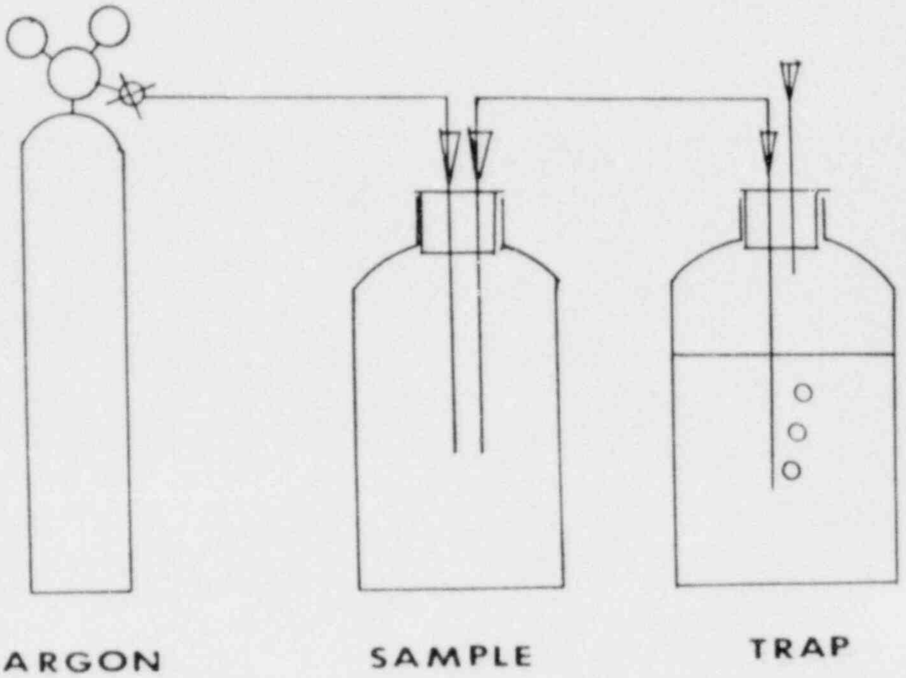

Figure C.3 Schematic of manifold used to flush sample bottle with argon gas.

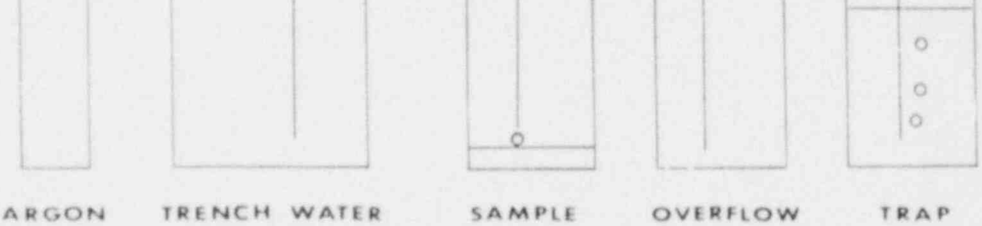

Figure C.4 Schematic of manifold used to transfer anoxic trench water from sampling container to sample bottle.

C.3.2 Sample Preparation for Sorption Experiments

Weighed amounts of solid phases were quantitatively transferred to the Teflon sample containers (Figure C.1). Empty containers were reserved for blanks and control samples.

All the materials needed for sample preparation are transferred into a glove box which is then sealed and purged of oxygen. Because of the extreme sensitivity of anoxic trench waters to oxygen, the glove box was purged with ultra high purity argon (O_2 < 1 ppm) for two to three days prior to use. A basic solution of pyrogallol remains nearly colorless for 10-15 minutes when the glovebox atmosphere is ready. About 20 mL of spiked anoxic trench water is added to the Teflon sample container by means of a plastic pipet. Measurements of pH and Eh on the spiked anoxic trench water, as well as preparation of K_d samples, were performed in the controlled atmosphere glovebox.

The Teflon containers are sealed with Teflon faced septa and enclosed in the Lucite containers before being removed from the glove box and placed in the tumbling unit.

The K_d samples are tumbled under an argon atmosphere until equilibrium is established. See Figure C.5. During the tumbling process the solid phase is disaggregated.

C.4 Counting

To monitor the progress of the sorption experiment with time, periodically the gamma ray spectra of the liquid phase is taken with a Ge(Li) detector. The samples are removed from the tumbler and centifuged for 20 minutes at 3000 rpm. The activity in the liquid phase is measured by shielding the solid phase from the Ge(Li) detector with a 3 x 3 x 1-1/2 inch lead brick. See Figure C.6.

C.5 Final Measurements and Calculations

A final count of the liquid phase is performed after disassembling the K_d containers in the argon-flushed glove box. The Eh and pH of each sample liquid phase is measured. The liquid phase is then filtered through a 0.2 μm membrane syringe filter. Ten mL of the liquid phase are pipetted into a sample bottle and concentrated hydrochloric acid (1 mL) is added to maintain the radioisotopes in solution. Plastic bottles, pipettes and syringes are used to avoid container surface adsorption. The acidified samples are then counted to measure the activity that remains in solution.

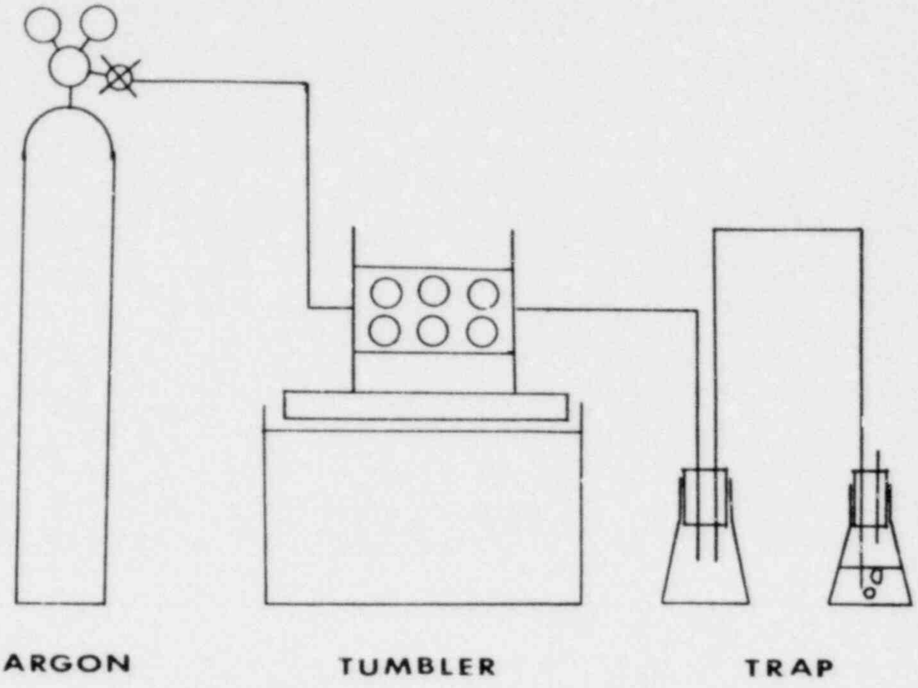

Figure C.5 Schematic of manifold used to tumble samples on a ball mill collar while maintaining samples in inert gas atmosphere.

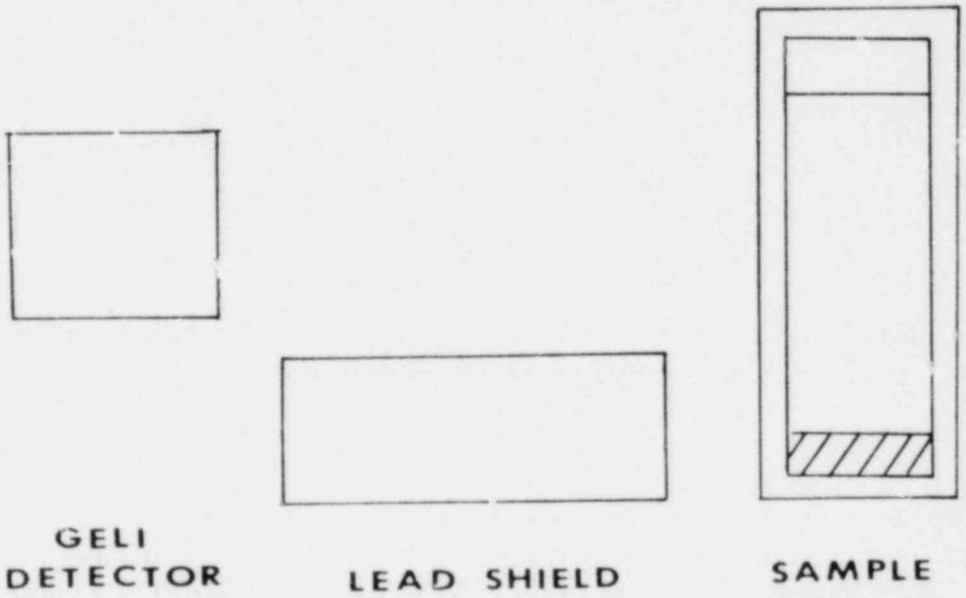

Figure C.6 Schematic of gamma ray counting arrangement used to monitor activity in solution.

The radionuclide sorption coefficient (K_d) is calculated according to the equation:

$$K_d = \frac{\text{activity on solid/unit weight}}{\text{activity in solution/unit volume}} = \frac{(A_r - A_i)}{A_i} \cdot \frac{V_\ell}{W_s}$$

A_r = initial activity in solution

A_i = activity in the sample solution

W_s = weight of solid in grams

V_ℓ = volume of liquid in mL

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