

EVALUATION OF ISOTOPE MIGRATION — LAND BURIAL

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

Status Report
October 1980 — September 1981

Richard F. Pietrzak, Kenneth S. Czycinski,
and Allen J. Weiss

NUCLEAR WASTE MANAGEMENT DIVISION
DEPARTMENT OF NUCLEAR ENERGY, BROOKHAVEN NATIONAL LABORATORY
UPTON, LONG ISLAND, NEW YORK 11973



Prepared for the U.S. Nuclear Regulatory Commission
Office of Nuclear Regulatory Research
Contract No. DE-AC02-76CH000016

EVALUATION OF ISOTOPE MIGRATION — LAND BURIAL

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

Status Report
October 1980 — September 1981

Principal Investigators:
R. Pietrzak, K.S. Czycinski,
and A.J. Weiss

Contributors:
James H. Clinton and Mary Kinsley

Manuscript Completed — February 1982
Date Published — March 1982

D.G. SCHWEITZER, HEAD
NUCLEAR WASTE MANAGEMENT DIVISION
DEPARTMENT OF NUCLEAR ENERGY, BROOKHAVEN NATIONAL LABORATORY, UPTON, NEW YORK 11973

PREPARED FOR THE U.S. NUCLEAR REGULATORY COMMISSION
OFFICE OF NUCLEAR REGULATORY RESEARCH
CONTRACT NO. DE-AC02-76CH00016
FIN A-3042

NOTICE

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, or any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for any third party's use, or the results of such use, of any information, apparatus, product or process disclosed in this report, or represents that its use by such third party would not infringe privately owned rights.

The views expressed in this report are not necessarily those of the U.S. Nuclear Regulatory Commission.

Available from
GPO Sale Program
Division of Technical Information and Document Control
U.S. Nuclear Regulatory Commission
Washington, D.C. 20555
and
National Technical Information Service
Springfield, Virginia 22161

ABSTRACT

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. This study is an attempt to monitor the behavior of existing low-level disposal sites, provide an understanding of significant factors which affect prediction of radionuclide movement along the groundwater flow paths, and assist in the development of criteria for the selection and licensing of future low-level disposal sites.

Brookhaven National Laboratory (BNL) began a field and laboratory testing program in 1976 sponsored by the U.S. Nuclear Regulatory Commission (USNRC), in cooperation with the U.S. Geological Survey (USGS), to study the existing commercial low-level radioactive waste disposal sites. This investigation measures the source terms (concentrations in solution) of radionuclides and other solutes in the disposal trench waters, and describes the physical and chemical properties of the site geochemistry that control the movement of radionuclides.

During the past year, radiochemical analyses of trench waters and sediment cores from the Barnwell disposal site were completed. Results of the trench water radiochemical analyses are similar to those reported for previous samplings. The trench water compositions reflect two processes; (1) interaction between the burial waste and infiltrating groundwaters and (2) the effects of bacterial decomposition of organic material. The extent to which groundwaters are changed reflects the length of time water accumulations persist in the trenches and the intensity of the processes, which in turn is a function of the saturation state and permeability of the local sediment.

Very low concentrations of ^{90}Sr and $^{238,239,240}\text{Pu}$ were found as dissolved species in some Barnwell trench waters. Tritium was the most abundant of the radionuclides and was found in all trench waters. Chemically bound as HTO , tritium would be the most mobile radionuclide.

Sediment cores from beneath four Barnwell disposal trenches were analyzed for radionuclides. Only the sediment core from beneath trench 2 showed gamma activity. ^{60}Co was found throughout the core from trench 2. Gross alpha and beta activities significantly above background and detectable concentrations of ^{90}Sr and $^{238,239,240}\text{Pu}$ were restricted to the uppermost 30 cm of the core from trench 2.

Batch sorption, K_d , tests were performed with materials from the Barnwell site. The batch K_d results for $^{134,137}\text{Cs}$, ^{60}Co and ^{241}Am are dependent on the ratio of soil to solution. However, the observed K_d for ^{85}Sr is not a function of the soil to solution ratio.

Recirculating water passed through a column of Hawthorne sediment (loop), from the Barnwell site, was used to determine K_d 's. The batch K_d 's for strontium and cesium were of the same magnitude but lower than the column loop results. The ^{60}Co and ^{132}Eu K_d 's differed by two orders of magnitude from batch results.

An attempt to measure radionuclide sorption coefficients using anoxic trench water and shale from the Maxey Flats disposal site was complicated by changes in the water chemistry. Oxygen diffusion into some chambers may have caused coprecipitation of radionuclides on ferric oxyhydroxides. Experiments have been initiated to measure the contribution of coprecipitation and sorption of radionuclides by the sediments from anoxic waters.

Cobalt complexes of EDTA, NTA, and DTPA were found to persist in a chemically reducing water/sediment environment which simulates the water chemistry of a Maxey Flats trench water. The anoxic trench environments do not rapidly destroy organo-cobalt complexes in solution. The concentration of chelating agents should be minimized in disposal trenches to minimize cobalt migration.

Experimental work was initiated to measure the chemical changes and radionuclide scavenging by the formation of ferric oxyhydroxide precipitates. The formation of substances which coprecipitate radionuclides may act as a retarding mechanism for radionuclide transport.

CONTENTS

ABSTRACT	iii
CONTENTS	v
FIGURES	vii
TABLES	ix
ACKNOWLEDGEMENTS	xi
PREVIOUS REPORTS	xiii
1. INTRODUCTION	1
1.1 Water and Sediment Analyses	1
1.2 Geochemistry.	2
1.2.1 Radionuclide Sorption.	2
1.2.2 Organo-Radionuclide Complexes in Anoxic Water-Soil Regimes.	4
1.2.3 Oxidation of Disposal Trench Waters.	5
1.3 Summary of the Year's Activities.	7
2. EXPERIMENTAL	9
2.1 Trench Water Source Term Investigations at the Barnwell Disposal Site: Strontium and Plutonium Analyses.	9
2.2 Radionuclide Analysis of Sediment Cores From Beneath Disposal Trenches at the Barnwell Disposal Site.	9
2.3 Batch Sorption Experiments - Barnwell Trench Waters and Hawthorne Sediment.	10
2.4 Recirculating Water "Loop" System Sorption Experiments - Barnwell Synthetic Trench Waters and Hawthorne Sediment	12
2.5 A Batch Radionuclide Sorption Method for Anoxic Trench Waters.	14
2.6 Organo-Radionuclide Complexes in Anoxic Water-Soil Regimes Using a Controlled Environment Chamber Experiment	16
2.7 Measurement of pH, Eh, and Alkalinity Changes for Trench Water Oxidation	19
2.8 Chemical Changes and Radionuclide Scavenging During the Oxidation of a Trench Water	20
3. RESULTS AND DISCUSSION	23
3.1 Trench Water Source Term Investigation at the Barnwell Disposal Site	23
3.2 Radionuclide Profiles of Sediment Cores From Beneath Trenches at the Barnwell Site.	24
3.2.1 Tritium.	24
3.2.2 Gamma Ray Spectra.	28
3.2.3 Gross Alpha and Beta Activity.	28
3.2.4 Strontium-90 and Plutonium Isotopes.	34

CONTENTS (Continued)

3.3	Sorption of Radionuclides From Solution	35
3.3.1	Barnwell Sediments and Trench Waters	35
3.3.2	Recirculating Water "Loop" System Sorption Results for Barnwell Disposal Site Sediment.	42
3.3.3	Sorption of Radionuclides From Trench Waters of Maxey Flats.	47
3.4	Stability of Organo-Radionuclide Complexes in Anoxic Water- Soil Regimes - Controlled Environment Experiments	56
3.5	Retention Mechanisms in Disposal Trench Environments.	59
3.5.1	pH, Eh, and Alkalinity Changes for Trench Water Oxidation.	59
3.5.2	Chemical Changes and Radionuclide Scavenging During the Oxidation of a Trench Water.	61
4.	CONCLUSIONS.	63
4.1	Trench Water and Sediment Analyses.	63
4.2	Radionuclide Sorption	63
4.3	Stability of Organo-Radionuclide Complexes in Anoxic Water Soil Regimes.	64
4.4	Chemical Changes During the Oxidation of Anoxic Trench Waters.	64
5.	CURRENT EXPERIMENTAL TASKS AND FUTURE DIRECTIONS	67
5.1	Program Objectives.	67
5.2	Water Analysis.	68
5.3	Sediment Analysis	68
5.4	Leaching of Waste Forms in Simulated Trench Environment	69
5.5	Radionuclide Transport and Retardation	69
5.5.1	Batch K_d Sorption Isotherms.	69
5.5.2	Column Retardation Factors	70
5.5.3	Diffusion Coefficients	70
5.6	Radionuclide Behavior in Anoxic Groundwater	70
5.6.1	Sorption of Radionuclides.	71
5.6.2	Iron Oxyhydroxide Precipitation.	71
5.6.3	Ferrous Sulfide Precipitation.	71
5.6.4	Metal Carbonate Precipitation.	71
6.	REFERENCES	73

FIGURES

1.1	Locator Map of the Barnwell Disposal Facility.	3
2.1	Schematic Diagram of the Recirculating "Loop" Apparatus.	13
2.2	(a) Schematic Drawing of the Controlled-Environment Apparatus Used for the Stability Experiments, and (b) Top View of the Controlled-Environment Chamber	17
3.1	Tritium Activity vs Depth - Barnwell Disposal Site Cores	25
3.2	Bulk Density Profiles of Barnwell Trench Cores	26
3.3	Moisture Content Profiles of Barnwell Trench Cores	27
3.4	Batch Sorption Test Results - ^{60}Co R_d vs Time - Barnwell Trench 6D1 Water and Hawthorne Sediment.	35
3.5	Batch-Sorption Test Results - ^{85}Sr R_d vs Time - Barnwell Trench 6D1 Water and Hawthorne Sediment.	36
3.6	Batch Sorption Test Results - ^{134}Cs R_d vs Time - Barnwell Trench 6D1 Water and Hawthorne Sediment.	36
3.7	Batch Sorption Test Results - ^{137}Cs R_d vs Time - Barnwell Trench 6D1 Water and Hawthorne Sediment.	37
3.8	Batch Sorption Test Results - ^{241}Am R_d vs Time - Barnwell Trench 6D1 Water and Hawthorne Sediment.	37
3.9	Batch Sorption Test Results - R_d vs Time - Barnwell Trench 6D1 Water and Hawthorne Sediment	38
3.10	Batch Sorption Test Results - ^{60}Co K_d vs Solution/Soil Ratio - Barnwell Trench 6D1 Water And Hawthorne Sediment	39
3.11	Batch Sorption Test Results - ^{85}Sr K_d vs Solution/Soil Ratio - Barnwell Trench 6D1 Water and Hawthorne Sediment	40
3.12	Batch Sorption Test Results - ^{134}Cs K_d vs Solution/Soil Ratio - Barnwell Trench 6D1 Water and Hawthorne Sediment	40
3.13	Batch Sorption Test Results - ^{137}Cs K_d vs Solution/Soil Ratio - Barnwell Trench 6D1 Water and Hawthorne Sediment	41
3.14	Batch Sorption Test Results - ^{241}Am K_d vs Solution/Soil Ratio - Barnwell Trench 6D1 Water and Hawthorne Sediment	41

FIGURES, Continued

3.15	Calibration of Peristaltic Pump for Flow Rate Setting vs Observed Volume Flow Rate.	42
3.16	Percent of Maximum Count Rate vs Time - Flow of a Tritiated Synthetic Barnwell Trench Water (6D1) Through an Undisturbed Sediment Core.	43
3.17	Column Flow Rates vs Tritium Maximum-Travel Time	44
3.18	Percent of Initial ^{152}Eu Count Rate in Effluent vs Time	45
3.19	Percent of Initial Count Rate vs Time (Radioisotope Mix) Repacked Column	45
3.20	Percent of Initial Count Rate vs Time (Radioisotope Mix) Intact Column	46
3.21	Percent Metal in Solution vs Time for Co and Zn Chelate Stability Experiments.	57
3.22	Percent Cobalt in Solution vs Time for CoEDTA Experiment After Addition of MnCl_2 Under Reducing Conditions.	59
3.23	Eh and pH of West Valley Trench 8 Water During Controlled Oxidation.	62
3.24	Total Dissolved Iron Concentrations in West Valley Trench 8 Water During Controlled Oxidation.	62

TABLES

2.1	Characterization Data for Solid and Liquid Phases Used in Batch Sorption Experiments - Barnwell Disposal Site.	11
2.2	Composition of Synthetic Barnwell Trench Water	12
2.3	Iron Concentrations in Maxey Flats Disposal Site Trench Waters Used in Sorption Experiments	14
2.4	Chemical Composition of Synthetic Trench Water	18
2.5	Initial Metal-Complex Concentrations Used in Environmental Chamber Experiment	19
3.1	Concentration of Dissolved Radionuclides in Trench Water Samples From the Barnwell Site	23
3.2	Gross Alpha and Beta Activities in a Sediment Core From Trench 2 at the Barnwell Site (10 Minute Count).	29
3.3	Gross Alpha and Beta Activities in a Sediment Core From Trench 2 at the Barnwell Site (1000 Minute Count).	30
3.4	Gross Alpha and Beta Activities in a Sediment Core From Trench 8 at the Barnwell Site (10 Minute Count).	31
3.5	Gross Alpha and Beta Activities in a Sediment Core From Trench 5 at the Barnwell Site (10 Minute Count).	32
3.6	Gross Alpha and Beta Activities in a Sediment Core From Trench 7 at the Barnwell Site (10 Minute Count).	33
3.7	Strontium-90 and Plutonium Isotope Concentrations in Sediment Core Samples From the Barnwell Site.	34
3.8	Comparison of Batch and Column Loop K_d for Barnwell Trench 6D1 Water and Hawthorne Sediment	47
3.9	pH and Eh of Maxey Flats Trench 19S Anoxic Water With ^{152}Eu Before and After the Experiment.	49
3.10	pH and Eh of Maxey Flats Trench 19S Anoxic Water With ^{85}Sr , $^{134,137}\text{Cs}$, and ^{60}Co Before and After the Experiment.	50
3.11	Isotope K_d and Solution/Solid Ratios of Maxey Flats Trench 19S Anoxic Waters.	51

TABLES, Continued

3.12	pH and Eh of Maxey Flats Trench 27 Anoxic Water With ^{85}Sr , $^{134,137}\text{Cs}$, and ^{60}Co Before and After the Experiment.	52
3.13	Isotopic K_d and Solution/Solid Ratios of Maxey Flats Trench 27 - Anoxic Waters.	53
3.14	pH and Eh of Maxey Flats Trench T-2E Anoxic Water With ^{85}Sr , $^{134,137}\text{Cs}$, and ^{60}Co Before and After the Experiment.	54
3.15	pH and Eh of Maxey Flats Trench T-2E Anoxic Water With ^{152}Eu Before and After the Experiment.	55
3.16	Isotopic K_d and Solution/Solid Ratios of Maxey Flats Trench T-2E - Anoxic Waters	56
3.17	Chelate Stability Constants and Sulfide Solubility Products. . .	58
3.18	Chemical Changes, Acid (H^+) Generating Potential of Ferrous Ions, and Buffering Capacities (Alkalinities in Trench Waters - Before and After Oxidation).	61

ACKNOWLEDGMENTS

The authors would like to express their appreciation to several members of the U.S. Geological Survey, J. Cahill, J. Robertson, and H. Zehner, for their help in obtaining the samples used in this study, as well as their helpful comments and suggestions during the progress of the work reported here.

The cooperation and assistance of J. Razor of National Waste Management Services, Incorporated and D. Ebenhack of Chemical Nuclear Corporation for their assistance during our sampling trips to the Maxey Flats, Kentucky, and Barnwell, South Carolina, disposal sites.

The authors wish to thank the following individuals from Brookhaven National Laboratory for the aid they supplied in many areas of this study: Carl I. Anderson, Beverly Nine, and James D. Smith for their skillful assistance in the laboratory; Charles Ruege and Barry Karlin for their valuable contribution to the fabrication of many of the devices used in the various studies; Walter W. Becker for his general assistance; Nancy Yerry and Katherine Becker for their skillful typing and help in the preparation of this manuscript.

PREVIOUS REPORTS

Weiss, A. J., and P. Colombo, Brookhaven National Laboratory, "Evaluation of Isotope Migration-Land Burial, Water Chemistry at Commercially Operated Low-Level Radioactive Waste Disposal Sites, Status Report Through September 30, 1979," NUREG/CR/1289, BNL-NUREG-51143 (1980). Available from the National Technical Information Service, Springfield, VA 22161.

Czyscinski, K. S., and A. J. Weiss, Brookhaven National Laboratory, "Evaluation of Isotope Migration-Land Burial, Water Chemistry at Commercially Operated Low-Level Radioactive Waste Disposal Sites, Status Report, October 1979-September 1980," NUREG/CR-1862, BNL-NUREG-51315 (1981). Available from the National Technical Information Service, Springfield, VA 22161.

EVALUATION OF ISOTOPE MIGRATION - LAND BURIAL
WATER CHEMISTRY AT COMMERCIALY OPERATED LOW-LEVEL
RADIOACTIVE WASTE DISPOSAL SITES
STATUS REPORT OCTOBER 1980 - SEPTEMBER 1981

1. INTRODUCTION

This report presents work performed during the 1981 fiscal year and updates previous program status reports (Weiss and Colombo, 1980; Czyscinski and Weiss, 1981). Based on data obtained to date, we have identified and described areas of further study in the program.

This research program provides data on the chemical and radionuclide composition of disposal trench waters at commercial low-level radioactive waste disposal sites. This information, together with the data on chemical behavior of radionuclides under simulated field conditions, will aid the NRC in licensing and regulation of waste disposal sites, as well as assist in efforts to model groundwater transport of radionuclides. The ability to make predictions on the rate of radionuclide movement along the groundwater flow path is an important factor in the development of these criteria.

A field and laboratory program was continued to study the existing commercial low-level radioactive waste disposal sites. This investigation will describe the physical and chemical properties of the geochemical systems relevant to isotope migration and define the source terms (concentrations in solution) of radionuclides and other solutes in trench waters at the sites.

1.1 Water and Sediment Analyses

The chemical and radionuclide composition of trench waters from commercial low-level radioactive waste disposal sites is important for an understanding of radionuclide migration. Four eastern commercial sites have been sampled: (1) Maxey Flats, KY, (2) West Valley, NY, (3) Barnwell, SC, and (4) Sheffield, IL. The Maxey Flats disposal site was sampled four times over a six-year period (1976-1981); the Barnwell site twice; the West Valley site three times; and the Sheffield site once.

These analyses are part of the source term data base studies of the commercial disposal sites. The well waters were also sampled to: (a) identify and characterize radionuclides that might be migrating along groundwater flow paths and (b) compare and contrast local groundwater compositions to those of the trench waters. Procedures for the collection, preservation, processing, and analysis of the trench waters have been developed to supplement standard methods when required. These procedures are continually updated as needed. The water analysis scheme includes radionuclide, inorganic (major, as well as minor cations and anions), and the organic components. Samples of trench water from the Barnwell site were collected in May, 1980. Analytical results for ^{90}Sr and plutonium isotopes present as soluble species in the trench waters are presented in this report for the Barnwell site.

An integral part of the research program is the analysis of sediment cores recovered from some of the commercial waste burial sites. Analysis of these cores in terms of their radionuclide profile as a function of depth beneath a burial trench is useful because it provides: (a) the field data required for verifying modeling calculations, (b) the information on the behavior of nonsorptive radionuclides, especially tritium, in the unsaturated zone above the water table, and (c) a comparison of results with laboratory sorption studies against the field situation.

Four cores, collected by the U. S. Geological Survey from beneath selected Barnwell disposal trenches (Figure 1.1), were analyzed. The results obtained include: (a) pore water tritium content, (b) total sediment and pore water gross alpha and beta activities, (c) isotopic analyses for ^{90}Sr and $^{238,239,240}\text{Pu}$ of selected core sections. Except for tritium, the radionuclide concentrations were very low.

1.2 Geochemistry

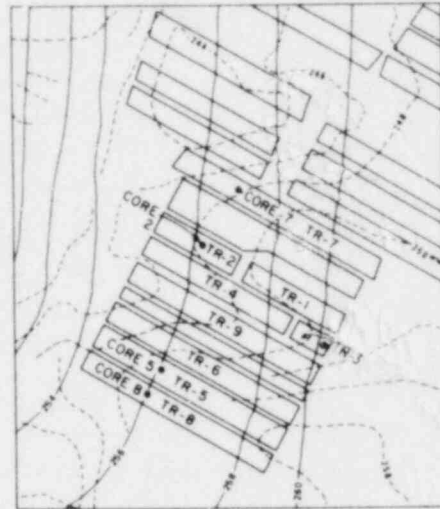
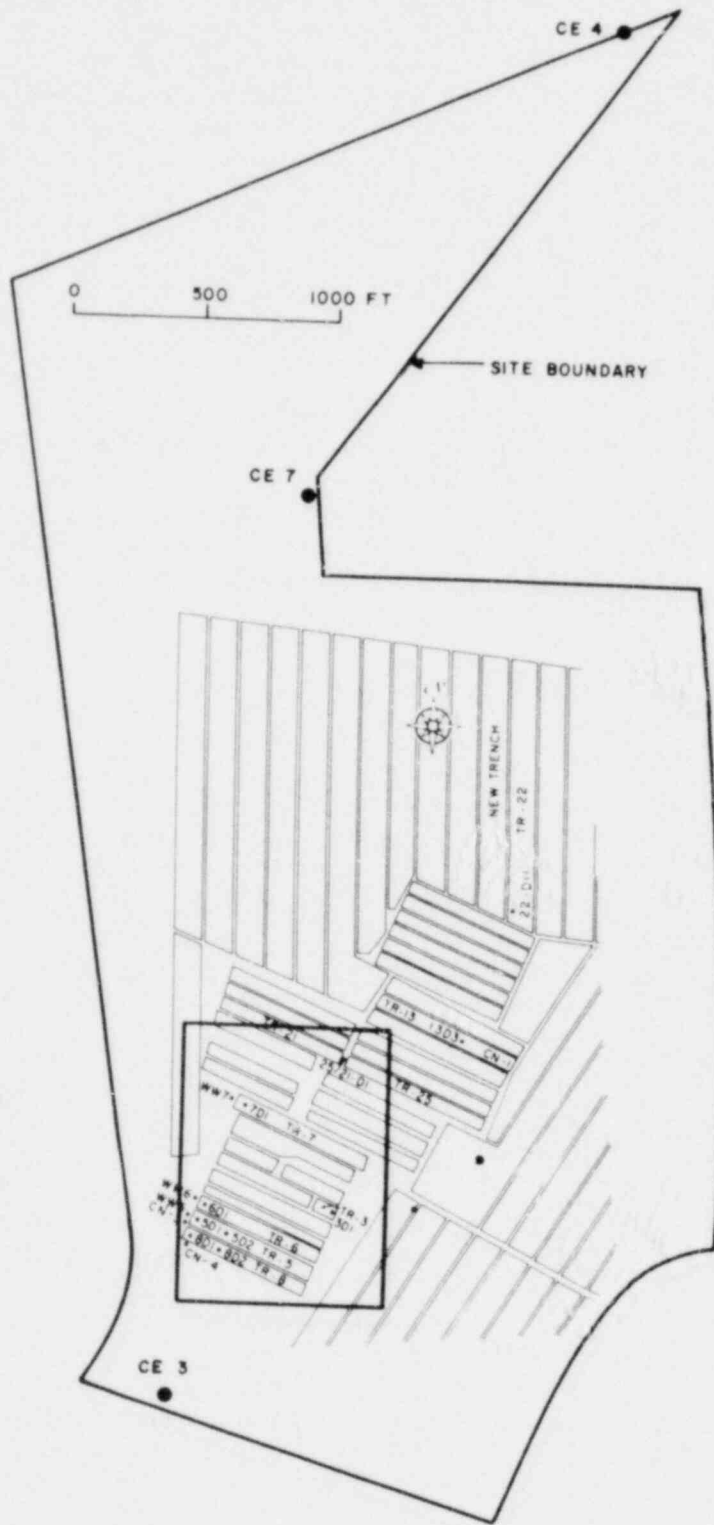
The geochemical aspects of radionuclide migration and retardation addressed in this study are: (a) radionuclide sorption, (b) the stability of cobalt complexes in anoxic water and (c) chemical changes and precipitation reactions which can affect radionuclide migration. Results obtained from these studies are expected to have direct application to modeling studies of the sites and to establish siting criteria and improved burial practices at future sites.

1.2.1 Radionuclide Sorption

The sorption capacity measurements of the sediment at commercial disposal sites is essential to the evaluation of the sediment characteristics for radionuclide retention. Laboratory determination of radionuclide retention by the sediment involves the use of either batch or column tests. The commonly used batch test involves tumbling a mixture of sediment with radionuclide spiked water.

The purpose of conducting batch sorption studies using site-specific materials from the Barnwell site is twofold: first, to characterize the sediment sorptive properties in the trench environment, as part of the source term investigations of commercial burial facilities, and second, to formulate general testing guidelines based on comparison of batch and column test results. Preliminary results for some of these batch tests were presented previously (Czyscinski and Weiss, 1981).

A flow-through recirculating water column test was also used to determine radionuclide sorption. The recirculating system avoids the grinding effects of tumbling which could change the average particle size of the sediment and its sorption capacity. The batch test results were compared against those determined for a small sediment column with a recirculating water system (a "loop" experiment). This loop experiment is essentially a batch experiment in that it is a closed recirculating system in which the radionuclides are allowed to reach a steady-state concentration in the solution and solid phases.



NOTE DASHED LINES REPRESENT ORIGINAL
GROUND CONTOURS
NOTE SOLID LINES REPRESENT PROPOSED
COMPLETED CONTOURS

Figure 1.1 Locator map of the Barnwell disposal facility.

Laboratory studies were continued to measure the radionuclide sorption capacity of shale from Maxey Flats under conditions which simulate the anoxic groundwater environment of the disposal trenches. These studies were performed using a batch technique which allows anaerobic bacterial process to function and thus minimize the effect of diffusion of air into sample solutions. The trench waters often contain large amounts of ferrous iron, which on exposure to air becomes oxidized, and subsequently precipitates as ferric oxyhydroxide. Radionuclides in the trench water often coprecipitate with the iron oxyhydroxides. The sensitivity of ferrous ion to oxidation requires that air be excluded during sample preparation procedures and subsequent manipulations. This study was designed to test the effectiveness of the proposed sorption measurement technique and to evaluate the sensitivity of the resulting sorption to the solution/solid ratio.

Removal of some radionuclides by sorption or coprecipitation with hydrous ferric oxides formed as a result of the oxidation of ferrous iron-rich anoxic groundwater presents the possibility of a serious experimental error. Results for the radionuclide sorption capacity of the sediment from anoxic groundwater would be erroneously high due to coprecipitation of radionuclides. Consequently, any sorption test using anoxic waters must prevent the oxidation of ferrous iron and subsequent precipitation of iron oxyhydroxide.

1.2.2 Organo-Radionuclide Complexes in Anoxic Water-Soil Regimes

Organic decontaminating solutions and other chemical wastes are placed into disposal trenches and contribute organic chelates to the trench waters. Subsurface migration of radionuclides and toxic metals as organo-metallic complexes could contaminate surrounding soils and groundwaters.

Enhanced migration of ^{60}Co through the groundwaters as a result of complexing (with EDTA)* has been reported in the literature (Means et al., 1978). Since this study at Oak Ridge National Laboratory, attention has been focused on the presence and behavior of organic chelating agents in disposal trench environments (Warren, 1974; Means et al., 1980; Tredge, 1975; 1977; Czyscinski and Weiss, 1981; Kirby, 1981; Cleveland and Rees, 1981). Most of this work has focused on the stability of the chelating agent rather than that of the complexed radioisotope, largely because demonstrating the existence of an organo-radionuclide complex in an actual trench water is a difficult analytical task. In this respect, gel filtration chromatographic experiments performed in this program (Czyscinski and Weiss, 1981), failed to convincingly demonstrate the existence of organo-radionuclide complexes in actual trench waters. The existence of such complexes in trench waters would not be surprising in that the widespread use of organic chelating agents in decontaminating solutions implies that a substantial portion of many radionuclides may be in a complexed state when placed in the disposal trenches, where they can be subsequently leached into the trench waters. The question of the existence and temporal stability of such complexes in the field situation remains unresolved.

*EDTA - Ethylenediamine tetraacetic acid.

Considerable work on trace metal complexes with EDTA, NTA*, and DTPA** in soil environments has been performed by workers concerned with plant nutrition (Reddy and Patrick, 1977; Sommers and Lindsay, 1979; Nowell and Lindsay, 1969; 1972, Lindsay, 1979). Much of this work has direct bearing on the behavior of similar complexes in disposal trench environments. The controlled environment studies (Reddy and Patrick, 1977) are of particular interest in this respect. In these studies, the anoxic pore water-soil regime of waterlogged soils was simulated in a laboratory-scale controlled environment chamber. Copper and zinc complexes (with EDTA and DTPA) were introduced and the amount of metal remaining in solution monitored as a function of time. Multiple experiments were performed at constant Eh conditions which ranged from well oxidized (+ 500 mv) to strongly reduced (-200 mv). Under reducing conditions, the metals were rapidly removed from solution. The authors maintain that sulfide ion generated in the anoxic water regime precipitated the trench metals as sulfides.

These experiments suggest that in disposal trenches where strongly anoxic water is present (such as those at the Maxey Flats and West Valley, disposal sites), the chemical environment may be capable of removing some radioisotopes from solution by this precipitation mechanism. For these experiments, ^{60}Co or ^{65}Zn in the form of a complex was added to the anoxic water, and the amount of cobalt in solution monitored as a function of time, for constant Eh and pH conditions corresponding to those in the actual disposal trenches. Cobalt was selected because it is a radioisotope common in the disposal trenches (Weiss and Colombo, 1980; Czyscinski and Weiss, 1981), and likely to be strongly complexed with organic chelating agents. Cobalt complexes of EDTA, NTA, and DTPA were studied by the methods of Reddy and Patrick (1977) to see if they are removed from solution. In addition, ^{65}Zn -EDTA was used to study the complex stability under the reducing conditions in our experimental chamber.

If results similar to those published (Reddy and Patrick, 1977) are observed, it would indicate that the strongly reducing, anoxic water regimes developed in some disposal sites can act to remove cobalt from organic complexes, and thereby help to prevent the enhanced migration due to complexing.

1.2.3 Oxidation of Disposal Trench Waters

The total radionuclide retention capacity of the geochemical system is the sum of all the mechanisms which can prevent radionuclide migration from disposal trenches. Sorption processes include the relatively rapid and reversible ion exchange at the surface of minerals and the relatively slow irreversible diffusion of ions into mineral matrices (Freeze and Cherry, 1979; Forstner and Wittmann, 1979). However, for the anoxic, chemically reducing

*NTA - Nitriiotriacetic acid.

**DTPA - Diethylenetriamine pentaacetic acid.

geochemical environments of some eastern disposal sites, Maxey Flats and West Valley, other retention mechanisms are possible. Precipitation reactions can coprecipitate radionuclides and can have a considerable effect on radionuclide retention. Sulfide ion generated by bacterial reduction of sulfite ion results in the coprecipitation of radionuclides by ferrous sulfide (FeS). Carbon dioxide, generated by the bacterial decomposition of organic waste, can also coprecipitate radionuclides as metal carbonates. In addition, trench waters migrating away from immediate trench environment and mixing with more oxidized groundwaters will precipitate iron oxyhydroxides. All these precipitation reactions can retain radionuclides.

Trench waters, in a strongly reducing regime, reflect a combination of two processes, (1) leaching of the burial wastes and, (2) bacterial degradation of organic components in the trench water. When these waters migrate from the immediate trench environment, mixing with local groundwater will result in alterations of the chemical systems. Understanding the chemical changes taking place along migration paths is important for several reasons:

- (a) to design laboratory sorption experiments,
- (b) to supply reliable input data to modeling efforts involving mass transport calculations, and
- (c) aid in the interpretation of field data which are correlated with modeling predictions.

For greatest reliability, the conditions for laboratory experiments should approximate those in the field situation as closely as possible. Sorption experiments using site-specific trench water and soils have been carried out in this program for some time. These determinations were designed to measure the retention behavior of the geochemical system in the trench proper. However, selecting experimental conditions for sorption determinations aimed at characterizing the retention behavior along migration paths requires a knowledge of the chemical changes resulting when these waters move away from the trench proper. This information is also required to formulate general testing guidelines for evaluating the sediment retention capacity at candidate disposal sites.

Modeling calculations of subsurface radionuclide transport involve mass transport parameters for which proper selection of input data is required for best results. Knowledge concerning the chemical evolution of trench waters along migration paths would allow judicious selection of sorption coefficients for such calculations. This selection process is particularly important if the results of modeling studies are to be compared against field data.

Trench waters found to be highly reducing chemical regimes share many characteristics in common with naturally occurring anoxic waters, such a low redox potential (Eh) and high titration alkalinity. They differ in one important aspect in that many of the trench waters contain high contents of dissolved ferrous iron (up to 1400 mg/L) derived from the waste. The oxidation of ferrous iron and subsequent precipitation of ferric oxyhydroxides is one

of the most acid generating reactions in nature. Therefore, even partial oxidation of trench waters during subsurface migration may result in large pH changes along the flow paths. In contrast, trench waters also contain high titration alkalinities (alkalinity can also be regarded as the acid neutralizing capacity) which would tend to buffer the pH. To determine the relative importance of these two mechanisms in controlling the pH during migration, trench waters were exposed to oxygen and the Eh, pH, and titration alkalinity measured after iron oxidation and precipitation occurred.

It is realized that the chemical system in these waters does not represent a condition expected to be duplicated in the field, except in the cases where diluted trench waters reach ground surface, either via springs or groundwater discharge into streams. However, this extreme case of oxidation should indicate the maximum changes possible and show the trends to be expected along migration paths.

Burial site trench waters may enter a less reducing environment, upon migration out of a trench, in which oxidation will occur. The changes in the oxidation states of various solutes affects their solubility. The most evident result of exposing an anoxic trench water to oxidizing conditions, is the precipitation of ferric oxyhydroxides as the ferrous iron is oxidized to the ferric state. Some radionuclides may be removed from solution by coprecipitation with the ferric oxyhydroxides. Coprecipitation may be a significant mechanism for retarding the migration of radionuclides. Sorption of heavy metals on ferric oxyhydroxides is an effective mechanism for the removal of trace metals from solution (Freeze and Cherry, 1979). Cobalt in natural waters would be expected to have a strong affinity for the hydroxyl group of $FeO(OH)$ incorporating itself into the outer surface by exchange of H^+ ion. For example, hydrous iron-manganese coatings of sediments and deep sea ferromanganese concretions were found to be enriched in cobalt (Forstner and Wittmann, 1979).

An experiment was performed to study the oxidation and coprecipitation process in a burial site trench water. The removal of radionuclides from solution will be measured as ferric oxyhydroxide precipitation from a trench water undergoes slow oxidation and will be reported in a subsequent report. The pH, redox potentials and dissolved iron concentrations were monitored while the experiment was in progress. Preliminary results are reported.

1.3 Summary of the Year's Activities

A detailed description and results of the work performed are given in this report. Brief descriptions of the research projects are summarized below.

Water and Sediment Analyses

- Trench waters from the Barnwell site were analyzed for their ^{90}Sr and $^{238},^{239},^{240}Pu$ concentrations.

- Sediment cores from beneath four Barnwell disposal trenches were analyzed for their radiochemical content as a function of depth. The tritium content of the sediment pore water was also determined.

Sorption Experiments

- Sediment and trench water from the Barnwell site were used for batch radionuclide sorption experiments.
- A recirculating water "loop column" was used to measure radionuclide sorption from a synthetic Barnwell trench water and Hawthorne sediment. The results were compared with batch sorption results.
- An attempt was made to measure radionuclide sorption using anoxic trench water and shale from the Maxey Flats site in specially designed containers to prevent oxidation of the trench water.

Anoxic Water Chemistry

- Experiments to measure the persistence of ZnEDTA, CoEDTA, CoNTA and CoDTPA complexes in shale and anoxic water mixtures that simulate a trench environment at Maxey Flats were performed. These experiments were designed to evaluate the enhancement of ^{60}Co migration attributed to complexing with EDTA.
- The pH, Eh, and alkalinity of anoxic waters from Maxey Flats and West Valley sites were measured before and after oxidation. The results provide information about the oxidation/reduction changes that could occur along migration paths and are important in the interpretation of data from field studies and modeling calculations.
- An experiment was designated to measure the Eh buffer potential of the ferric/ferrous iron couple and the coprecipitation of radionuclides on ferric oxyhydroxides. Anoxic trench water from the West Valley site, containing a high concentration of ferrous iron, was allowed to slowly oxidize. During the oxidation processes, the changes in the radionuclide and ferrous iron concentrations and in pH and redox potential were monitored as a function of time.

2. EXPERIMENTAL

2.1 Trench Water Source Term Investigations at the Barnwell Site - Strontium and Plutonium Analyses

Waters from the trenches were analyzed for their dissolved radionuclides after filtration through a 0.45 μm membrane filter. Radiochemical measurements are made on an acidified aliquot of the filtrate. Strontium-90 is determined by radiochemically separating strontium from the trench water sample and counting the in-growth of yttrium-90 with a low-level beta counter. Plutonium isotopes are radiochemically separated from other alpha emitting radionuclides by anion exchange chromatography and electroplated onto a counting disc. Plutonium isotopes on the disc are measured by alpha spectroscopy with a surface barrier silicon detector.*

2.2 Radionuclide Analysis of Sediment Cores from Beneath Disposal Trenches at the Barnwell Site

Gamma-ray spectra [Ge(Li) detector] of the sealed, wet, whole, approximately 30-cm-long, sediment core sections were taken to determine and identify gamma emitting radionuclides present. Gross gamma-ray spectra of the sealed whole core sections showed only a very small concentration of ^{60}Co at the top of the trench 2 core. Any plan to separate the pore water and sediment to determine the radionuclide phase distributions would be futile. Hopefully, more sensitive and detailed analysis would supply positive results even if at low activity levels. Earlier plans by Czyscinski and Weiss (1981), to determine the mineral radionuclide associations were abandoned. Most radionuclides did not reach even the top sediment core sections in appreciable concentrations.

After the preliminary gamma-ray scan, the sediment core sections were subdivided into small cylinders, approximately 2.5 cm in diameter by 5 cm in length. The cylinders were kept in preweighed glass weighing bottles equipped with a ground glass lid to retain the moisture.

A detailed description of the distillation apparatus and procedure used to determine the tritium content of the pore water has been described earlier (Czyscinski and Weiss, 1981). Briefly water was vacuum distilled from the core plugs. The tritium activity of the distillate was determined by liquid scintillation counting. The sediment cores were completely dried and used for subsequent analyses.

After the pore water was removed by distillation, the cylindrical plugs were gamma-ray counted on a Ge(Li) detector. A detailed description of the calibration standards and the gamma ray analysis will be given in a subsequent report.

* ^{90}Sr and $^{238,239,240}\text{Pu}$ analyses were performed by EAL Laboratories, Richmond, California.

Gross alpha and beta activity was determined on samples of approximately one-half gram removed from the core samples after gamma-ray analyses. Material was removed from several portions of the cylindrical sample so that a representative subsample was obtained for counting. The sediment material was placed in a two-inch-diameter planchet, dispersed in water and then dried under an IR lamp. Ten-minute counts were taken to get an estimate of the gross activity in the cores and select procedures for more detailed analyses. A low-level alpha-beta gas flow proportional counter (Canberra) with a 2 π configuration was used for the measurements. A measure of natural background activity in the sediments was obtained by counting several uncontaminated sediment samples of similar mineral composition and texture from the area immediately surrounding the disposal site.

Strontium and plutonium analyses were made on samples which had significant gross beta or alpha activity. These samples were from the upper portion of Core 2 and the "hot spots" from Cores 7 and 8. Ten gram samples were used for the analysis. Strontium-90 was determined by radiochemically separating strontium from the sediment samples, waiting for the ⁹⁰Y to achieve a steady-state in-growth activity, and determining the ⁹⁰Y beta activity with a low-level gas flow proportional counter.

Plutonium isotopes in ten-gram sediment samples were radiochemically separated from other alpha-emitting radionuclides by anion exchange chromatography and electroplated onto a counting disc. Plutonium isotopes on the disc are measured by alpha spectroscopy with a silicon surface barrier detector. The chemical yield and alpha counting efficiency was determined by the addition of an internal ²³⁶Pu or ²⁴²Pu standard.

2.3 Batch Sorption Experiments - Barnwell Trench Waters and Hawthorne Sediment

Sample preparation and experimental procedures for handling anoxic waters have been described previously (Czyscinski and Weiss, 1981). For the more oxidized trench waters from Barnwell, the sample preparation procedure is identical except that the use of an argon atmosphere to prevent oxidation is not necessary.

The sediment was a silty-sand from the disposal site (Hawthorne formation). It was supplied by J. Cahill (U.S. Geological Survey) and was sampled from a depth corresponding to the trench bottoms. The sediment composition is presented in Table 2.1.

Trench 6D1 water, (collected May, 1980), was selected based on the results of inorganic and radiochemical analyses which showed it to have a composition intermediate between the extremes shown by the analyses of many trench waters from Barnwell (Czyscinski and Weiss, 1981). Complete results of the inorganic and radiochemical analyses of the trench waters are presented elsewhere (Czyscinski and Weiss, 1981). Table 2.1 shows the major components of the trench water.

Table 2.1

Characterization Data for Solid and Liquid Phases
Used in Batch Sorption Experiments - Barnwell Disposal Site

Soil Phase		Liquid Phase	
Silty-Sand (Hawthorne Formation)		Trench Water-6D1 (mg/L)	
Sand:silt:clay	75:10:15	Titration Alkalinity (as CaCO ₃)	86
Surface Area - (m ² /g)	0.3-13	Chloride	13.3
Cation Exchange Capacity (meq/100 g)	6.0	Sulfate	44.5
Organic carbon (wt %)	0.03	Calcium	14
Extractable Iron (wt %)	0.2-0.3	Magnesium	1.4
Carbonate (wt %)	0.0	Potassium	3.0
Mineral Content		Sodium	28
Quartz	85%	Iron	<1
Mica	5-10%	pH	6.1
Kaolinite	5-10%	Eh _{NHE} (mV)	+350
Feldspar	<2%		
Goethite	<5%		
Hematite	<5%		
Heavy Minerals	<2%		

The batch experiments were set up with a variable solution/soil ratio ranging from 20/1 to less than 5/1. As mentioned earlier, one of the reasons for performing these experiments is to compare the results of batch and column experiments. By increasing the amount of soil relative to water in the batch tests, it may be possible to extrapolate any trend observed in the results to the solution/soil ratio to be expected in a column experiment. In this way, a prediction for the column test can be derived from batch test results. The solution/soil ratio of 20/1 was included so that results of the Barnwell batch studies can be compared against the anoxic water batch tests performed with Maxey Flats and West Valley trench waters and soils which were performed for this solution/soil ratio by (Weiss and Colombo, 1980). The isotopes used were the same as used for previous sorption experiments; namely, ⁶⁰Co, ⁸⁵Sr, ¹³⁷Cs, ¹³⁴Cs, ²⁴¹Am, and ¹⁵²Eu, and their concentrations are the same in all the samples.

After the samples were prepared, they were monitored periodically (gamma counting of the liquid phase) during the 119-day contact time. At the end of this period, the majority of the samples had reached steady-state conditions. The sample containers were then disassembled for final counting of the separated liquid phases.

2.4 Recirculating Water "Loop" System Sorption Experiments - Barnwell Synthetic Trench Water and Hawthorne Sediment

A synthetic trench water was prepared for these experiments. The composition was derived from the water analyses of Barnwell disposal site - trench 6D1 - collected May 1980 and reported (Czyscinski and Weiss, 1981). The composition of the synthetic water is shown in Table 2.2.

Table 2.2

Composition of Synthetic Barnwell Trench Water^a

Cations	Concentration mmoles/L	Anions	Concentration mmoles/L
Na ⁺	1.43	HCO ₃ ⁻¹	0.40
K ⁺	0.030	SO ₄ ⁻²	0.19
NH ₄ ⁺	0.084	Cl ⁻¹	1.83
Ca ⁺²	0.30	NO ₃ ⁻¹	0.37
Mg ⁺²	0.41		
Mn ⁺²	0.008		

SiO₂ = 0.096 mmoles/L^b

^aThe composition of the synthetic trench water was formulated to resemble water from trench sump 6D1 at Barnwell, SC. The pH of the solution is adjusted to 6.0 with hydrochloric acid.

^bAdded as sodium metasilicate Na₂SiO₃·9H₂O.

A synthetic "trench water" was used because this experiment is a first attempt at using the loop experimental design. It was thought desirable to avoid using actual trench water until the technique is mastered in order to avoid exhausting the limited stock of trench waters.

A silty sand (Hawthorne formation) was used from the Barnwell disposal site (supplied by J. Cahill - U. S. Geological Survey). The sediment was obtained at a depth equivalent to the trench bottoms.

An intact piece of undisturbed core material was force fitted into a Lucite cylinder thereby restricting the flow along the sides of the column. The columns were conditioned to the synthetic groundwater by adding fresh 50-mL aliquots of synthetic groundwater each day for a week, Figure 2.1.

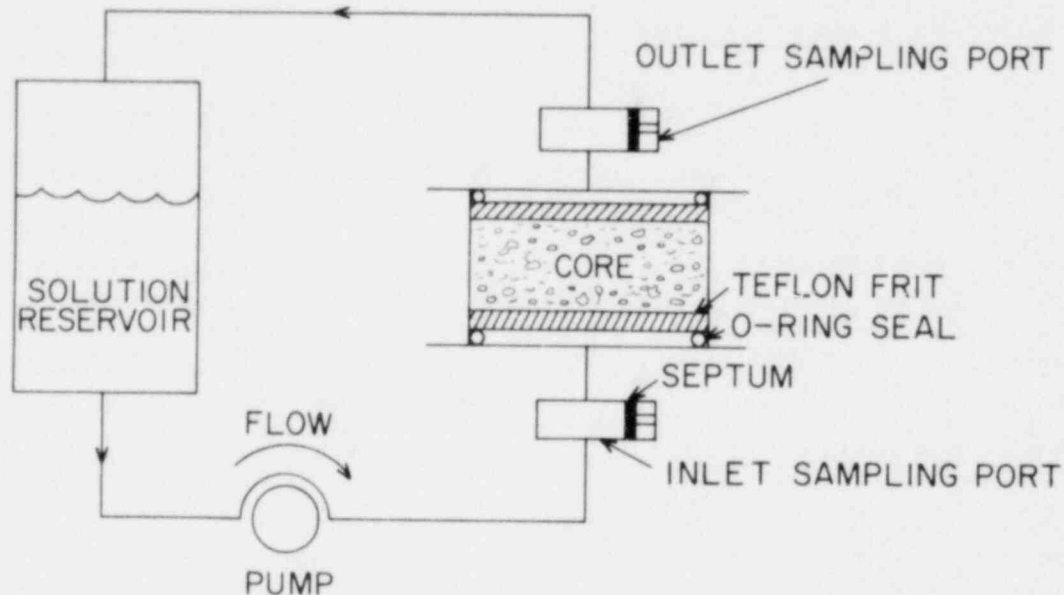


Figure 2.1 Schematic diagram of the recirculating "loop" apparatus.

Water flow through the column was characterized by measuring the rates at which tritiated water moved through the system. Approximately 0.1 μCi of tritiated water (0.1 mL) was injected into the water stream through the entrance port just beneath the column. Contamination of the water reservoir was avoided by connecting the column outlet stream directly to a waste bottle. By means of a 1-mL hypodermic syringe, water samples (0.1 mL) were removed periodically from the column outlet sampling port. The samples were then added to 10 mL of Instagel liquid scintillation cocktail and counted in a LSC system for 10 minutes (Searle Analyzer 92 Liquid Scintillation Counter).

The isotopes selected were those used in previous batch experiments; namely, ^{60}Co , ^{85}Sr , $^{134,137}\text{Cs}$, ^{241}Am and ^{152}Eu . The radioisotope-column-type combinations used were as follows:

1. ^{152}Eu alone - repacked core material;
2. ^{241}Am , ^{85}Sr , $^{134,137}\text{Cs}$ and ^{60}Co - repacked core material;
3. ^{241}Am , ^{85}Sr , $^{134,137}\text{Cs}$ and ^{60}Co - intact core material.

Tracer solutions were prepared by evaporating under an infra red lamp 0.1 mL of 20 μCi , isotope carrier free, 0.5 M HCl solutions (8 M HNO_3 in the case of ^{241}Am) to dryness. The residue was wetted with 0.25 mL of concentrated HCl and the solution again evaporated to dryness. The chloride salts were then dissolved in 150 mL of synthetic groundwater.

Several scoping experiments were performed to characterize the behavior of the selected radionuclides, and to compare these results with those obtained from earlier batch experiments. The columns were conditioned by recirculating synthetic groundwater. The flow rates for an intact core column were determined by the time required for tritiated water to pass through the core. Radionuclide sorption tests were conducted by adding a spike to the reservoir and monitoring the column effluent as a function of time. A 1-mL aliquot was removed daily from the sampling port above the column. The sample was counted for its radionuclide content with a Ge(Li) detector using a pulse height analyzer.

2.5 A Batch Radionuclide Sorption Method for Anoxic Trench Waters

Water samples for the determination of radionuclide sorption were collected from the disposal site, using the anoxic collection procedure described in an earlier report (Weiss and Colombo, 1980). These waters were stored in glass bottles in a nitrogen atmosphere to preserve the trench redox conditions, and at approximately 4°C to minimize bacterial activity. The water samples used in the sorption experiments are listed Table 2.3. Analyses of the inorganic components of these waters were reported earlier (Czyscinski and Weiss, 1981).

Table 2.3

Iron Concentrations in Maxey Flats Disposal Site Trench Waters
Used in Sorption Experiments

Trench No.	Collection Date	Iron (mg/L)	$\frac{[\text{Fe}^{+2}]}{[\text{Fe}^{+3}]}$
19S	11/79	58	30
27	11/79	1400	39
T-2E	11/79	1.6	---

Chemical reactions related to microbial activity continue during the sorption test. The three principal types of reactions that could affect the sorption capacity of the sediment are, (1) the degradation of organic substances, (2) the reduction of nitrate ion, and (3) the reduction of sulfate ion (Freeze and Cherry, 1979). Hence, even with waters that contain low concentrations of ferrous iron, maintaining anoxic conditions may be necessary for a realistic test of sorption capacity (Forstner and Wittmann, 1979). The

purpose of this experiment is to test a procedure proposed for maintaining water conditions that simulate the disposal trench environment.

Samples representative of the sediment at the Maxey Flats site were supplied by the United States Geological Survey. Unweathered Nancy Shale was obtained from trench 46 at an approximate depth of 20 feet. The chemical and physical characteristics of the Nancy Shale were reported earlier (Czyscinski and Weiss, 1981).

A detailed description of the improved experimental apparatus and sample preparation procedures for working with anoxic waters was reported earlier (Czyscinski and Weiss, 1981). Briefly, the procedure is as follows: spiked trench waters are prepared by evaporating radionuclide tracer solutions to dryness, converting the tracers to chloride salts by evaporation with hydrochloric acid, and dissolving the dry salts in the trench waters. The spiked trench water is added to shale chips in Teflon containers. Containers without shale chips are used for control solutions. All sample handling procedures involving anoxic waters are performed under an inert atmosphere. 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 experiment. Radionuclide activity in solution is measured while shielding the solid phase from the Ge(Li) detector. When the concentration of radionuclides in solution remains nearly constant, the experiment is terminated. At the end of each test, the experimental solutions are processed by (1) centrifuging the samples, (2) filtering the liquid phase through 0.2 μm filters, and (3) counting an acidified aliquot of the liquid phase to determine the amount of radionuclide in solution. These steps avoid interference from radionuclides sorbed on the solid phase. The amount of radionuclides initially in solution are determined from acidified control samples.

For this series of tests, five sample sets were prepared. Each sample set was prepared using a trench water spiked with ^{152}Eu , or a mixture from the following group of radionuclides: ^{241}Am , ^{85}Sr , ^{134}Cs , ^{137}Cs , and ^{60}Co . Aliquots (10 mL) of each solution were used to determine the initial radionuclide concentrations (samples 1SC and 2SC). Control samples (1AC and 2AC) of the spiked trench waters (20-mL) were kept in Teflon containers and treated in the same manner as the K_d samples. These spiked, anoxic solutions, without shale, were prepared to evaluate the degree of wall adsorption of radionuclides. Samples for sorption determinations contained 20 mL of spiked anoxic trench water and varying amounts of shale so that the solution to solid ratio (mL/g) varied from approximately 3 to 26.

Containers containing trench water and shale samples for sorption determinations (tumbled in an argon atmosphere) were periodically monitored to measure the radionuclide content remaining in solution. When steady-state concentrations of the radionuclides in solution were reached, the samples were disassembled in a glove box flushed with ultrahigh purity argon, and the pH, Eh, and activity of each sample solution were measured.

Aliquots (10 mL) of the filtered solutions were acidified (1 mL of 6 M HCl) and counted by gamma-ray spectroscopy using a Ge(Li) detector to determine the final radionuclide concentrations in solution.

2.6 Organo-Radionuclide Complexes in Anoxic Water-Soil Regimes Using a Controlled Environment Chamber

A controlled-environment chamber (Fig. 2.2), similar to the chamber of Patrick et al. (1973) was used in these experiments. It consists of a Lucite container [(a) A]* and lid (b). The lid contains gas inlet and outlet tubes [(b) C] and six air-tight ports [(b) A] that accommodate five electrodes [(b) A] and a septum [(b) B]. A double junction, saturated calomel electrode is used as reference electrode for the redox and sulfide electrodes. Two platinum electrodes monitor the redox potential. Nitrogen gas [(a) D] or nitrogen-air mixtures control the redox conditions. A silver-silver sulfide specific-ion electrode monitors sulfide ion concentrations. A combination pH electrode monitors hydrogen ion concentrations. The pH is controlled by the addition of dilute acid or base. The acid or base is added and the chamber solution is sampled by hypodermic syringes connected to needles inserted through the septum port. Several pH-mV meters [(a) E] record the electrode readings. A magnetic stirrer and stirring bar [(a) F] mix the soil-water contents during the experiments.

The trench water selected for these experiments was that from trench 32 at Maxey Flats. Eh-pH considerations by Czyscinski and Weiss (1981) indicate that this water is in equilibrium with iron sulfide. When this water was collected, field measurements indicated the presence of sulfide ion in the sample Weiss and Colombo, (1980). Black particulate matter was also observed in the sample. Presumably, this is iron monosulfide, which is commonly observed in such environments. It was decided to use a simulated water for the first experiment because the supply of actual trench water on hand was limited.

A synthetic trench water was prepared with a composition similar to water from trench 32 at Maxey Flats. Chemical analyses of this trench water have been reported (Czyscinski and Weiss, 1981). The chemical composition of the synthetic trench water is reported in Table 2.4. The pH is adjusted to 7.0 with dilute H₂SO₄. The sulfate salts and sulfuric acid supply the sulfate source for bacterial reduction and sulfide production.

*[(a) A] refers to Item A in Section (a) of Figure 2.2.

A-CONTROLLED ENVIRONMENT CHAMBER
 B-CHAMBER HEAD WITH ELECTRODES AND SEPTUM PORT
 C-GAS TRAP
 D-GAS
 E-Eh AND pH METERS
 F-MAGNETIC STIRRER

A-ELECTRODE PORTS
 B-SEPTUM PORT
 C-GAS-INLET AND OUTLET

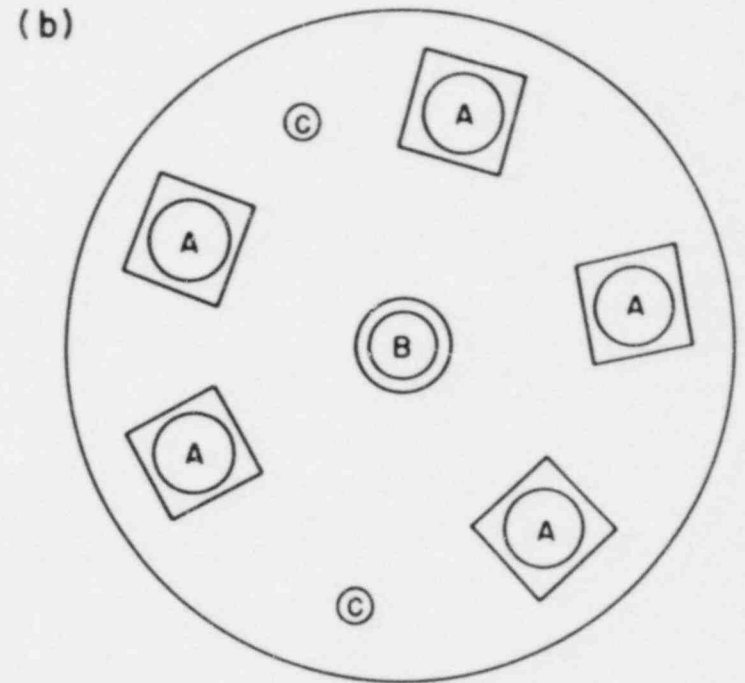
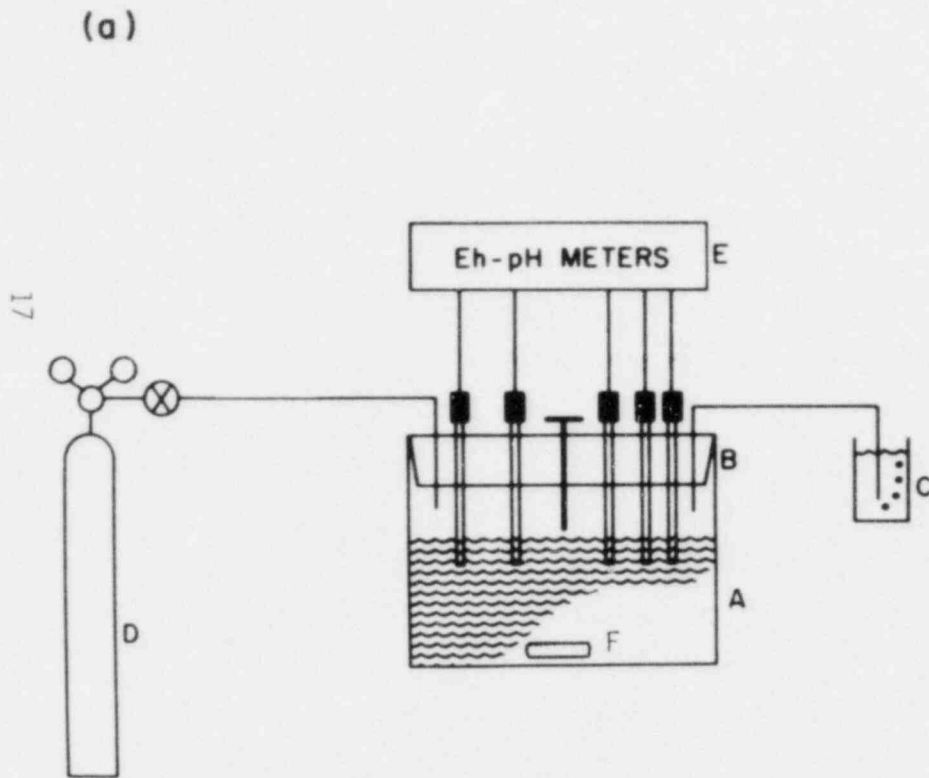


Figure 2.2 (a) Schematic drawing of the controlled-environment apparatus used for the stability experiments and, (b) top view of the controlled-environment chamber.

Table 2.4

Chemical Composition of Synthetic Trench Water^a

Cations	Concentration mmoles/L	Anions	Concentration mmoles/L
Na ⁺	35.0	HCO ₃ ⁻	35.0
K ⁺	4.0	Cl ⁻	10
Ca ⁺²	1.0	SO ₄ ⁻²	20.5
Mg ⁺²	22.5		

^aSimilar to the composition of Maxey Flats trench 32 water.

The solid phase is Nancy Shale from the Maxey Flats disposal site. The shale is disaggregated by ultrasonic agitation. Nancy Shale is an illitic shale with small amounts of quartz, feldspars, and kaolinite and is approximately half silt and half clay in particle size distribution. Characterization data for the shale was reported earlier (Czyscinski and Weiss, 1981).

Equimolar solutions approximately 2×10^{-2} M of cobaltous chloride and NTA, DPTA or EDTA was prepared and spiked with tracer ⁶⁰CoCl₂. An aliquot of a spiked solution was added to the controlled environment chamber such that the initial Co complex concentration in the chamber was approximately 10^{-4} mol/L. Also, a zinc sulfate-⁶⁵Zn-EDTA solution was used as the radionuclide spike in an experiment similar to the Co-complex experiment.

One liter of synthetic trench water, 25 g of disaggregated shale, and approximately 10 g of clam meat (organic source for bacterial degradation) are placed in the chamber. The lid is sealed onto the chamber with silicone sealant and the electrodes are fitted into their ports. Nitrogen gas is bubbled through the solution in the chamber to purge oxygen from the system. The Eh, pH, and sulfide electrodes are monitored while anoxic conditions develop from bacterial degradation of the organic material. The pH is maintained at 7.0 ± 0.2 by adding 1N H₂SO₄. Most experiments are run at the lowest redox conditions, as indicated by the Eh and sulfide electrodes, that are established by the soil-water system. When the desired redox conditions are stabilized, a small aliquot of a tagged stock solution is added through the septum port to give the initial concentrations listed in Table 2.5. The solution is sampled within a couple of minutes and thereafter periodically. The samples are filtered through disposable 0.45 μ m filter assemblies (Gelman Acrodisc) to remove particulate material. The dissolved radionuclide concentrations are determined by gamma-ray counting of the filtrates. Aliquots of the tagged stock solutions are counted as references.

Table 2.5

Initial Metal-Complex Concentrations
Used in Environmental Chamber Experiment

Metal Complex	Concentration (Molarity, M)
CoEDTA (0 mV, NHE) ^a	2.5x10 ⁻⁴
CoDTPA	2.5x10 ⁻⁴
CoEDTA	1.0x10 ⁻⁴
CoNTA	2.0x10 ⁻⁴
ZnEDTA	2.5x10 ⁻⁴

^aExperiments were performed under low-redox conditions (approx. -200 mV and -250 mV, NHE) with one under relatively more oxidizing conditions (approx. 0 mV, NHE).

Five experiments were performed under low redox conditions (approx. -200 mV and -250 mV, NHE) including one under relatively more oxidizing conditions (approx. 0 mV, NHE). The low redox conditions were maintained for CoEDTA, CoNTA, CoDTPA, and ZnEDTA experiments. The more oxidizing condition was used for a CoEDTA experiment. The Eh was adjusted to this condition by adding air through the septum port with a hypodermic syringe and needle.

Manganous ion (as MnCl₂) in an amount slightly higher than the cobalt concentration, is added to the reducing CoEDTA experiment after about 300 hours. Sufficient synthetic trench water is added to 1000 mL. This solution is also sampled periodically filtered, and counted for gamma activity of ⁶⁰Co or ⁶⁵Zn.

2.7 Measurement of pH, Eh, and Alkalinity Changes During Trench Water Oxidation

Anoxic trench waters from Maxey Flats and West Valley were used for these experiments. Waters from the experimental interceptor trenches at Maxey Flats were included because these waters have already undergone some migration along groundwater flow paths. Water from Maxey Flats trenches 33L4 and 33L18 were also studied because of the abnormal pH in these trenches, which are a result of the solidification agents used in them (Weiss and Colombo, 1980).

All disposal trenches, the well UB1A (5/78), and one experimental trench (MF-IT2) were sampled anaerobically. The other trenches and well UB1A (11/79) were sampled aerobically. West Valley trenches 3, 4, 5, 8, and 9 were all sampled anaerobically. Eh measurements were made in the field using platinum

electrodes. Measurements of pH were made either in the field or in the laboratory. In the laboratory, all waters were filtered by an anaerobic filtration procedure and measurements for pH and alkalinities were performed immediately. The anaerobic filtration procedure and analytical procedures were described earlier by Weiss and Colombo (1980). Portions of the filtrates were acidified with nitric acid and analyzed for total dissolved iron by atomic absorption.

Aliquots were removed from the anaerobic and aerobic sample bottles, placed in beakers, and stirred with a magnetic stirrer for several hours. A reddish-brown precipitate appeared in the beakers. Oxidation was complete when no more precipitate appeared in the supernates and the Eh values stabilized. The supernates were filtered through 0.45 μm filter assemblies (Gelman Acrodisc) and analyzed for pH, Eh, and alkalinities.

2.8 Chemical Changes and Radionuclide Scavenging During the Oxidation of a Trench Water

The slow oxidation of a selected trench water was carried out in a controlled environment chamber described in Section 2.6 and illustrated in Figure 2.2.

The trench water selection for this experiment was based on two considerations, namely the chemical composition of the water and the availability of sufficient quantity for the experiment. Water collected from trench 8 at the West Valley disposal site was used because it is representative of anoxic trench waters with a high content of dissolved ferrous iron. Analytical data for this sample was reported previously (Weiss and Colombo, 1980). Trench water was transferred anoxically from a collection bottle into the controlled environment chamber that had been purged with nitrogen gas. After the Eh and pH of solutions remained essentially constant, a mixed radioisotope solution (spike) containing ^{241}Am , ^{85}Sr , ^{134}C , ^{137}C , and ^{60}Co was added to the trench water. The flow of nitrogen gas into the chamber was then stopped. This allowed oxidation of trench water to take place at a slow rate as air entered the chamber by leaking past the seals around probes and the chamber lid. Changes in Eh and pH were monitored by probes in the chamber.

Two-mL aliquots were removed periodically and filtered through a 0.45 μm filter membrane (Gelman Acrodisc). The filtrates were acidified with concentrated HNO_3 and counted to monitor changes in radioisotope activities. A 125 cm^3 closed-end, coaxial lithium-drifted germanium detector was used for measuring radionuclide activity. Eh and pH of solution was measured at each sampling period. The experiment was continued until radioisotope activities, Eh and pH had reached steady-state levels.

At the termination of the experiment the contents of the chamber were filtered through a tared 0.45 μm membrane filter (millipore). The solution was acidified with concentrated HNO_3 and preserved for analysis. The filters were dried, weighed and dissolved in concentrated HNO_3 . The residue from the filter was dissolved in 2.5 mL of concentrated HCl . Solid residues

adhering to the interior surface of the chamber were removed by vigorous scrubbing and rinsing with 6 M HCl. Insoluble residues from the rinse solution were removed by filtration through a 0.45 μm membrane filter (millipore). The filtered chamber rinse solution and the solution from the dissolved filters were combined, diluted to 15 mL, and counted for radionuclide activity.

3. RESULTS AND DISCUSSION

3.1 Trench Water Source Term Investigation at the Barnwell Disposal Site

Results of the radiochemical analyses are presented in Table 3.1 along with data from a previous sampling trip in March 1979.

Table 3.1
Concentration of Dissolved Radionuclides
in Trench Water Samples From the Barnwell Site,^a
[pCi/L (+2%)^b]

Radionuclide	Date	Trench 3D1	Trench 5D2	Trench 6D1	Trench 8D2
Gross alpha	3/79	<1.4 E1	<1.4 E1	1.6 E1 (65)	<9 E0
	5/80	c	c	1.5 E1 (67)	c
Gross beta	3/79	<2.8 E1	4.1 E2 (8.3)	<2.8 E1	7.9 E2 (6.6)
	5/80	c	c	<3.6 E1	c
Tritium	3/79	1.2 E4 (6.5)	9.9 E6 (<1)	5.7 E5 (<1)	4.8 E8 (<1)
	5/80	c	c	6.1 E5 (13)	c
⁶⁰ Co	3/79	<2.2 E1	1.3 E2 (18)	<2.2 E1	2.6 E1 (69)
	5/80	c	c	<2.7 E1	c
¹³⁴ Cs	3/79	<2.1 E1	<2.4 E1	<2.2 E1	<2.2 E1
	5/80	c	c	<2.1 E1	c
¹³⁷ Cs	3/79	<2.3 E1	1.6 E2 (14)	<2.2 E1	<2.5 E1
	5/80	c	c	<2.2 E1	c
²³⁸ Pu ^d	3/79	e	1.4 E0 (56)	e	1.9 E0 (40)
	5/80	c	c	<3.6 E-1	c
^{239,240} Pu ^d	3/79	e	<2.8 E-1	e	4.6 E-1 (110)
	5/80	c	c	<2.8 E-1	c
⁹⁰ Sr ^d	3/79	e	4.2 E1 (10)	e	3.7 E1 (18)
	5/80	c	c	<4.3 E0	c

Radionuclide	Date	Trench 8D3	Trench 13D4	Trench 18D5	Trench 25/21D1
Gross alpha	3/79	c	c	c	<1.4 E1
	5/80	1.1 E1	8.8 E0 (100)	<8.5 E0	1.0 E1 (90)
Gross beta	3/79	c	c	c	1.0 E2 (27)
	5/80	9.6 E2 (4.8)	<3.6 E1	<3.6 E1	<3.6 E1
Tritium	3/79	c	c	c	3.7 E5 (<1)
	5/80	7.8 E8 (<1)	<7.3 E2	<7.1 E2	2.2 E5 (8.3)
⁶⁰ Co	3/79	c	c	c	<2.2 E1
	5/80	3.7 E2 (9.4)	N.D.	<2.4 E1	<2.8 E1
¹³⁴ Cs	3/79	c	c	c	<2.2 E1
	5/80	3.4 E1 (24)	N.D.	<2.3 E1	<2.4 E1
¹³⁷ Cs	3/79	c	c	c	<2.5 E1
	5/80	5.1 E2 (7.4)	N.D.	<2.1 E1	<2.5 E1
²³⁸ Pu ^d	3/79	c	c	c	4.6 E0 (18)
	5/80	5.6 E-1 (80)	7.4 E-1 (80)	<3.6 E-1	4.6 E0 (20)
^{239,240} Pu ^d	3/79	c	c	c	<2.8 E-1
	5/80	<2.8 E1	9.3 E-1 (30)	<2.8 E-1	2.8 E-1 (114)
⁹⁰ Sr ^d	3/79	c	c	c	9.3 E0 (78)
	5/80	4.8 E1 (10)	<4.6 E0	<4.6 E0	<4.6 E0

^aSamples were filtered through a 0.45 µm Millipore filter.

^bNumber in () = +2% counting uncertainty.

^cNot sampled on this date.

^dAnalyses performed by EAL Laboratories, Richmond, California.

^eAnalysis not performed.

The most abundant of the observed radionuclides was tritium. The highest concentrations of ^{238}Pu and ^{90}Sr were observed in trench 25/21 D1 and trench 8D3, respectively. In general, except for tritium, radionuclide concentrations in the Barnwell trench water samples are exceedingly small and often undetectable.

3.2 Radionuclide Profiles of Sediment Cores From Beneath Trenches at the Barnwell Site

The source of radionuclides is the waste emplaced in the trenches. Water accumulates in the trenches due to rainfall infiltration. Accumulated water stays in the trenches long enough to leach the waste and develop high tritium concentrations. The concentration of dissolved radionuclides in the trench water, from trenches 5, 7, and 8 above the sediment cores, were reported earlier (Weiss and Colombo; 1980, Czyscinski and Weiss, 1981), and are shown in Table 3.1. It has not been possible to collect water from trench 2. The concentration of the nonsorptive isotope tritium would be the maximum concentration expected in the pore water of sediments directly below the disposal trench. The tritium concentration in the trench waters are high relative to environmental levels observed in rainwater (NCRP, 1975; Freeze and Cherry, 1979). The concentrations of ^{137}Cs , ^{60}Co , ^{90}Sr and ^{238}Pu are not much greater than those observed for fallout from nuclear weapon testing (Eisenbad, 1973). This situation is characteristic of all the trench waters that have been analyzed from Barnwell (Weiss and Colombo, 1980; Czyscinski and Weiss, 1981).

3.2.1 Tritium

The tritium content of the sediment pore water as a function of depth has been reported earlier (Czyscinski and Weiss, 1981), but is given here for sake of completeness, Figure 3.1, along with core bulk densities and moisture contents. The sediment cores are uniform in texture throughout their length (coarse sands) and show no significant changes in bulk densities or moisture contents, Figures 3.2 and 3.3.

The maximum pore water tritium concentrations are similar to those observed in the trench waters (Figure 3.1 and Table 3.1). The tritium distribution in the sediment core exhibits a minimum at approximately ten meters followed by an increase in tritium concentrations with increasing depth. This profile may represent diluted trench water moving downward through the unsaturated sediment. Rainfall in the southeastern United States is the heaviest in the late winter and early spring months. Rainwater infiltrates the trench caps, briefly accumulates in the trenches, and subsequently migrates downward through the sediment toward the underlying water table.

Based on a hydraulic conductivity of 10^{-5} cm/s, water will migrate approximately three meters in one year period under saturated flow conditions and less under unsaturated flow conditions (Law 1970). 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 trenches 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.

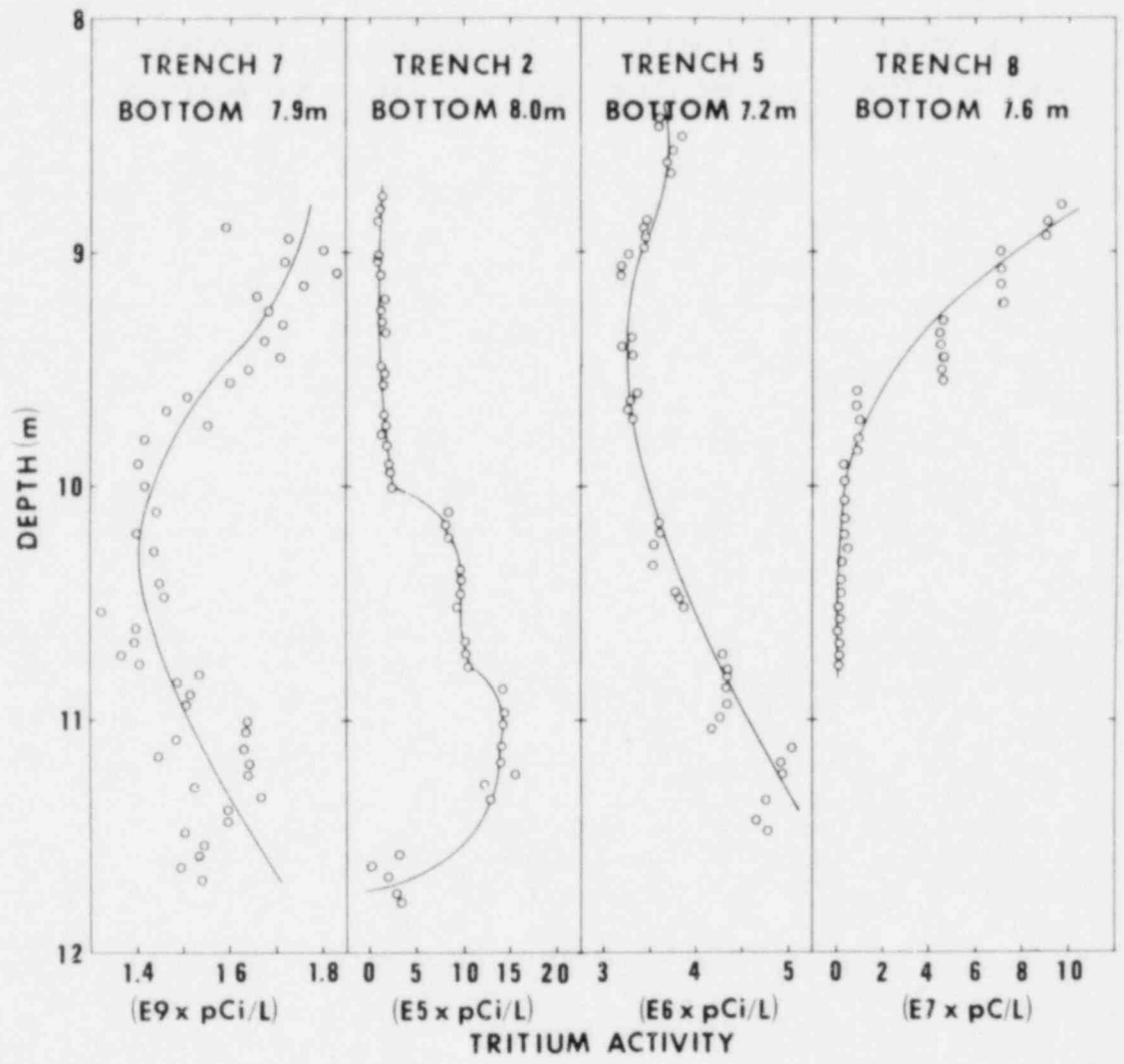


Figure 3.1 Tritium activity vs depth - Barnwell disposal site cores.

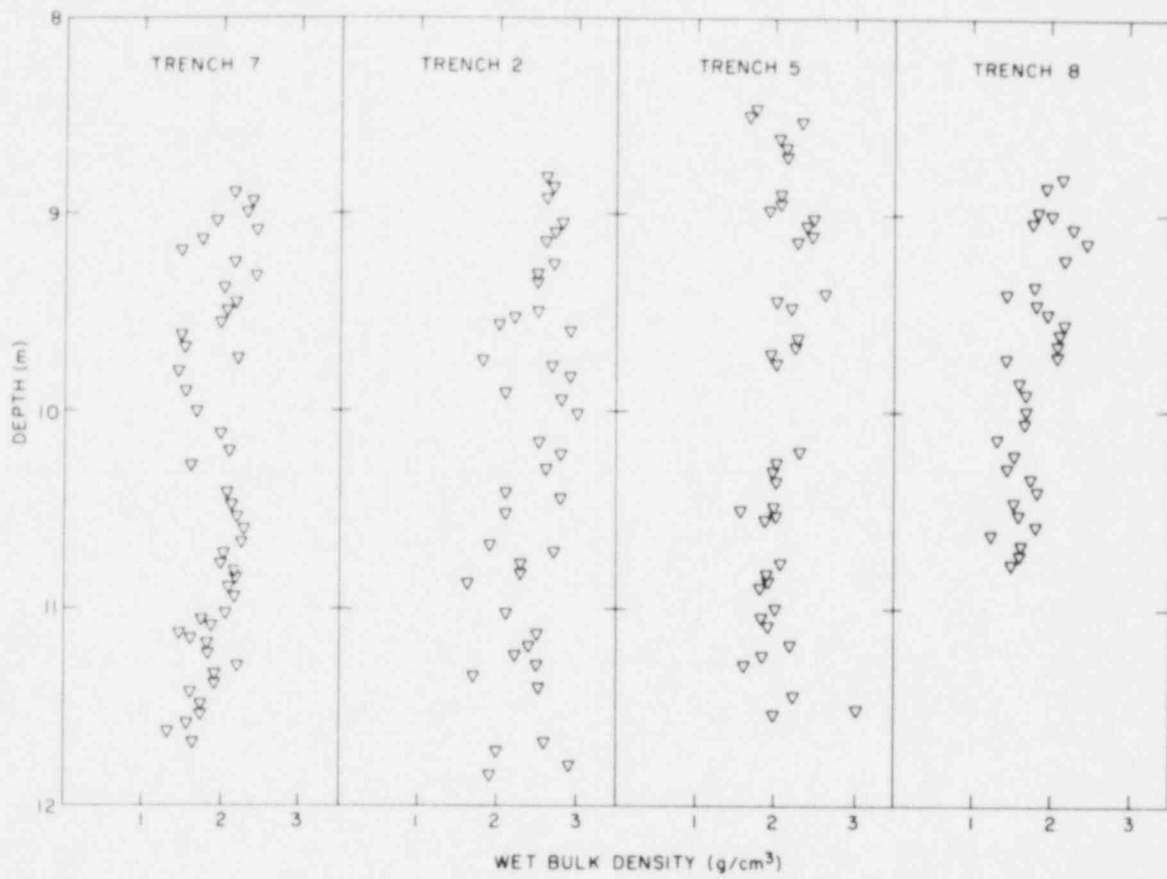


Figure 3.2 Bulk density profiles of Barnwell trench cores.

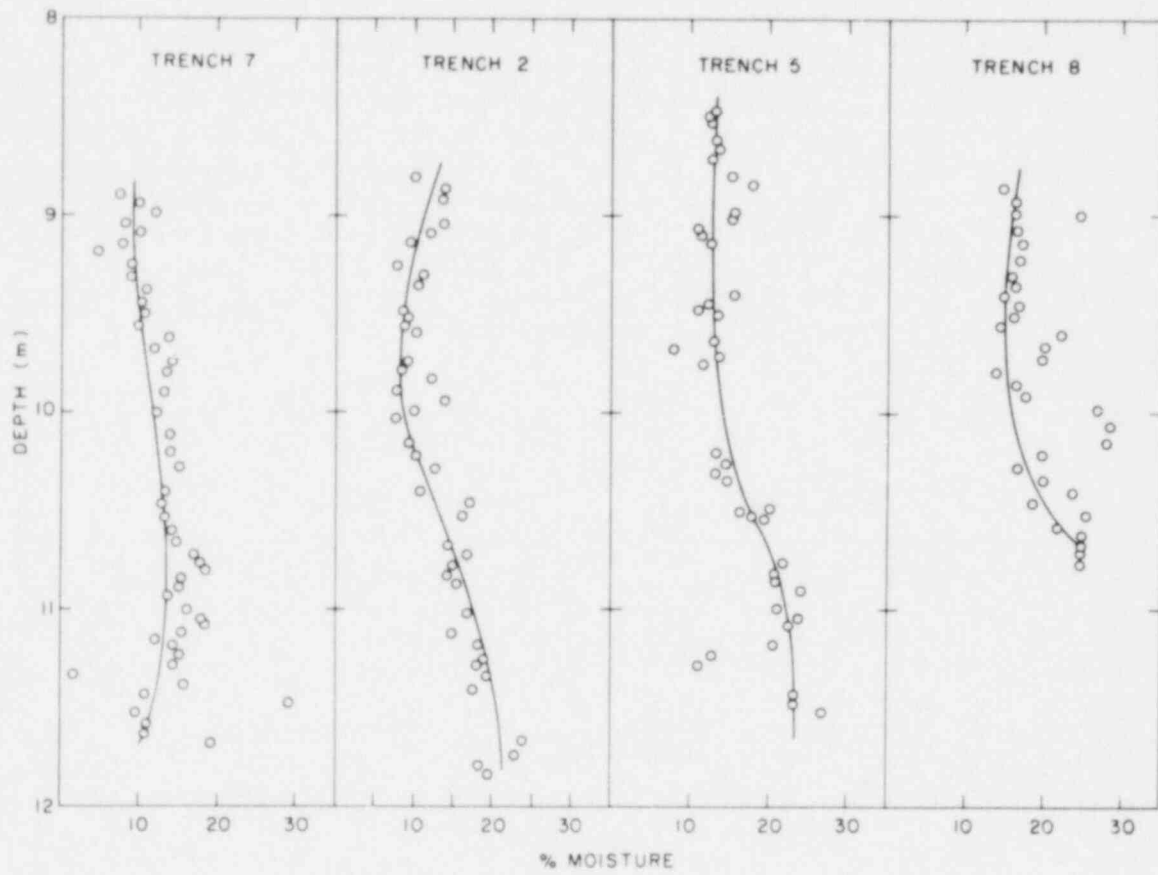


Figure 3.3 Moisture content profiles of Barnwell trench cores.

3.2.2 Gamma Ray Spectra

Preliminary results for gamma-ray spectroscopy showed that ^{60}Co was present throughout the entire length of the core taken from beneath trench 2 at the Barnwell site. The qualitative results showed that the highest concentrations are present in the uppermost 30 cm section of the core. Quantitative results will be reported later.

3.2.3 Gross Alpha and Beta Activity

The results for gross alpha and beta activities in trench core sediments are shown in Tables 3.2, 3.3, 3.4, 3.5, and 3.6. An uncontaminated sediment core had an average gross beta activity of 8 pCi/g with a 6% 2 sigma counting uncertainty and a gross alpha activity of 1.4 pCi/g with a 15% 2 sigma counting uncertainty for a 1000 minute counting period. Only the core from beneath trench 2 showed gross activities significantly above the levels in the uncontaminated samples. The activity is restricted to the uppermost 30 cm of the core, at a vertical distance of approximately 8.75 meters below the land surface. Count rates slightly higher than background were also found in two places in the cores from trench 7 and trench 8. The gross activity in most segments of these cores probably represent statistical fluctuations at background activity levels in the sandy sediments.

Table 3.2

Gross Alpha and Beta Activities in a Sediment Core
From Trench 2^a at the Barnwell Site
(10 minute count)

Depth (m)	Gross Beta ^b Activity [pCi/g(+2 σ%)] ^d	Gross Alpha ^c Activity [pCi/g(+2 σ%)] ^d
8.76-8.81	94(12)	<10 ^e
8.81-8.86	141(10)	30(80)
8.86-8.92	97(12)	<10
9.02-9.04	29(24)	<10
9.04-9.09	18(34)	<10
9.09-9.14	8(66)	<10
9.20-9.25	<4 ^e	<10
9.25-9.30	<4	<10
9.30-9.35	6(80)	<10
9.45-9.49	<4	<10
9.49-9.52	10(44)	<10
9.52-9.56	<4	<10
9.56-9.60	<4	<10
9.70-9.74	5(86)	<10
9.74-9.78	11(50)	<10
9.78-9.83	27(28)	24(88)
9.83-9.91	5(88)	<10
9.91-9.94	11(50)	<10
9.94-10.01	9(50)	<10
10.01-10.03	16(76)	<10
10.11-10.16	<4	<10
10.16-10.22	13(50)	<10
10.22-10.29	9(60)	<10
10.36-10.41	<4	<10
10.41-10.46	15(32)	<10
10.46-10.52	15(32)	<10
10.52-10.67	1(60)	<10
10.67-10.72	<4	<10
10.72-10.77	14(42)	<10
10.77-10.82	7(80)	<10
10.92-10.87	8(66)	<10
10.97-11.02	7(66)	<10
11.02-11.12	7(66)	<10
11.12-11.18	<4	<10
11.18-11.23	4(56)	<10
11.23-11.28	6(74)	<10
11.28-11.34	8(66)	<10
11.34-11.40	10(54)	<10
11.59-11.67	10(52)	<10
11.67-11.74	13(44)	24(88)
11.74-11.79	12(48)	<10
11.79-11.84	11(48)	<10

^aTrench bottom 8.0 meters.

^bCounting time = 10 m., efficiency = 38.0%, transmission factor = 0.8.

^cCounting time = 10 m., efficiency = 23.8%, transmission factor = 0.1.

^dNumber in () = + 2 σ% counting uncertainty.

^eDetection limit = + 3 σ% counting uncertainty.

Table 3.3

Gross Alpha and Beta Activities in a Sediment Core
From Trench 2^a at the Barnwell Site
(1000 minute count)

Depth (m)	Gross Beta ^b Activity [pCi/g(+2 σ%)] ^d	Gross Alpha ^c Activity [pCi/g(+2 σ%)] ^d
8.76-8.81	100(1)	12(13)
8.81-8.86	150(1)	18(11)
8.86-8.92	99(1)	15(11)
9.02-9.04	26(2)	20(10)
9.04-9.09	11(5)	11(15)
9.09-9.14	8(6)	10(16)

^aTrench bottom 8.0 meters.

^bCounting time = 1000 m, ^β efficiency = 38.0% ,
transmission factor = 0.8.

^cCounting time = 1000 m, ^α efficiency = 23.8% ,
transmission factor = 0.1.

^dNumber in () = + 2 σ% counting uncertainty.

Table 3.4

Gross Alpha and Beta Activities in a Sediment Core
From Trench 8^a at the Barnwell Site
(10 minute count)

Depth (m)	Gross Beta ^b Activity [pCi/g(+2 σ%)] ^d	Gross Alpha ^c Activity [pCi/g(+2 σ%)] ^d
8.80-8.87	6(64)	<10 ^e
8.87-8.93	6(70)	<10
8.93-8.99	<4	<10
8.99-9.07	5(89)	<10
9.07-9.14	<4	<10
9.14-9.22	<4	<10
9.22-9.30	<4	<10
9.30-9.35	7(33)	<10
9.35-9.40	7(71)	<10
9.40-9.45	<4	<10
9.45-9.50	<4	<10
9.50-9.55	9(62)	<10
9.55-9.60	8(64)	<10
9.60-9.66	7(68)	<10
9.66-9.72	9(18)	<10
9.72-9.79	<4	36(25)
9.79-9.85	7(60)	20(97)
9.85-9.91	10(48)	<10
9.91-9.98	9(45)	24(87)
9.98-10.06	9(54)	<10
10.06-10.14	7(63)	20(97)
10.14-10.21	12(39)	24(87)
10.21-10.27	4(56)	<10
10.27-10.33	4(43)	<10
10.33-10.40	4(68)	<10
10.40-10.46	5(78)	<10
10.46-10.52	10(55)	<10
10.52-10.57	15(37)	36(25)
10.57-10.62	18(31)	28(79)
10.62-10.67	14(38)	24(87)
10.67-10.72	10(51)	28(74)
10.72-10.77	8(61)	28(79)
10.77-10.82	5(76)	<10

^aTrench bottom 8.0 meters.

^bCounting time = 10 m, β efficiency = 38.0% , transmission factor = 0.8.

^cCounting time = 10 m, α efficiency = 23.8% , transmission factor = 0.1.

^dNumber in () = + 2 σ% counting uncertainty.

^eDetection limit = + 3σ counting uncertainty.

Table 3.5

Gross Alpha and Beta Activities in A Sediment Core
From Trench 5^a at the Barnwell Site
(10 minute count)

Depth (m)	Gross Beta ^b Activity [pCi/g(+2%) ^d]	Gross Alpha ^c Activity [pCi/g(+2%) ^d]
8.43-8.46	6(62)	<10 ^e
8.46-8.50	<4	<10
8.50-8.53	7(60)	<10
8.56-8.62	5(65)	<10
8.62-8.66	<4	<10
8.66-8.71	4(89)	28(79)
8.86-8.91	5(70)	20(97)
8.90-8.94	7(57)	<10
8.94-8.98	8(50)	<10
8.98-9.02	8(50)	<10
9.02-9.06	5(67)	<10
9.06-9.10	9(37)	24(87)
9.10-9.14	6(56)	20(97)
9.37-9.40	<4	<10
9.40-9.44	<4	20(97)
9.44-9.47	<4	24(87)
9.60-9.63	<4	<10
9.63-9.67	<4	24(87)
9.67-9.71	<4	24(87)
9.71-9.75	9(56)	<10
10.16-10.20	7(66)	<10
10.20-10.25	<4	<10
10.25-10.30	6(76)	<10
10.30-10.34	8(76)	20(97)
10.46-10.48	9(57)	<10
10.48-10.50	9(56)	<10
10.50-10.52	6(72)	<10
10.52-10.54	6(69)	<10
10.72-10.76	13(41)	<10
10.76-10.81	8(59)	<10
10.81-10.86	9(55)	24(87)
10.86-10.90	11(54)	20(97)
10.95-10.99	10(57)	<10
10.99-11.04	11(53)	20(97)
11.04-11.08	12(48)	24(87)
11.12-11.18	8(74)	24(87)
11.18-11.23	14(43)	<10
11.23-11.28	7(81)	<10
11.35-11.43	8(61)	<10
11.43-11.48	10(50)	<10
11.48-11.53	8(54)	24(87)

^aTrench bottom 8.0 meters.

^bCounting time = 10 m, ϵ efficiency = 38.0%, transmission factor = 0.8.

^cCounting time = 10 m, α efficiency = 23.8%, transmission factor = 0.1.

^dNumber in () = + 2% counting uncertainty.

^eDetection limit = + 3% counting uncertainty.

Table 3.6

Gross Alpha and Beta Activities in a Sediment Core
From Trench 7^a at the Barnwell Site
(10 minute count)

Depth (m)	Gross Beta ^b Activity [pCi/g(+2%)] ^d	Gross Alpha ^c Activity [pCi/g(+2%)] ^d
8.89-8.94	<4	<10 ^e
8.94-8.99	18(28)	<10
8.99-9.04	<4	24(87)
9.04-9.09	<4	<10
9.09-9.14	6(66)	28(79)
9.14-9.19	7(68)	<10
9.19-9.25	<4	<10
9.25-9.31	<4	<10
9.31-9.38	15(68)	<10
9.38-9.45	8(48)	24(87)
9.45-9.50	7(58)	<10
9.50-9.56	<4	28(79)
9.56-9.62	<4	<10
9.62-9.68	9(48)	<10
9.68-9.74	<4	20(97)
9.70-9.80	6(80)	<10
9.80-9.90	9(53)	<10
9.90-10.01	6(62)	<10
10.01-10.11	5(73)	<10
10.11-10.20	8(53)	20(97)
10.20-10.28	6(74)	<10
10.28-10.36	9(57)	<10
10.41-10.47	8(57)	<10
10.47-10.53	13(46)	<10
10.53-10.60	12(44)	<10
10.60-10.66	7(72)	<10
10.66-10.72	5(85)	20(97)
10.72-10.76	8(65)	<10
10.76-10.80	7(62)	20(97)
10.80-10.84	8(58)	<10
10.84-10.89	17(72)	20(97)
10.89-10.93	5(71)	<10
10.93-10.97	16(40)	<10
11.02-11.05	10(59)	20(97)
11.05-11.08	16(38)	24(87)
11.08-11.12	7(46)	28(79)
11.12-11.15	10(56)	<10
11.15-11.18	12(46)	<10
11.18-11.23	12(48)	<10
11.23-11.28	11(50)	<10
11.28-11.33	9(62)	<10
11.33-11.38	11(54)	<10
11.38-11.43	6(71)	20(97)
11.43-11.48	7(63)	<10
11.48-11.53	5(85)	<10
11.53-11.58	44(20)	<10
11.58-11.63	10(48)	<10
11.63-11.68	9(50)	<10
11.68-11.76	10(55)	<10

^aTrench bottom 8.0 meters.

^bCounting time = 10 m, ϵ efficiency = 38.0%, transmission factor = 0.8.

^cCounting time = 10 m, ϵ efficiency = 23.8%, transmission factor = 0.1.

^dNumber in () = $\pm 2\%$ counting uncertainty.

^eDetection limit = $\pm 3\%$ counting uncertainty.

3.2.4 Strontium-90 and Plutonium Isotopes

Radiochemical analyses for ^{90}Sr and $^{238,239,240}\text{Pu}$ were made on the upper portion of Core 2 and the "hot spots" from Cores 7 and 8. Results are shown in Table 3.7. Low concentrations of ^{90}Sr occurred in the upper parts of the core taken from beneath trench 2. The maximum concentration of ^{90}Sr was at the 8.86-8.92 m level or approximately 0.9 m below the disposal trench bottom. Detectable amounts of Pu isotopes occurred in the core from below trench 2 at the 9.02 to 9.14 meter levels. Generally soluble plutonium is more strongly sorbed than strontium (Ames and Rai, 1978). The occurrence of plutonium at depths greater than that observed for strontium may suggest that the plutonium is carried by the groundwater as colloidal particles.

Table 3.7

Strontium-90 and Plutonium Isotope Concentrations
in Sediment Core Samples From the Barnwell Site

Trench	Depth (m)	Concentration ^a [pCi/g (2 % Error)]			Percent Yield	
		^{238}Pu	$^{239,240}\text{Pu}$	^{90}Sr	Pu	Sr
2	8.76-8.81	<0.002 ^b	<0.001	<0.2	26	47
2	8.81-8.86	<0.002	<0.002	0.49 (10)	24	74
2	8.86-8.92	<0.002	<0.001	0.59 (10)	22	67
2	8.02-9.04	<0.001	<0.001	0.34 (16)	60	46
2	9.04-9.09	<0.002	<0.002	<0.2	64	46
2	9.09-9.14	0.23 (12)	0.063 (2.0)	<0.2	26	79
2	9.78-9.83	<0.001	<0.001	0.26 (20)	62	40
7	11.53-11.58	<0.001	<0.001	<0.2	72	51
8	10.57-10.62	<0.001	<0.001	<0.04	67	50
Blank	---	<0.001	<0.01	<0.03	56	61

^aDetection limit given as pCi/g.

^bAnalyses performed by EAL Corporation.

3.3 Sorption of Radionuclides From Solution

3.3.1 Barnwell Trench Waters and Hawthorne Sediment

Figures 3.4 to 3.8 show the behavior of the samples as a function of time. The term R_d is used to describe the sorption, rather than K_d , because the measurements shown are only approximate. During the course of the experiment, activity in the liquid phase was measured by centrifuging the sample containers to sediment the solid phase and then shielding the detector from the solid during the actual counting. This is an adequate method for monitoring the sorption behavior with time, but it does not produce the most accurate results. More specifically, the activity associated with small amounts of the soils which do not settle to the bottom of the containers is consequently counted with the liquid phase. The apparently random deviation of some points from the general trend of the data is probably due to this effect. Accurate measurements of the liquid phase activity are performed on aliquots taken from the containers when the experiment is terminated. These final measurements are referred to as K_d results, however, the term is used to refer to the laboratory measurements only and does not carry any thermodynamic implications.

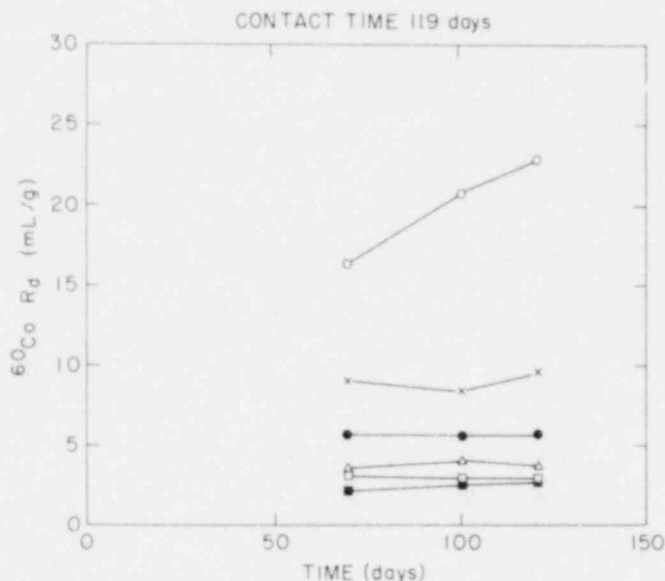


Figure 3.4 Batch sorption test results - ^{60}Co R_d vs time - Barnwell trench 60l water and Hawthorne sediment. Solution to soil ratios: o, 20.4; X, 10.0; ●, 6.55; △, 5.00; □, 3.98; and ■, 3.33, 2.87, 2.50, 2.22, 2.00, 1.82, and 1.67.

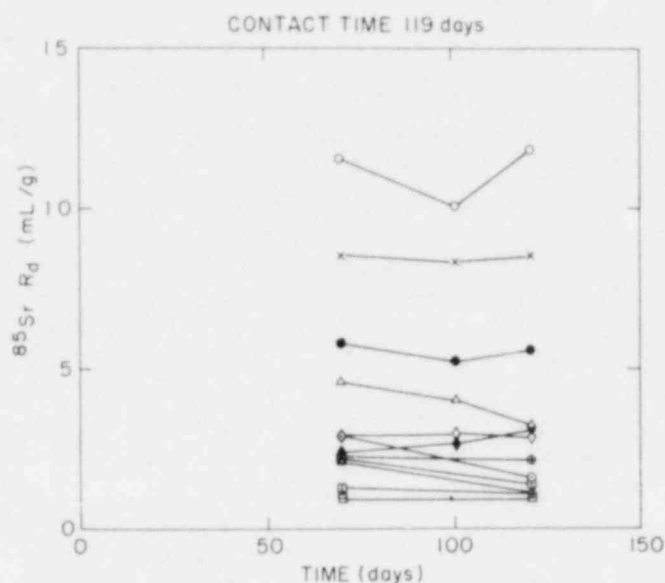


Figure 3.5 Batch-sorption test results - ^{85}Sr R_d vs time - Barnwell trench 6D1 water and Hawthorne sediment. From top to bottom, in order of appearance, solution to soil ratios: o, 20.4; X, 10.0; ●, 6.55; △, 5.00; □, 3.98; ■, 3.33; o, 2.87; △, 2.50; ●, 2.22; ●, 2.00; △, 1.82; □, 1.67.

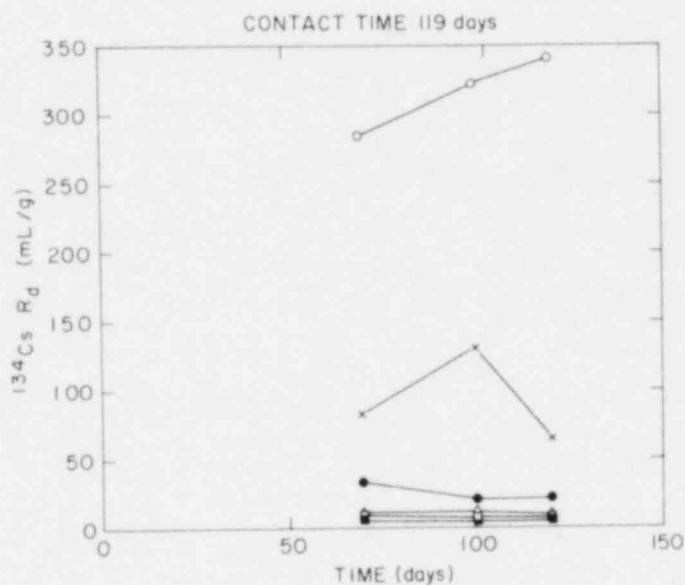


Figure 3.6 Batch sorption test results - ^{134}Cs R_d vs time - Barnwell trench 6D1 water and Hawthorne sediment. Solution to soil ratios: o, 20.4; X, 10.0; ●, 6.55; △, 5.00; □, 3.98; ■, 3.33, 2.87, 2.50, 2.22, 2.00, 1.82, 1.67.

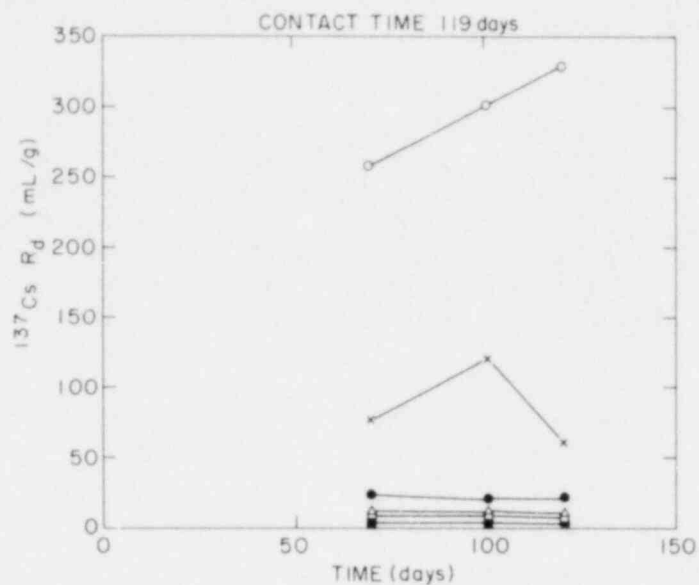


Figure 3.7 Batch sorption test results - ^{137}Cs R_d vs time - Barnwell trench 6D1 water and Hawthorne sediment. Solution to soil ratios: o, 20.4; X, 10.0; ●, 6.55; Δ , 5.00; \square , 3.98; \blacksquare , 3.33, 2.87, 2.50, 2.22, 2.00, 1.82, 1.67.

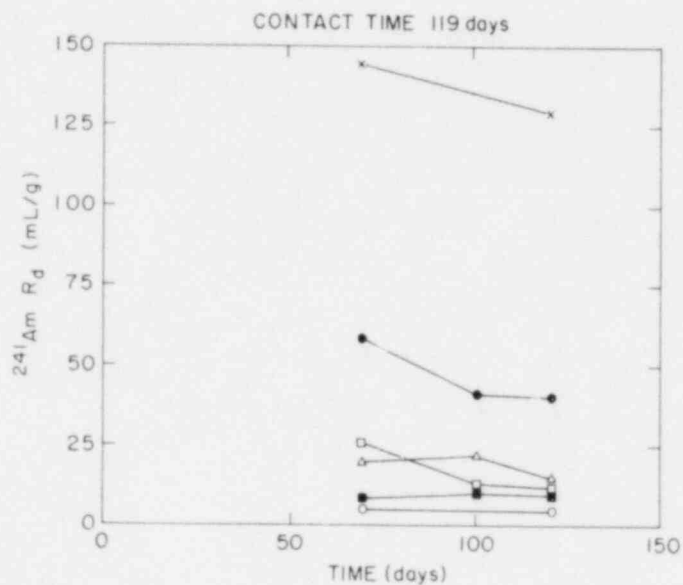


Figure 3.8 Batch sorption test results - ^{241}Am R_d vs time - Barnwell trench 6D1 water and Hawthorne sediment. Solution to soil ratios: o, 20.4; X, 10.0; ●, 6.55; Δ , 5.00; \square , 3.98; \blacksquare , 3.33; o, 2.87, 2.50, 2.22, 2.00, 1.82, 1.67.

The length of time required to achieve a steady state for sorption was evaluated by determining the concentration of radionuclides remaining in solution.

These time studies, shown in Figures 3.4-3.8, indicate no significant changes in sorption for contact times in excess of two months (after correction for decay). Due to malfunctions of the counting equipment, no measurements were obtained during the early period of the experiment. Steady-state conditions may have been reached in much less than two months, particularly for ^{85}Sr and ^{60}Co ; the isotopes which showed the most rapid equilibration time in experiments using the anoxic trench waters as discussed (Weiss and Colombo, 1980).

The relative behavior of the isotopes was consistent for all the samples; americium showed the highest sorption followed by cesium, with strontium and cobalt showing essentially the same results. The typical pattern is shown in Figure 3.9.

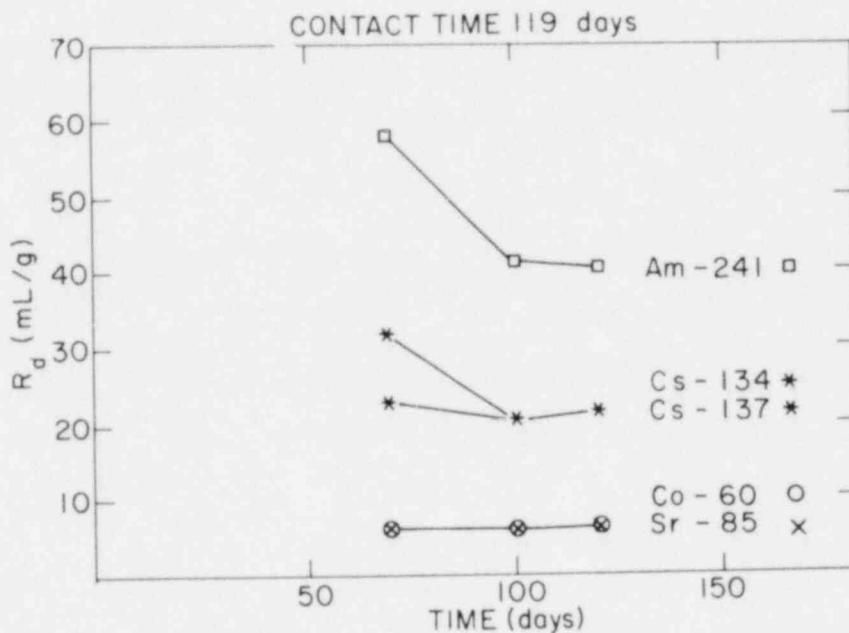


Figure 3.9 Batch sorption test results - R_d vs time - Barnwell trench 6D1 water and Hawthorne sediment.

Figures 3.10-3.14 show the final sorption measurements (performed on aliquots of the liquid removed from the sample containers) plotted as functions of the solution/soil ratio. The observed K_d behavior is linear for ^{85}Sr , exhibits maxima for $^{134,137}\text{Cs}$ and ^{241}Am , and shows asymptotic behavior for ^{60}Co . The reasons for these varied behavior patterns are not apparent. If a particular sorbate behaves according to ideal exchange behavior, the observed K_d should not vary significantly when the solution/soil ratio is changed, as long as the sorbate concentration remains constant and the exchange capacity of the solid is not exceeded. This simple ion exchange behavior is exhibited by strontium only. Simple exchange behavior is approached as the solution/soil ratio decreases for the ^{60}Co experiments. For the cesium and americium results, the reason for the maxima is not readily explained.

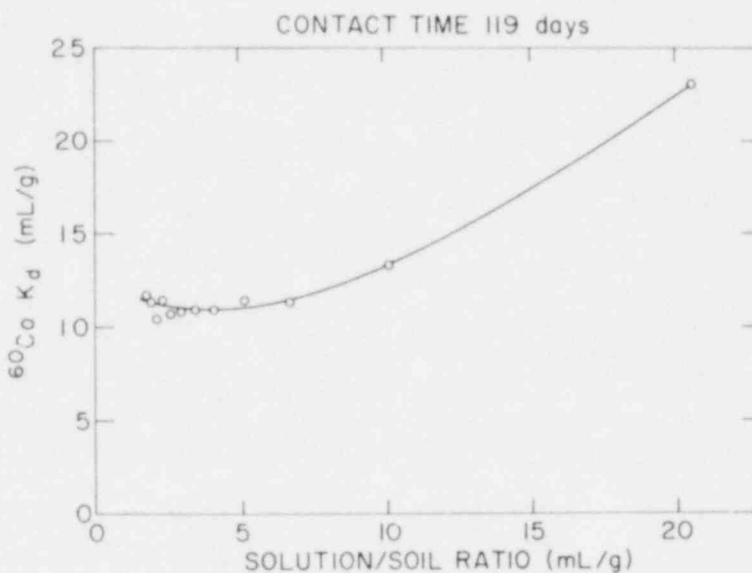


Fig. 3.10 Batch sorption test results - ^{60}Co K_d vs solution/soil ratio - Barnwell trench 6D1 water and Hawthorne sediment.

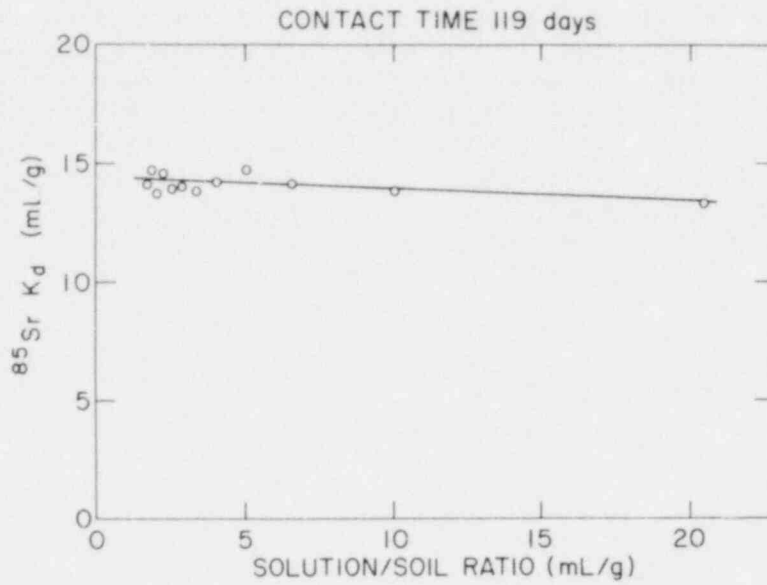


Figure 3.11 Batch sorption test results - ^{85}Sr K_d vs solution/soil ratio Barnwell trench 6D1 water and Hawthorne sediment.

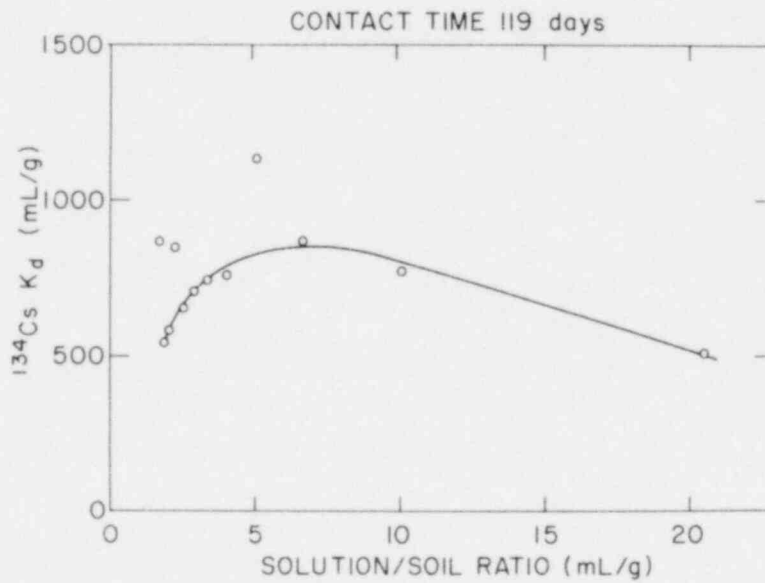


Figure 3.12 Batch sorption test results - ^{134}Cs K_d vs solution/soil ratio - Barnwell trench 6D1 water and Hawthorne sediment.

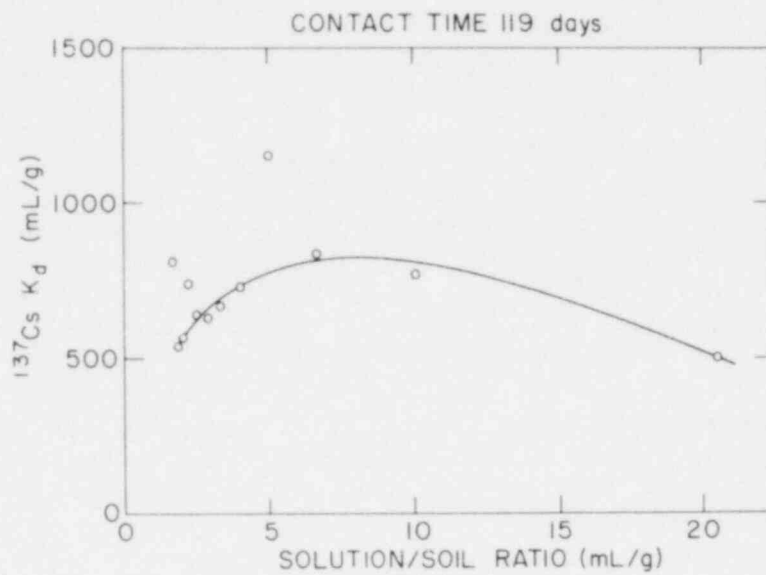


Figure 3.13 Batch sorption test results - $^{137}\text{Cs } K_d$ vs solution/soil ratio - Barnwell trench 6D1 water and Hawthorne sediment.

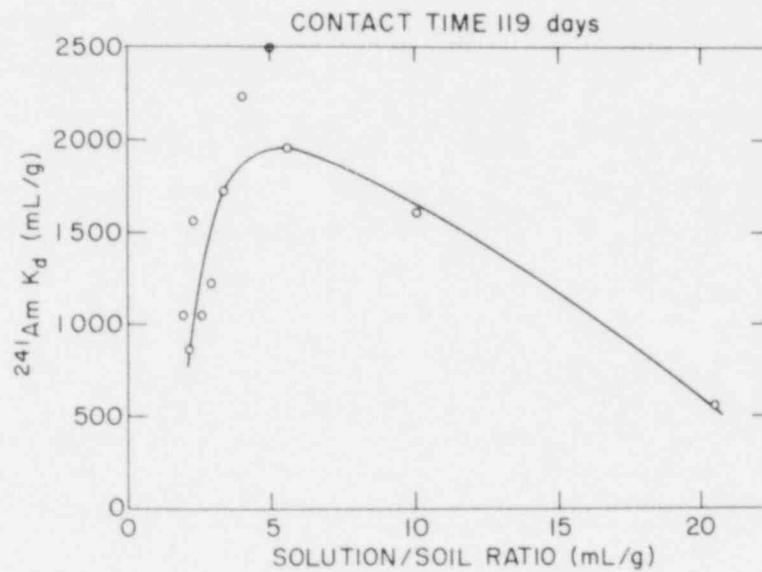


Figure 3.14 Batch sorption test results- $^{241}\text{Am } K_d$ vs solution/soil ratio - Barnwell trench 6D1 water and Hawthorne sediment.

Using the strontium and cobalt results to predict K_d results for the flow-through column experiments is relatively straightforward, in that an extrapolation is made to the appropriate solution/soil ratio. In these cases, a K_d value of approximately 12 and 15 mL/g would be expected for cobalt and strontium, respectively, for column experiments under equivalent conditions. Predictions for cesium and americium behavior are not as straightforward.

3.3.2 Recirculating Water "Loop" System Sorption Results for Barnwell Synthetic Trench Water and Hawthorne Sediment

Flow Rates - The appearance of a pulse of tritiated water in the column effluent was used to measure the rate at which the water front moves through the column. Since water movement is controlled by the pumping rate through the column, volume flow rates were measured for a series of settings on the Manostat pump (see Figure 3.15). Spikes of tritiated water were introduced into the column and the count rates in the effluent monitored with time for a series of different flow rates. A plot of the travel time of the tritium peak through the column as a function of the water flow rates is shown in Figure 3.16, where the count rate for each sample is displayed as a percent of the maximum count rate observed.

$$\% \text{ of tritium maximum} = \frac{\text{sample count rate}}{\text{maximum count rate observed}} \times 100$$

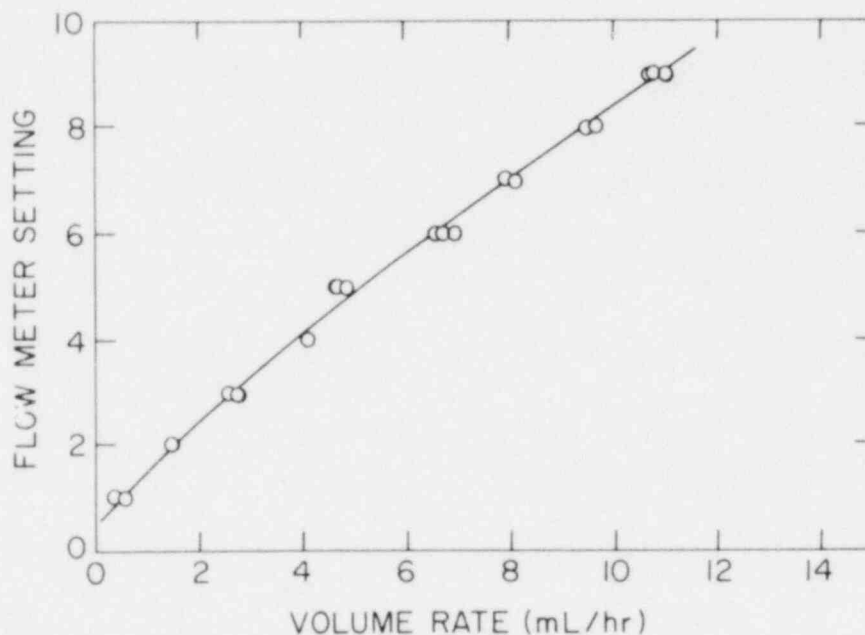


Figure 3.15 Calibration of peristaltic pump for flow rate setting vs observed volume flow rate.

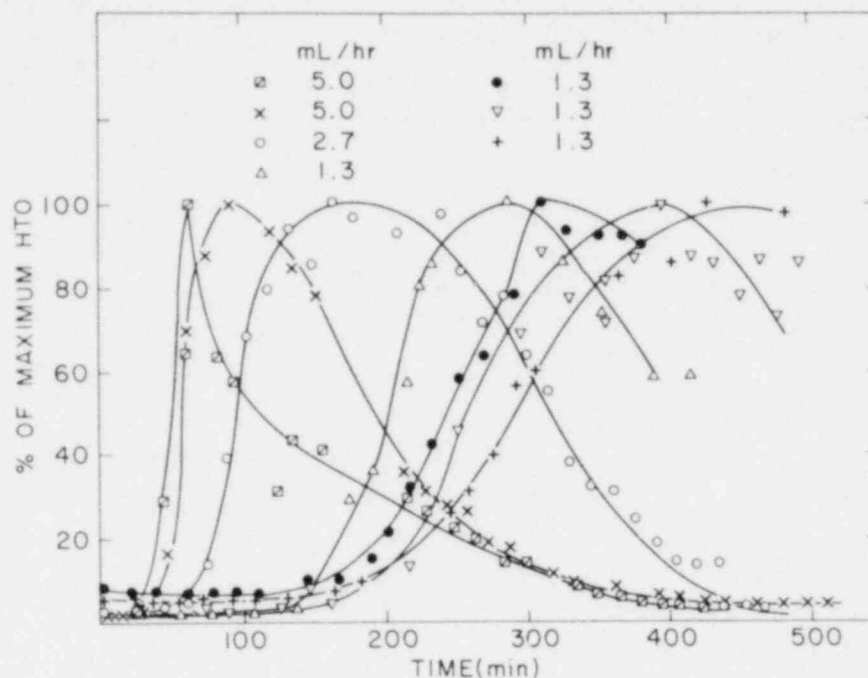


Figure 3.16 Percent of maximum count rate vs time - flow of a tritiated synthetic Barnwell trench water (6D1) through an undisturbed sediment core. (1-1/4 in. diam. x 1 in. - Hawthorne formation, silty sand) from the Barnwell site.

The maximum tritium count rate for the same pumping rate did not remain constant, Figure 3.17. The variability at which the initial rise and maximum count rate occurs cannot be fully explained by variability of the water pumping rate. Column permeability was apparently changing as the column aged. Small amounts of clay may have moved to seal the smaller pores, either within the column or along the sides. These results imply the need to age columns before reliable sorption data can be obtained.

Sorption coefficients can be obtained either by, (1) measurements of radioisotope contents in the solid and liquid phases after an experiment, or (2) by use of the simple chromatographic equation;

$$V_w = V_N[1 + K_d(\rho/\epsilon)]$$

where:

V_w = linear water velocity - distance the water front has moved through a column

V_N = linear radionuclide velocity - distance a radionuclide front has moved through a column

K_d = radionuclide sorption coefficient (mL/g)

ρ = bulk density (g/cm³)

ϵ = porosity.

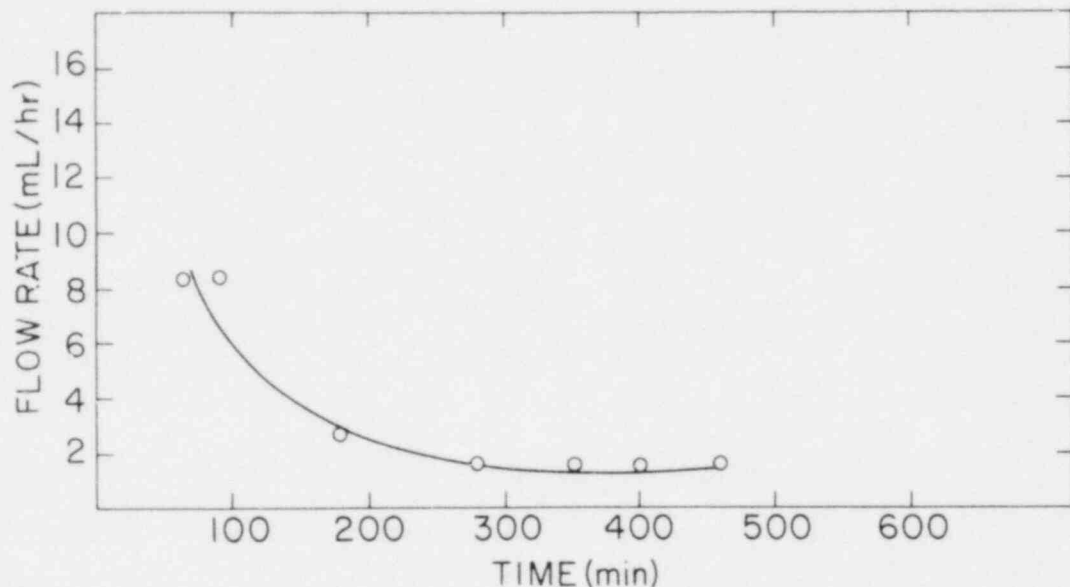


Figure 3.17 Column flow rates vs tritium maximum-travel time.

The flow rate variations indicate that sorption coefficients are more accurately determined by treating the loop experiment as a batch test and making calculations from measurements of radioisotope concentrations in the liquid reservoir after steady-state conditions have developed.

Radionuclide Sorption Results - Results for the loop tests using repacked and intact core material are shown in Figures 3.18-3.20. As mentioned above, three determinations were performed, two determinations using repacked core material with ¹⁵²Eu and the isotope mix, and one using an undisturbed core and the isotope mix.

After 10 days, ¹⁵²Eu concentrations in the water reached nearly constant levels (Figure 3.18). For the experiment with the isotope mix, ²⁴¹Am showed a similar rapid sorption onto the core material, with the concentration in the liquid immediately dropping to levels below the detection limit (Figure 3.19).

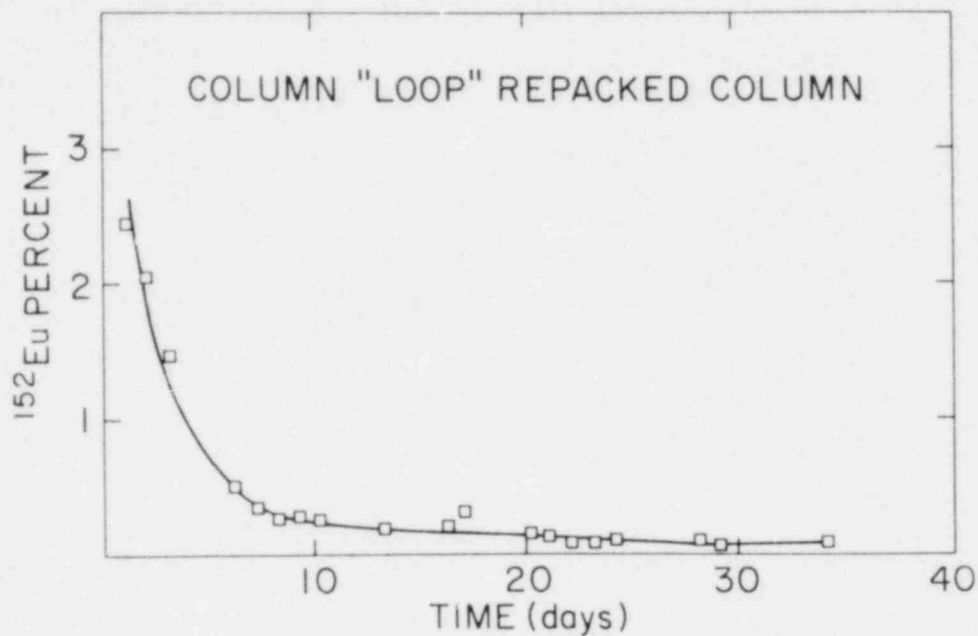


Figure 3.18 Percent of initial ¹⁵²Eu count rate in effluent vs time.

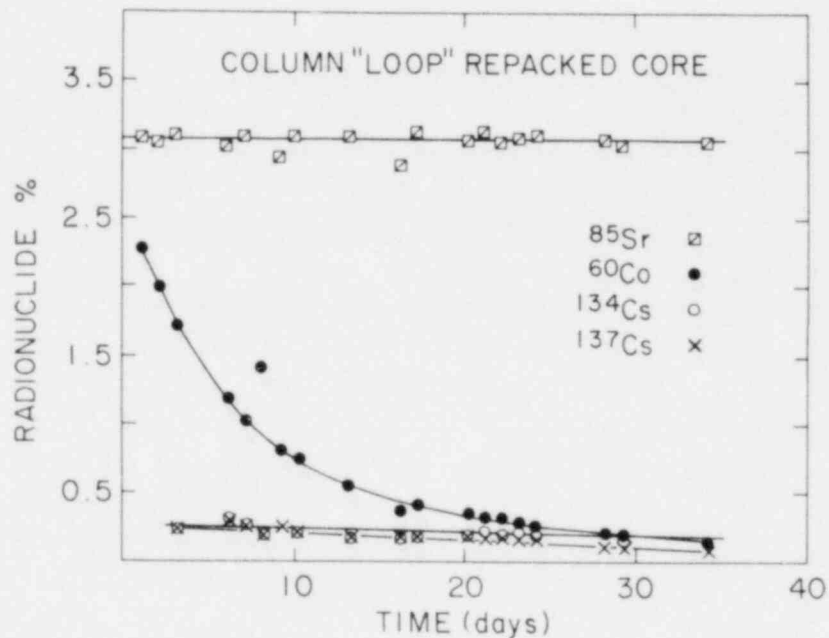


Figure 3.19 Percent of initial count rate vs time (radioisotope mix) repacked column (1-1/4-in. diam. x 0.5 in. - Hawthorne formation, silty sand) and synthetic Barnwell trench water (6D1) - recirculating water flow.

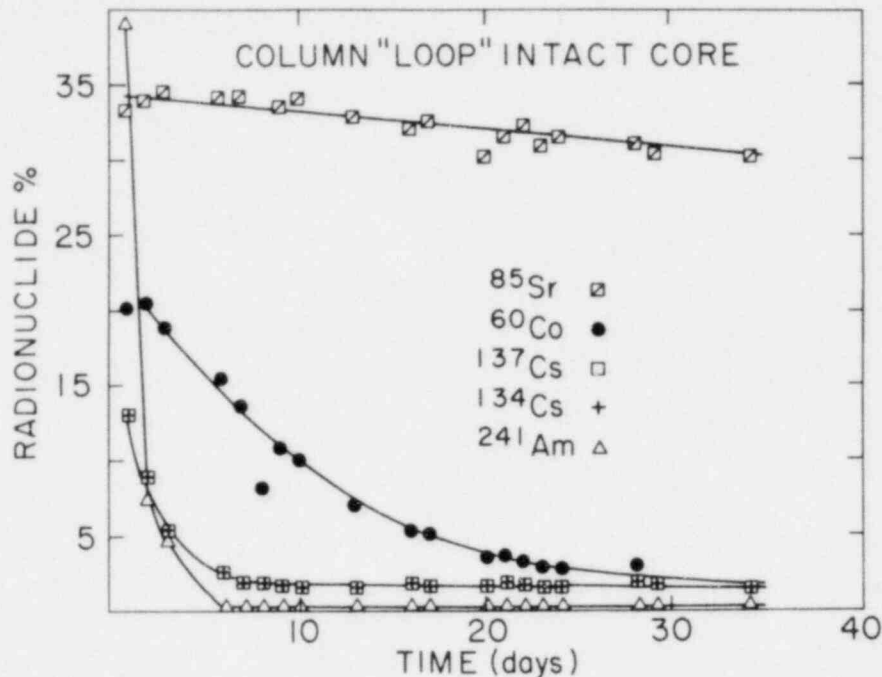


Figure 3.20 Percent of initial count rate vs time (radioisotope mix) intact column (1-1/4-in. diam. x 0.5 in. - Hawthorne formation, silty sand) and synthetic Barnwell trench water (6D1)-recirculating water flow.

The ^{85}Sr activity in solution remained at a constant level, as did ^{134}Cs and ^{137}Cs . However, ^{60}Co continued to be removed from solution through a longer time interval. For ^{85}Sr and $^{134,137}\text{Cs}$, the rapid attainment of steady-state conditions indicates that their behavior is governed by simple ion exchange processes in the soil, in agreement with the results of systematic studies of Sr and Cs sorption on minerals (Meyer, 1980). Ion exchange processes may also control ^{152}Eu behavior, but steady-state conditions are established in a longer time span suggesting that the sorption may involve more than ion exchange equilibria. Slower surface adsorption kinetics or solution redox changes may also be involved.

The third column (intact sediment and the isotope mix) showed similar qualitative behavior for the radionuclides (Figure 3.20). In this case, the relatively slower sorption of ^{241}Am , and $^{134,137}\text{Cs}$ may be due to the presence of small fractures in the core or channeling along the column sides, which effectively decrease the water-soil contact time for each cycle through the column.

Assuming the radionuclide concentrations in the column effluent at steady-state conditions are equivalent to liquid phase concentrations in batch tests, sorption coefficients can be calculated for these loop tests. Table 3.8 shows the "loop" column coefficients compared with batch coefficients reported previously. The coefficients for batch determinations are for a

solution/soil ratio of 15:1, equivalent to the ratio for the loop determination. For strontium and cesium, coefficients agree within a factor of 3. Due to low concentrations in solution, accurate values for the sorption coefficients of ^{241}Am and ^{152}Eu cannot be obtained. The poor agreement for cobalt is unexpected and not easily explained. During batch determinations, changes may occur in the liquid phase resulting in a very different chemical regime than that in the loop system which may in turn affect the cobalt behavior.

Table 3.8

Comparison of Batch and Column Loop K_d for Barnwell Trench 6D1 Water and Hawthorne Sediment

Isotope	Batch K_d^a (mL/g)	Column Loop K_d^b (mL/g)
^{241}Am	1150	>1200 ^d
^{85}Sr	14	35
^{134}Cs	670	960
^{137}Cs	670	960
^{60}Co	18	1100
^{152}Eu	37 ^c	>1200 ^d

^aTrench 6D1 water (collected May 1980).

^bSynthetic 6D1 water and repacked Hawthorne sandy silt-solution/soil ratio 15:1.

^cContainer wall sorption effects have not been fully investigated for ^{152}Eu .

^dBecause the activity in solution was only slightly above background, an accurate K_d could not be calculated.

Vine et al. (1980) reported some comparative data for Sr and Cs sorption coefficients determined by loop and batch sorption techniques using crushed tuff as the solid phase. For Sr, the batch technique showed generally higher results while cesium showed generally greater sorption in the loop determination. More detailed comparisons are not possible without considerably more experimental data.

3.3.3 Sorption of Radionuclides From Trench Waters From Maxey Flats

Results for each trench water are given in the following sections. Since leakage of air into the sample containers could destroy the anoxic character of the solution, the changes in pH and Eh were measured for each sample. As a result, some change in Eh might be expected.

3.3.3.1 Trench 19S Water

Results of pH and Eh measurements for Maxey Flats trench 19S water before and after the equilibration, are shown in Tables 3.9 and 3.10. Three of the four control samples could not be kept in an anoxic condition.

The samples containing shale and spiked with ^{152}Eu had pH and Eh values that differed from the original field and laboratory results, but were still in the reducing region relative to an exposed sample of the same water (Table 3.9). However, the samples containing shale and the radionuclide mixture (^{85}Sr , $^{134,137}\text{Cs}$, and ^{60}Co) had Eh values which ranged from the reducing redox region, characteristic of this anoxic trench water, to Eh values in the vicinity of the air oxidized sample, probably due to air leakage into the containers (Table 3.10). In all cases, no reddish brown precipitate of ferric oxyhydroxide was observed. Coprecipitation of the radionuclides probably did not occur due to the low initial ferric iron content of the trench water (Table 2.3).

Table 3.9

pH and Eh of Maxey Flats Trench 19S Anoxic Water
With ^{152}Eu Before and After the Experiment

Sample	pH		Eh(mV) ^a	
	Before	After	Before	After
1SC ^b	7.10	---	-87	---
2SC	7.10	---	-87	---
1AC ^c	7.10	8.09	-87	+308
2AC	7.10	7.90	-87	+297
1 ^d	7.10	7.58	-87	+37
2	7.10	7.59	-87	+84
3	7.10	7.48	-87	-60
4	7.10	7.44	-87	+18
5	7.10	7.42	-87	+95
6	7.10	7.43	-87	-7
Field ^e	6.70	---	+57	---
Lab ^f	6.90	---	+25	---
Air Oxidized ^g	8.52	---	+397	---

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

^bSamples 1SC and 2SC are solutions of spiked anoxic trench water acidified with 6M HCl to serve as preserved experimental controls to determine initial radionuclide concentration.

^cSamples 1AC and 2AC are spiked anoxic trench waters alone. They were equilibrated along with the shale-water solutions prepared for sorption determinations to estimate radionuclide adsorption on container walls.

^dSamples 1-6 are shale and spiked anoxic trench water equilibrated for the sorption determination.

^e"Field" sample - measurements were made while sampling the trench water at Maxey Flats, KY.

^f"Lab" sample - unspiked anoxic trench water.

^gAnoxic water exposed to air until ferric oxyhydroxide has precipitated completely.

Table 3.10

pH and Eh of Maxey Flats Trench 19S Anoxic Water
With ^{85}Sr , $^{134,137}\text{Cs}$, and ^{60}Co Before and After the Experiment

Sample	pH		Eh(mV) ^a	
	Before	After	Before	After
1SC ^b	7.10	---	-87	---
2SC	7.10	---	-87	---
1AC ^c	7.10	7.47	-87	-20
2AC	7.10	7.54	-87	+377
1 ^d	7.10	7.75	-87	+370
2	7.10	7.22	-87	+324
3	7.10	7.32	-87	+71
4	7.10	7.28	-87	+196
5	7.10	7.27	-87	+39
6	7.10	7.41	-87	+217
Field ^e	6.70	---	+57	---
Lab ^f	6.70	---	+25	---
Air Oxidized ^g	9.17	---	+397	---

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

^bSamples 1SC and 2SC are solutions of spiked anoxic trench water acidified with 6M HCl to serve as preserved experimental controls to determine initial radionuclide concentration.

^cSamples 1AC and 2AC are spiked anoxic trench waters alone. They were equilibrated along with the shale-water solutions prepared for sorption determinations to estimate radionuclide adsorption on container walls.

^dSamples 1-6 are shale and spiked anoxic trench water equilibrated for the sorption determination.

^e"Field" sample - measurements were made while sampling the trench water at Maxey Flats, KY.

^f"Lab" sample - unspiked anoxic trench water.

^gAnoxic water exposed to air until ferric oxyhydroxide has precipitated completely.

The sorption results given in Table 3.11 are erratic and not a simple function of the solution to solid ratio or the Eh of solution. The disagreement for the ^{134}Cs and ^{137}Cs K_d results is a measure of the experimental error which ranged from approximately 4 to 51%.

Table 3.11

Isotopic K_d and Solution/Solid Ratios
of Maxey Flats Trench 19S Anoxic Waters

Sample	Solution/Soil	K_d (mL/g)			
	(mL/g)	^{134}Cs	^{137}Cs	^{60}Co	^{152}Eu
1	26.1	380	340	2.7	1.1 E4
2	6.68	2770	1600 ^a	23	1.1 E4
3	4.40	2600	2500	12	1.4 E4
4	3.34	2400	2100	4.5	1.4 E4
5	2.86	3300	3000	10	0.4 E4
6	2.94	1000	1400	5.3	b

^aThe large difference between the K_d result for ^{134}Cs and ^{137}Cs cannot be accounted for at this time.

^bSample lost.

3.3.3.2 Trench 27 Water

The pH and Eh results for Maxey Flats trench 27 water are given in Table 3.12. The control samples without shale could not be kept in an anoxic condition for the duration of the experiment probably due to insufficient microbial activity and air leakage into the containers. The samples which contained spiked anoxic trench 27 water and shale had pH and Eh values which differed from the original field and laboratory measurements. However, four of these samples remained in the reducing region relative to air-exposed samples of the same trench water. The remaining two samples had pH and Eh values which were midway between the initial solution values and those for an air-oxidized sample of the same trench water. Some radionuclides may have coprecipitated due to oxidation of this ferrous iron-rich water (1400 mg/L Fe, 39 [Fe²⁺/Fe³⁺]) and subsequent precipitation of ferric hydroxide as a reddish-brown precipitate was found in these samples. This appears to be strongly reflected in the ^{60}Co results (Table 3.13) where two of the ^{60}Co results are unusually high. However, the samples with the highest Eh do not correspond to those with the largest ^{60}Co K_d results. The results for ^{241}Am , ^{85}Sr , and $^{134,137}\text{Cs}$ do not appear to be affected by changes in the solution Eh. Results for other radionuclides were not strongly affected by pH and Eh changes during the experiment. There may be a systematic decrease in sorption for the ^{241}Am , ^{134}Cs , and ^{137}Cs , but the data are inadequate for a clear evaluation. Differences between ^{134}Cs and ^{137}Cs K_d results are a measure of the experimental error characteristic of the test procedure and ranged from 2 to 6%.

Table 3.12

pH and Eh of Maxey Flats, KY, Trench 27 Anoxic Water With ^{85}Sr , ^{134}Cs , and ^{60}Co Before and After the Experiment

Sample	pH		Eh(mV) ^a	
	Before	After	Before	After
1SC ^b	6.63	---	-24	---
2SC	6.63	---	-24	---
1AC ^c	6.63	2.48	-24	+518
2AC	6.63	2.62	-24	+487
1 ^d	6.63	5.88	-24	+108
2	6.63	5.22	-24	+172
3	6.63	6.24	-24	+102
4	6.63	5.93	-24	+87
5	6.63	3.64	-24	+317 ^h
6	6.63	3.87	-24	+317 ^h
Field ^e	5.90	---	+140	---
Lab ^f	6.60	---	+17	---
Air Oxidized ^g	2.97	---	+557	---

^aEh(mV) is the potential for a platinum electrode immersed in the specimen relative to a normal hydrogen reference electrode at 25°C.

^bSamples 1SC and 2SC are solutions of spiked anoxic trench water acidified with 6M HCl to serve as preserved experimental controls to determine initial radionuclide concentration.

^cSamples 1AC and 2AC are spiked anoxic trench waters alone. They were equilibrated along with the shale-water solutions prepared for sorption determinations to estimate radionuclide adsorption on container walls.

^dSamples 1-6 are shale and spiked anoxic trench water equilibrated for the sorption determination.

^e"Field" sample -- measurements were made while sampling the trench water at Maxey Flats, KY.

^f"Lab" sample -- unspiked anoxic trench water.

^gAnoxic water exposed to air until ferric oxyhydroxide has precipitated completely.

^hA reddish-brown precipitate was found in samples 5 and 6.

Table 3.13

Isotopic K_d and Solution/Solid Ratios
of Maxey Flats Trench 27 - Anoxic Waters

Sample	Solution/Soil	K_d (mL/g)				
	(mL/g)	^{241}Am	^{85}Sr	^{134}Cs	^{137}Cs	^{60}Co
1	19.8	200	<0.1	560	550	1.3
2	9.94	160	2.6	430	440	2700 ^a
3	6.58	350	0.75	600	570	13
4	4.99	63	1.2	730	720	13000 ^a
5	4.02	91	0.15	160	150	0.54
6	3.33	6.9	<0.1	190	180	0.62

^aThe reason for the anomalously high results of the second and fourth samples were not definitely identified.

3.3.3.3 Experimental Trench T-2E Water

The pH and Eh results for experimental trench T-2E water are given in Tables 3.14 and 3.15. Bacterial processes caused a lowering of the Eh of the trench water during storage because the Eh values of the initial solution used to prepare samples for K_d determination was much lower than those observed in the field. The initial Eh value could not be maintained probably due to air leakages into the containers. The final Eh results ranged from below those observed in the field to near that observed for an air oxidized sample. Coprecipitation of radionuclides probably did not occur since the reddish brown precipitate of ferric oxyhydroxide was not observed when the samples were disassembled in an argon-filled glove box. The sorption results are erratic and show no systematic trend with variations in the solution to solid ratio (Table 3.16). The difference between the ^{134}Cs and ^{137}Cs K_d results are a measure of experimental errors characteristic of the test procedure. The errors had an average value of 22%.

Table 3.14

pH and Eh of Maxey Flats Trench T-2E Anoxic Water With
 ^{85}Sr , $^{134,137}\text{Cs}$, and ^{60}Co Before and After the Experiment

Sample	pH		Eh(mV) ^a	
	Before	After	Before	After
1SC ^b	7.18	---	-128	---
2SC	7.18	---	-128	---
1AC ^c	7.18	7.32	-128	+287
2AC	7.18	7.31	-128	-1
1 ^d	7.18	7.14	-128	+263
2	7.18	7.45	-128	+364
3	7.18	7.13	-128	+369
4	7.18	7.09	-128	+71
5	7.18	7.13	-128	+252
6	7.18	7.24	-128	+155
Field ^e	6.6	6.6	+270	---
Lab ^f	5.5	5.5	+270	---
Air Oxidized ^g	7.47	7.47	+403	---

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

^bSamples 1SC and 2SC are solutions of spiked anoxic trench water acidified with 6M HCl to serve as preserved experimental controls to determine initial radionuclide concentration.

^cSamples 1AC and 2AC are spiked anoxic trench waters alone. They were equilibrated along with the shale-water solutions prepared for sorption determinations to estimate radionuclide adsorption on container walls.

^dSamples 1-6 are shale and spiked anoxic trench water equilibrated for the sorption determination.

^e"Field" sample - measurements were made while sampling the trench water at Maxey Flats, KY.

^f"Lab" sample - unspiked anoxic trench water.

^gAnoxic water exposed to air until ferric oxyhydroxide has precipitated completely.

Table 3.15

pH and Eh of Maxey Flats Trench T-2E Anoxic Water
With ^{152}Eu Before and After the Experiment

Sample	pH		Eh(mV) ^a	
	Before	After	Before	After
1SC ^b	7.20	---	-103	---
2SC	7.20	---	-103	---
1AC ^c	7.20	7.64	-103	+296
2AC	7.20	7.59	-103	+302
1 ^d	7.20	7.20	-103	+318
2	7.20	7.31	-103	+318
3	7.20	7.31	-103	+319
4	7.20	8.08	-103	+352
5	7.20	7.75	-103	+345
6	7.20	7.56	-103	+346
Field ^e	6.60	---	-103	---
Lab ^f	5.50	---	+270	---
Air Oxidized ^g	7.97	---	+403	---

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

^bSamples 1SC and 2SC are solutions of spiked anoxic trench water acidified with 6M HCl to serve as preserved experimental controls to determine initial radionuclide concentration.

^cSamples 1AC and 2AC are spiked anoxic trench waters alone. They were equilibrated along with the shale-water solutions prepared for sorption determinations to estimate radionuclide adsorption on container walls.

^dSamples 1-6 are shale and spiked anoxic trench water equilibrated for the sorption determination.

^e"Field" sample -- measurements were made while sampling the trench water at Maxey Flats, KY.

^f"Lab" sample -- unspiked anoxic trench water.

^gAnoxic water exposed to air until ferric oxyhydroxide has precipitated completely.

Table 3.16

Isotopic K_d and Solution/Solid Ratios
of Maxey Flats Trench T-2E - Anoxic Waters

Sample	Solution/Solid (mL/g)	K_d (mL/g)				
		^{85}Sr	^{134}Cs	^{137}Cs	^{60}Co	^{152}Eu
1	25.5	67	1300	870	130	1.7 E5
2	6.68	65	2800	1300	330	3.6 E4
3	4.44	4.0	600	540	230	2.6 E4
4	3.34	3.6	4100	4200	<0.1	3.1 E4
5	3.84	2.7	660	620	270	2.1 E4
6	2.50	2.7	1500	1500	150	1.6 E4

3.4 Stability of Organo-Radionuclide Complexes in Anoxic Water-Soil Regimes - Controlled Environment Experiments

Synthetic trench water was used in the experiments because the trace organic, cobalt, and zinc concentrations in disposal trench waters are poorly known. The synthetic trench water avoids complications arising from reactions of the metals with unknown compounds in disposal trench waters. Maxey Flats trench 32 was selected because characterization data is available and field measurements detected sulfide (Czyscinski and Weiss, 1981). Also, laboratory Eh-pH measurements confirm that the water is in equilibrium with iron sulfide (Czyscinski and Weiss, 1981).

The behavior of complexed metals as a function of time are shown in Figure 3.21. The CoEDTA chelate is stable in the more oxidizing experiment (0 mV, NHE). The CoEDTA systems shows very small gradual decreases in metal concentration. The CoEDTA (-250 mV, NHE) and CoNTA systems show initial rapid decreases in metal concentrations followed by an asymptotic approach to steady-state conditions. The ZnEDTA system shows a rapid initial decrease in metal concentration, there is a slower decrease to undetectable levels of soluble metal. In the reducing systems, the order of stability of the cobalt complexes is DTPA > EDTA > NTA. The order correlates with the stability constants found in Table 3.18.

These experiments do not show the sharp decreases in trace metal concentrations observed by Reddy and Patrick (1977) for EDTA and DTPA chelates of copper and zinc under high-sulfide, low-redox conditions in their flooded soil systems. These metals were not removed from solution in their experiments under oxidized (-500 mV, NHE) conditions and they propose that the sulfide ions, generated in the anoxic water systems, precipitates trace metal sulfides. Calculations indicate that our solutions are not saturated with CoS. These calculations are based on soluble metal concentrations determined from stability constants, the sulfide ion concentration, and the metal sulfide

solubility products (Table 3.17). Sulfide ion concentrations were determined from the sulfide electrode measurements. The sulfide electrode was calibrated by the procedure of Berner (1963). These calculations are limited by the reliability of the constants and the absence of competing reactions in the solutions.

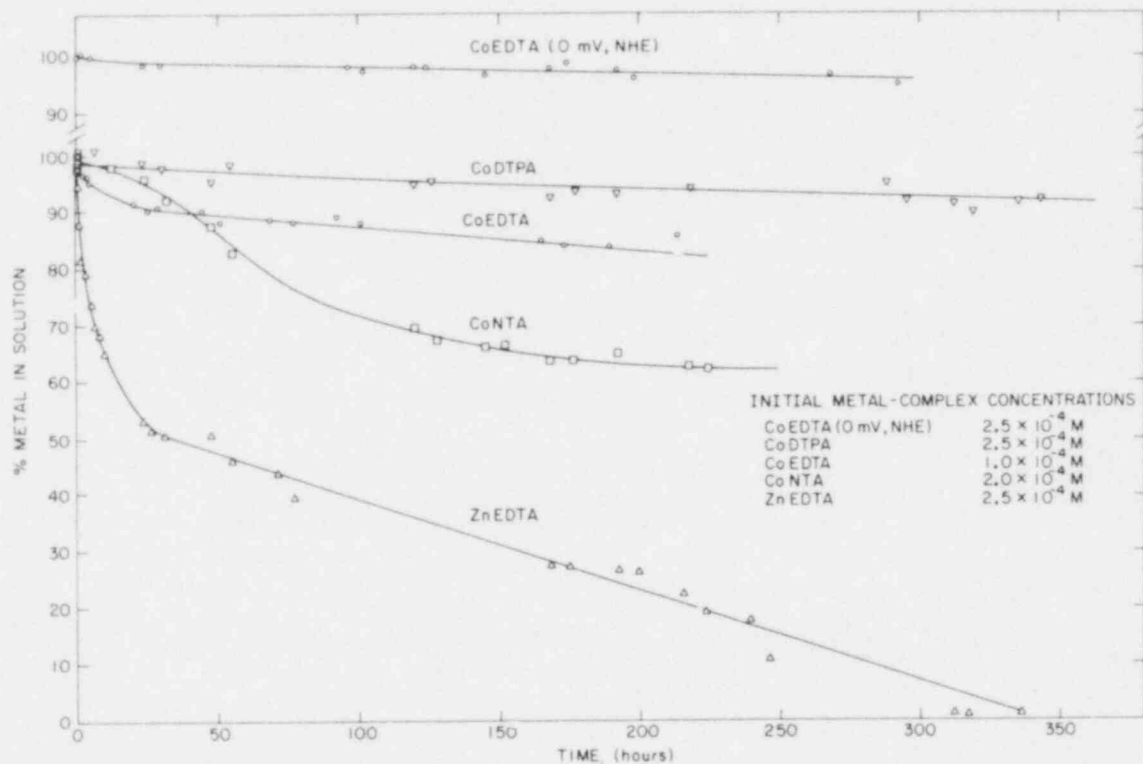


Figure 3.21 Percent metal in solution vs time for Co and Zn chelate stability experiments. The Eh for the experiments are approximately -200 mV, NHE for ZnDTPA, CoNTA, CoDTPA, and -250 mV, NHE for CoEDTA, except where indicated. The pH was maintained at approximately 7.

Table 3.17

Chelate Stability Constants and Sulfide Solubility Products^a

	$\log K_{0.1}^b$ MHL	$\log K_{0.1}^c$ ML	pK_{sp}^d
Co NTA	10.8	---	CoS 20.4-24.7
Co EDTA	19.2	15.6	ZnS 22-26
Co DTPA	24.1	22.8	
Zn EDTA	19.4	15.9	CuS 35.2-37.4
Zn DTPA	--	23.9	
Cu EDTA	21.7	18.8	
Cu DTPA	26.2	21.4	

^aLindsay, 1979, Anderegg, 1977, Sillen and Martell, 1964 and 1951.^b $K_{0.1}$ = stability constant for protonated ligand species at 0.1 ionic strength.^c $K_{0.1}$ = stability constant for the dissociated ligand at 0.1 ionic strength.^d K_{sp} = solubility product at zero ionic strength.

Since the CoEDTA chelate is stable in the more oxidizing experiment, the decreased metal concentrations in the low redox systems can be attributed to processes arising from the reducing environment. The metals are probably not sorbed on the soil or container walls since less cobalt sorp under reducing conditions than under oxidizing conditions in a Nancy Shale-trench water-EDTA system. Other chemical reactions probably compete with the sulfide precipitation reactions and metal chelate stability, since the stability constants and solubility products for cobalt and zinc are very similar. However, the reported values are not accurate and may explain the experimental differences.

Manganous compounds in soils become soluble when soil systems are reduced and the manganous ions compete for chelating ligands (Lindsay, 1979). Figure 3.22 shows the results from adding $MnCl_2$ to the reducing CoEDTA system. The data is normalized to the time the manganese salt is added. A small decrease (approx. 15%) in the cobalt concentration is observed.

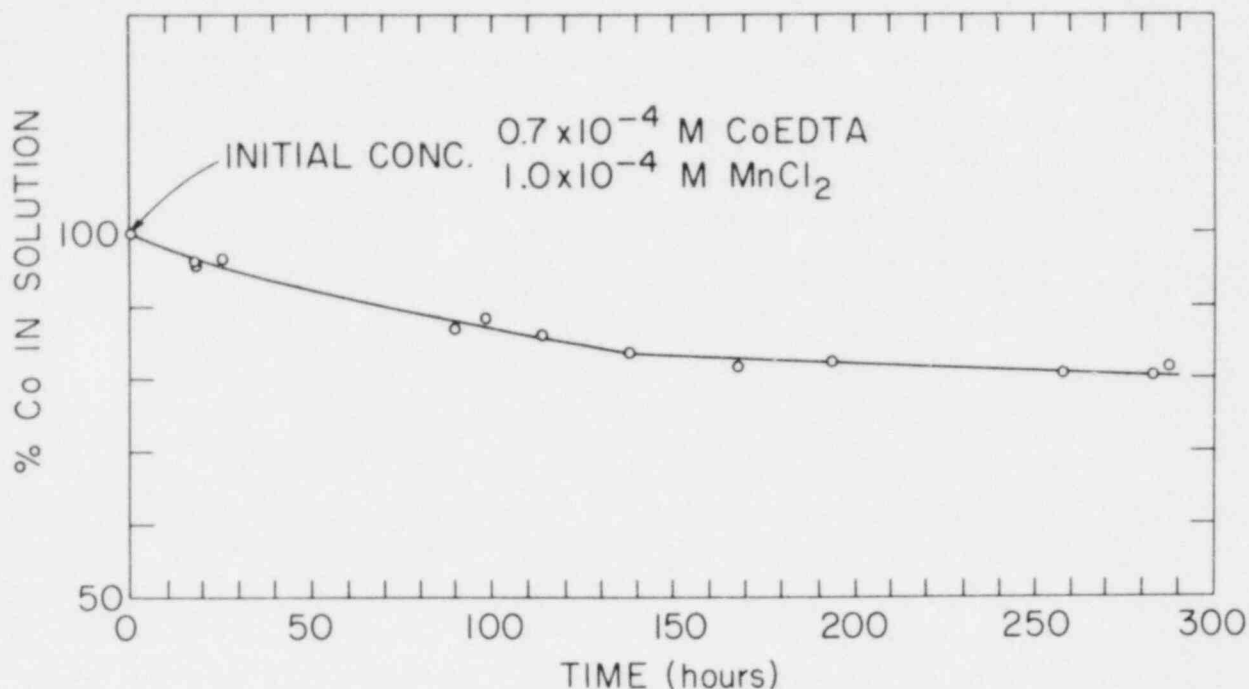


Figure 3.22 Percent cobalt in solution vs time for CoEDTA experiment after addition of MnCl_2 under reducing conditions. The pH was maintained at approximately 7.0.

3.5 Retention Mechanisms in Disposal Trench Environments

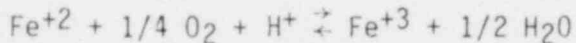
3.5.1 pH, Eh, and Alkalinity Changes During Trench Water Oxidation

The pH, Eh and titration alkalinities of these waters were measured when they were collected (Czyscinski and Weiss, 1981). Table 3.18 shows the values for pH, Eh, and titration alkalinities before and after complete oxidation, along with the initial total dissolved iron contents.

For the majority of trench waters, oxidation resulted in a pH increase, the notable exception being the water from Maxey Flats, disposal trench 27 which contains very high dissolved total iron concentrations. Slight decreases in pH were also observed for the Maxey Flats trenches 33L4 and 33L18. These trenches are not representative, however, in that cement was used as a solidification agent in trench 33L4 (trench water pH = 11.6) and urea formaldehyde in trench 33L18 (trench water pH = 2.4). The pH changes observed are a result of two competing processes, (1) the loss of CO_2 resulting from exposure of the waters to the low partial pressure of CO_2 in open air and (2) the ferrous iron oxidation and precipitation reactions. These two processes are discussed below.

During the development of an anoxic water regime, bacterial degradation processes liberate carbon dioxide which raises the P_{CO_2} of pore water microenvironment (Stumm and Morgan, 1970). Waters undergoing these processes are observed to show a pH decrease relative to their initial pH (Gardner, 1971). Upon exposure to air, the pH of naturally occurring anoxic waters normally rises, as a result of CO_2 loss and subsequent adjustments of the chemical system (Czyscinski, 1975).

The original mechanism which would decrease the pH is the oxidation of dissolved ferrous iron. According to the following generalized equations (Stumm and Morgan, 1970; Singer and Morris, 1969),



for each equivalent of ferrous iron oxidized and precipitated, two equivalents of hydrogen ion are released. However, the resulting acidity can be neutralized by the pore water alkalinity. Assuming that all the dissolved iron is in the ferrous state and available for oxidation and precipitation, some simple calculations show the relative magnitude of acid generation due to oxidation of Fe^{2+} versus the trench water buffering capacity due to its alkalinity. Table 3.18 shows some representative trench waters and the meq/L of H^+ which could be generated from ferrous iron oxidation, and the meq/L of neutralizing capacity available from the titration alkalinity.

Trench water pH changes resulting from oxidation are easily interpreted in terms of these competing mechanisms. For waters with high dissolved iron and alkalinity (MF-19S, WV-5,8,4 for example), the buffering capacity available is well in excess of that required to neutralize the H^+ liberated during iron oxidation. The exception is Maxey Flats trench 27, where the acidity generated by iron oxidation is well in excess of the buffering capacity. Consequently, when this water is oxidized, a sharp pH drop results. In the waters relatively low in dissolved iron (MF-IT 5, 4 and MF-32 for example) but with high alkalinity, exposure to air results in a release of excess P_{CO_2} , developed due to bacterial processes and a subsequent pH rise. Naturally occurring anoxic waters show this behavior, as mentioned previously.

Table 3.18

Chemical Changes, Acid (H⁺) Generating Potential of Ferrous Ions, and Buffering Capacities (Alkalinities in Trench Waters - Before and After Oxidation)

Trench Water	Date Collected	pH		Eh (mV, NHE)		Total Fe (mg/L)	H ⁺ (meq/L)	Titration Alkalinity (meq/L)	
		Before	After	Before	After			Before	After
MF-195 ^a	5/78	6.9	8.52	30	400	115	8.2	18	17
MF-195	11/79	7.2 ^b	8.59	60	390	60	4.3	18	17
MF-27	5/78	6.6	3.05	20	560	1150	82.4	6.6	---
MF-27	10/79	5.9	2.97	140	550	1400	100.	6.0	---
MF-32	11/79	5.6	8.97	-60	370	0.4	<0.1	34	42
MF-33L4	5/78	12.1	11.6	-10	190	0.3	<0.1	32	2.
MF-33L18	5/78	2.4	2.23	520	610	194 ^c	0	0	0
MF-IT-2	10/79	5.5	7.97	270	400	1.6	0.1	6.0	1.4
MF-IT-3	10/79	6.8 ^b	8.05	---	420	1.2	0.1	9.0	1.4
MF-IT-4	10/79	7.2 ^b	8.05	---	390	0.5	<0.1	6.0	1.3
MF-IT-5	10/79	7.5 ^b	8.11	---	410	0.2	<0.1	6.4	---
MF Well UB1A	5/78	6.6	7.85	270	440	<0.1	<0.1	1.0	1.0
MF Well UB1A	11/79	6.4 ^b	7.68	---	420	<0.1	<0.1	0.6	0.9
WV-3 ^d	10/78	7.3	8.12	0	400	56	4.0	35	42
WV-4	10/78	6.5	7.84	50	420	150	11.	160	9.4
WV-5	11/77	7.1	7.78	240	330	260	19.	20	24
WV-5	10/78	6.7	7.37	40	410	540	39.	46	33
WV-8	11/77	6.7	8.01	90	400	130	9.3	41	29
WV-8	10/78	6.9	8.19	-10	400	130	9.3	40	30
WV-9	11/77	7.3	8.65	70	380	72	5.2	30	28
WV-9	10/78	6.7	8.47	20	390	57	4.1	32	23

^aMF = Maxey Flats disposal site.

^bWV = No field measurements were made. Measurements were made immediately after anaerobic filtration. Iron exists as Fe³⁺.

^dWV = West Valley disposal site.

3.5.2 Chemical Changes and Radionuclide Scavenging During the Oxidation of a Trench Water

Preliminary results of the oxidation experiment are shown in Figures 3.23 and 3.24. Analysis of the amount of radionuclides removed from solution by coprecipitation are in progress. However, the redox data is worthy of some comment.

During the course of the oxidation process the Eh, pH, and iron content in solution were monitored. Precipitation of ferric oxyhydroxides began within one hour after the beginning of the experiment and continued for ninety-six hours. The rate of change of the measured Eh was relatively slow until the total iron content dropped below approximately 25 mg/L, after which the Eh electrode readings increased at a more rapid rate. The relatively slow redox change observed during oxidation may be due to the consumption of oxygen by the kinetically rapid ferrous iron oxidation reaction. When the dissolved ferrous iron concentration is high, oxygen diffusing into the water is rapidly scavenged, thereby preserving the oxygen depleted environment. As the dissolved iron content decreases, the capacity of this process also decreases, to the point where oxygen diffuses into the water at a faster rate than it can be consumed by the ferrous iron oxidation process, and the redox conditions become rapidly more oxidizing.

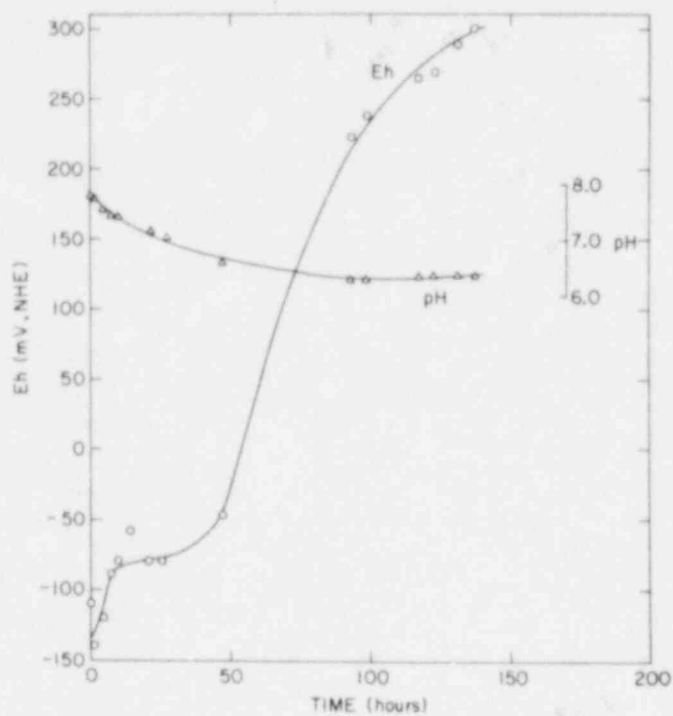


Figure 3.23 Eh and pH of West Valley trench 8 water during controlled oxidation.

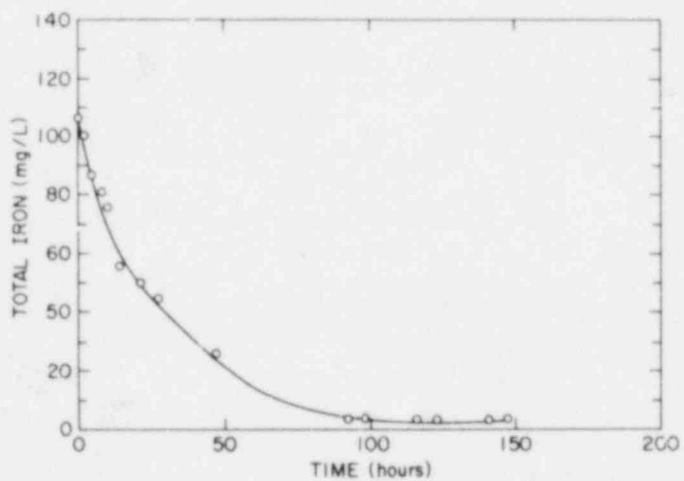


Figure 3.24 Total dissolved iron concentrations in West Valley trench 8 water during controlled oxidation.

4. CONCLUSIONS

4.1 Trench Water and Sediment Analyses

Radionuclide concentrations in Barnwell trench waters are low relative to those for Maxey Flats (Table 2.2, Czyscinski and Weiss 1981) and West Valley trench waters (Table 5.30, Weiss and Colombo 1980). Tritium concentrations are high compared to the gross alpha and beta activity levels but still orders of magnitude lower than those observed at Maxey Flats and West Valley. Low radionuclide activities are found at Barnwell because water does not accumulate in the burial trenches due to the relatively more permeable sediments.

Tritiated water was found in all the sediment cores from beneath the Barnwell site disposal trenches. The maximum tritium concentrations are similar to those found in the trench waters. A minimum in the tritium concentrations, 10 meters beneath the burial trenches, may represent a profile of diluted trench water moving downward through the unsaturated sediment. Only the sediment core from beneath Barnwell trench 2 showed significant radionuclide activities.

Significant gross alpha and beta activities were restricted to the uppermost 30 cm of the Barnwell trench 2 core. This uppermost part of the Barnwell trench 2 core contained detectable concentrations of ^{90}Sr and $^{238,239,240}\text{Pu}$.

4.2 Radionuclide Sorption

Results for batch K_d with materials from Barnwell appear to be dependent on the ratio of soil and solution for some isotopes. The observed K_d behavior for ^{85}Sr is linear and nearly constant. However, the results for ^{241}Am are clearly nonlinear. In the range of soil/solution ratios appropriate for an intact core of Barnwell Hawthorne sediment saturated with solution, the data is nearly linear but sharply dependent on the soil/solution ratio. The observation for ^{241}Am could be an artifact of the experimental method and needs to be further investigated.

Strontium and cesium sorption coefficients determined with a recirculating water "loop" column experiment agreed within a factor of 3 for materials from the Barnwell disposal site. Poor agreement for ^{60}Co cannot be easily explained by the authors.

A procedure for measuring radionuclide sorption coefficients for anoxic trench waters was tested using materials from the Maxey Flats site. The experimental procedure appears capable of maintaining anaerobic conditions during most of the determinations. However, the K_d results were erratic and showed no systematic trend with variations in the solution/solid ratio or the Eh of solution. In addition, observations on the oxidation of a West Valley trench 8 water sample, suggest that changes in the Eh of solution may be insensitive to significant changes in the iron content. Significant ferric

oxyhydroxide precipitation may occur before large (>50 mV) changes in the Eh occur. Radionuclide coprecipitation could occur with small changes in the solution Eh. The ferric/ferrous oxidation reduction couple may act as a Eh buffer for some trench waters. Consequently, a better measure of the sample integrity would be to measure the iron concentration in solution. The observed radionuclide sorption coefficients may be a combination of coprecipitation with ferric oxyhydroxide and sorption on the shale. Since no further significant improvements in this test procedure are planned, this type of experimental work will be terminated. Subsequent experiments will be designed to control the water chemistry and measure the contribution of precipitation reactions as well as measure radionuclide sorption by the sediments from anoxic waters.

4.3 Stability of Organo-Radionuclide Complexes in Anoxic Water Soil Regimes

Some conclusions can be drawn from these experiments concerning the behavior of some organo-radionuclide complexes in the anoxic, chemically reducing geochemical environments found in many disposal trenches. Cobalt complexes are persistent in these environments. Anoxic, chemically reducing trench environments do not rapidly destroy organo-cobalt complexes in solution. The relative stability of Co-EDTA, Co-DTPA, and Co-NTA follows the trend of their stability constants. The order of increasing stability of cobalt complexes is DTPA>EDTA>NTA. Zn-EDTA is not stable in these environments. The Zn is removed from solution presumably by sulfide precipitation (Reddy and Patrick, 1977). Consideration of stability constants and solubility products alone cannot reconcile the disparity in behavior between Zn and Co shown in the experiments. An empirical approach appears to be the only way to extend the results of these experiments to other radionuclides. To minimize enhanced migration of Co in disposal trenches, the concentration of organic chelating agents should be minimized.

4.4 Chemical Changes During the Oxidation of Anoxic Trench Waters

Some conclusions can be drawn from the pH and Eh changes resulting from the oxidation of anoxic trench waters in terms of, (1) laboratory sorption testing, and (2) modeling studies of trench water migration with respect to both radionuclide retention and chemical evolution of groundwaters along migration paths.

For laboratory sorption experiments, the pH range of interest for testing purposes is from 6-8. The Maxey Flats trenches which show pH changes significantly outside these limits (27, 33L-4 and 33L-18) are atypical of the anoxic water geochemical regimes present in the majority of trenches. For generalized testing guidelines, the 6-8 pH range should be used in laboratory sorption testing of candidate sediment where anoxic trench waters are anticipated. For more oxidized environments (represented by the Barnwell trench waters), pH changes shown by trench waters exposed to air are also similar to the anoxic water results (Czyscinski and Weiss, 1981). Therefore, the pH limits proposed for testing would appear to be applicable to both oxidized and strongly reduced water systems.

The application to modeling studies involving mass transport is less direct. Sorption coefficients selected for use in calculations must be selected from among those available in the literature. For the most reliable results, the data selected should be that corresponding most closely to expected conditions along migration paths. The results presented here should be useful in making judicious selection of sorption input data. However, because the data shown represent end points of trench water evolution, its use is limited. Information concerning changes in trench water composition during oxidation would be more useful, in terms of selecting input data for modeling and also for comparing field data against laboratory experimental data and modeling predictions.

The preliminary results for the chemical changes and radionuclide scavenging during the oxidation of a trench water suggest that high ferrous iron contents in disposal trench waters may function as redox buffers in the field situation. During subsurface migration, the trench waters mix with surrounding shallow waters that are generally high in dissolved oxygen. The ferrous iron oxidation and precipitation would rapidly consume oxygen in the surrounding groundwaters and still preserve the low Eh condition. Coprecipitation of radionuclides on the ferric oxyhydroxides would act as a natural scavenging mechanism to immobilize the contaminants. Results on the coprecipitation of radionuclides will be given in a subsequent report.

5. CURRENT EXPERIMENTAL TASKS AND FUTURE DIRECTIONS

5.1 Program Objectives

The initial objectives of this program were to routinely sample and analyze trench waters from commercial waste burial sites. Sufficient information was to be generated as source term data for input into numerical modeling efforts. The characteristics of the geochemical and geological regimes at the disposal sites were studied. Microorganisms played an important part in the degradation of organic waste. Microorganisms active in trench water leachates had been identified and their abundance and distribution was enumerated (Weiss and Colombo, 1980). The effects of various microbial processes on the transformation and migration of radionuclides was studied especially with regard to tritium and ^{14}C (Francis et al., 1980). The source term characterization part of the research program has been reoriented to more effectively assist modeling efforts and answer specific questions about the present situation at the disposal sites.

The current research program is an effort to provide data on the chemical and radionuclide contents of disposal trench waters at commercial low-level radioactive waste disposal sites, and to provide information on the chemical behavior of radionuclides under simulated field conditions. This research support will aid the NRC in the licensing and regulation of waste disposal sites, as well as assist in efforts to model the groundwater transport of radionuclides. These objectives will be pursued in four task areas: (1) Radionuclide and chemical analyses of trench waters and sediments. A monitoring effort will focus on the measurement of concentrations of radionuclides, chelating agents and major inorganic ions, and on in-situ chemical measurements of trench waters at Maxey Flats. Water taken from previously unsampled trenches at Barnwell will also be analyzed. In addition, sediment cores taken from beneath trenches at Sheffield will be analyzed; (2) Sorption of radionuclides using site specific materials will be performed. Retardation factors will be determined from column core experiments, adsorption isotherms will be determined by batch experiments and the measurement of diffusion constants will be initiated; (3) Radionuclide leaching rates of waste forms will be studied under simulated trench conditions; (4) A study of the chemical behavior of radionuclides in anoxic trench water will include an investigation of precipitation reactions and an evaluation of the stability of radionuclide chelates under simulated field conditions.

The new emphasis is to understand the effective radionuclide retention mechanisms operating in the geochemical environment. Through such knowledge, appropriate criteria can be established for the selection of future sites. Also, effective remedial action can be taken to modify the trench design at existing burial sites to take advantage of the geochemical environment to enhance radionuclide retention. Work in progress and future planned experiments are briefly described below.

5.2 Water Analysis

The water chemistry at each disposal site is controlled by a very complex interaction of the mineral composition of the sediment, leaching of the wastes, and bacterial degradation of organic matter. Modification of the burial sites, decommissioning efforts at Maxey Flats, and new burial trenches at Barnwell, require continued effort to characterize the inorganic, organic, and radiochemical compositions of the trench waters. A second analysis of the trench waters at Sheffield would be desirable to confirm earlier results.

Data on the chemical and radionuclide composition of trench waters at commercial low-level radioactive waste disposal sites are required for an understanding of radionuclide migration under field conditions. Furthermore, the characterization of trench water chemistry will provide the information on source terms which is required to model transport of radionuclides in ground-water systems at the various disposal sites. We plan to continue our efforts to characterize the trench waters at Maxey Flats, Sheffield, and Barnwell. Since the Maxey Flats site is currently being decommissioned, our trench water monitoring efforts may help in evaluating the changes that might occur in the trench water chemistry as a result of decommissioning. The anaerobic sampling procedure developed at BNL will be used to sample trench waters.

Field measurements of pH, Eh, dissolved oxygen, sulfide, and conductance will be made during the sampling operation. Analyses of dissolved constituents will include radionuclides (gamma-ray emitters, tritium, ^{90}Sr , and $^{238,239,240}\text{Pu}$), carrier cations (Sr, Cs, Co), and major inorganic constituents (e.g., Na, K, NH_3 , Ca, Mg, Ba, Fe, Cl^{-1} , SO_4^{-2} , HCO_3^{-1}). Analyses for organic chelating agents (e.g., EDTA, NTA, DTPA, TTHA)* will be performed on selected trench waters.

5.3 Sediment Analysis

Radiochemical analysis of core collected from beneath the disposal trenches will provide field data on the migration of radionuclides from burial trenches. This data is essential for the evaluation of results from modeling radionuclide transport.

Radiochemical analysis of sediment cores recovered from beneath the disposal trenches at Sheffield will be initiated upon receipt from the USGS. The cores will be analyzed for radionuclides as a function of depth. The analyses will include gross alpha and beta activity, gamma-ray spectroscopy, and isotopic analyses for ^{90}Sr and $^{238,239,240}\text{Pu}$. A more detailed

*EDTA - ethylenediaminetetraacetic acid.

NTA - nitrolotriacetic acid.

DTPA - diethylenetriaminepentaacetic acid.

TTHA - tetraethylenetriaminehexaacetic acid.

understanding of radionuclide migration at the site would be obtained in addition to confirming the validity of laboratory sorption experiments.

5.4 Leaching of Waste Forms in Simulated Trench Environment

The leaching rate of solidified waste could be a controlling mechanism in the transport of radionuclides by the groundwater. Standard tests (IAEA) are intended for the comparison of leach rates of solidification agents and not to predicate the actual leach rate of radionuclides by groundwater. Leaching radionuclides from solidified waste under conditions which closely resemble the trench environment would provide the source term for radionuclides based on laboratory tests.

Synthetic trench water conditioned with site specific sediments will be used to leach waste forms. The radionuclide content of the leachate water, sediment, and waste form will be determined. The results for radionuclide leaching will be expressed as the cumulative fraction released as a function of total leaching time. The study will be initiated with cement solidified ion exchange resin waste forms. Leaching of sodium sulfate and boric acid solidified waste will subsequently be performed under both oxic and anoxic water conditions. In addition, the results will provide source term information for the modeling of groundwater radionuclide transport. Sorption of radionuclides from leachate solutions on site specific sediments will be performed in future experiments.

5.5 Radionuclide Transport and Retardation

Realistic prediction of radionuclide transport by model calculations requires the retardation coefficients of different chemical species of radionuclides. Radionuclide retardation factors, sorption isotherms, and diffusion coefficients are desirable for modeling calculations of disposal sites. Tests of the applicability of such laboratory generated data could be made by comparison of calculated transport with the radionuclide profile of sediment cores taken from beneath burial trenches.

5.5.1 Batch K_d Sorption Isotherms

Confidence in modeling radionuclide transport from a disposal site is increased by a detailed knowledge of radionuclide sorption isotherms. Sorption isotherms for site specific materials from the Barnwell site will be established. The techniques described by Relyea et al. (1970), to determine K_d by the batch method will be followed. Sediment and radionuclide spiked trench water at a constant sediment/water ratio will be equilibrated in plastic containers. The initial radionuclide concentration of the trench water will be varied to provide the necessary data to determine the sorption isotherms (Travis and Etier, 1981). K_d 's will be calculated from the equilibrium concentration of radionuclides remaining in solution and that sorbed on the sediment.

5.5.2 Column Retardation Factors

Retardation factors provide relative information on the magnitude of retardation of a reactive radionuclide by sorption on sediment compared to that for a nonsorptive radionuclide such as tritium or ^{22}Na . Dynamic column tests provide the most realistic retardation factors. Methods described by Relyea et al. (1980), will be used to determine radionuclide retardation factors in our investigation. Intact soil cores and trench water from the Barnwell site will be used in the experiments. The sides of the cores will be sealed to the core liners to block channeling along the sides. Water flow through the core will be upward to create a saturated soil condition. Measurement of the column pore volume will be made by determining the volume required for passage of a tritiated water spike at a fixed flow rate. A constant radionuclide concentration will be maintained in the inflowing trench water and the effluent water will be monitored for its radionuclide content. The effluent volume (V_{50}) corresponding to $C/C_0 = 0.5$ will be used to calculate the radionuclide retardation factor (R_f). Here, C equals the effluent radionuclide concentration and C_0 equals the influent radionuclide concentration. The radionuclide retardation factor will be calculated as the ratio of the radionuclide effluent volume to column pore volume. For radionuclides that are strongly retained by the core material, the position of the radionuclide front will be determined by segmenting and analyzing the column sections. The position of the radionuclide front in the core relative to that of a nonreactive tracer can be used to estimate the radionuclide retardation factor in a given soil system.

5.3.3 Diffusion Coefficients

Preliminary experiments will be initiated to measure radionuclide diffusion coefficients in site-specific sediments using a diffusion cell. Sorptive and nonsorptive radionuclides will be used to determine the effects of sorption on radionuclide diffusion. The data on diffusion coefficients can also be used to estimate radionuclide retardation factors.

5.6 Radionuclide Behavior in Anoxic Groundwater

The retention of radionuclide by the soil is the sum of all mechanisms which can retard radionuclide migration. Precipitation reactions characteristic of anoxic reducing groundwater environment can coprecipitate some radionuclides. Sorption processes are only part of the possible retardation mechanisms. As trench water comes in contact with more oxidized groundwater, iron oxyhydroxides form and coprecipitate some radionuclides. Other processes which occur in anoxic chemically reducing groundwater environments are the generation of carbon dioxide by biodegradation of organic materials and the generation of sulfide ion by the reduction of sulfate ion. Subsequently formation of insoluble metal carbonates and ferrous sulfide, FeS , can also coprecipitate some radionuclides. Field measurements have shown the presence of free sulfide in solution and black particulate matter in Maxey Flats trench waters (Czyscinski and Weiss, 1981; Weiss and Colombo, 1980). Also, active

sulfate reducing microorganisms were identified in trench waters (Czyscinski and Weiss, 1981; Weiss and Colombo, 1980). A program to study and evaluate the relative importance of sorption and precipitation reactions on the retardation of radionuclide migration is briefly described below.

5.6.1 Sorption of Radionuclides

A radionuclide spiked trench water will be equilibrated with sediment in an argon atmosphere (Czyscinski and Weiss, 1981). The pH, Eh, sulfide, and iron contents of the trench will be monitored. Aliquots of the water phase will be removed periodically to measure the radionuclide concentrations. A K_d sorption coefficient will be calculated for the steady-state radionuclide concentration.

5.6.2 Iron Oxyhydroxide Precipitation

Anoxic waters are generally rich in ferrous iron. Diffusion of oxygen into anoxic water can oxidize ferrous ions, and the subsequent precipitation of ferric oxyhydroxide will coprecipitate some radionuclides. The efficiency of the precipitation process for site specific anoxic trench waters will be studied in a controlled environment chamber where the pH, Eh, and sulfide ion concentration will be monitored. Ferrous iron and total iron concentrations will be measured to follow changes in the water chemistry. Air will be allowed to diffuse into the chamber containing radionuclide spiked trench water. Aliquots of the aqueous phase will be measured for radionuclide content by gamma-ray spectroscopy to follow the coprecipitation processes. The precipitate will also be collected and counted for gamma ray activity.

5.6.3 Ferrous Sulfide Precipitation

Anoxic trench water will be maintained in a controlled environment chamber under an atmosphere of argon and by the addition of slurried organic matter to keep bacterial processes active. The pH of the solution will be kept constant by making periodic adjustments with sulfuric acid. Sulfide generation will be promoted by the periodic addition of sulfate and suitable sulfate reducing bacteria. The water conditions will be monitored by the use of pH, Eh, and sulfide electrodes, as well as making periodic measurements of ferrous iron and total iron concentrations. The concentrations of radionuclides remaining in solution will be measured by gamma-ray spectroscopy of aliquots removed from the chamber during the experiment.

5.6.4 Metal Carbonate Precipitation

Anoxic water will be monitored in a controlled environment chamber under an atmosphere of argon and slurried organic matter to keep bacterial processes active. Water conditions will be monitored by the use of pH, Eh, sulfide, and carbonate sensitive electrodes as well as making periodic measurements of the iron and calcium concentrations. When a steady-state condition for the solution has been achieved, the carbon dioxide content of the atmosphere will be increased. Aliquots of the solution filtered through 0.45 μm

filters will be examined by gamma-ray spectroscopy to determine the concentration of radionuclides in solution.

These efforts will provide data to evaluate and quantify the importance of in situ retention mechanisms and their effect on the retardation of radionuclide migration by the specific geochemical conditions of particular disposal sites.

6. REFERENCES

- Ames, L. L., and D. Rai, Radionuclide Interactions With Soil and Rock Media, pp. 108-137 and 166-203, EPA 520/6-78-007 (1978).¹
- Anderegg, G., Critical Survey of Stability Constants of EDTA Complexes, IUPAC Chemical Data Series No. 14, Pergamon Press, New York (1977).¹
- Berner, R. A., "Electrode Studies of Hydrogen Sulfide in Marine Sediments," Geochim. et Cosmochim. Acta 27, 563-575 (1963).¹
- Cleveland, S. M., and T. F. Rees, "Characterization of Plutonium in Maxey Flats Radioactive Trench Leachates," Science, 212, 1506 (1981).¹
- Cotton, F. A. and G. Wilkinson, Advanced Inorganic Chemistry, p. 421, Interscience Publishers - John Wiley & Sons, New York (1966).¹
- Champlin, J. F., "The Transport of Radioisotopes by Fine Particulate Matter in Aquifers," Doctoral Dissertation, Georgia Institute of Technology (1969). Available from University Microfilms, Ann Arbor, MI.
- Champlin, J. F., and G. G. Eichelz, "Fixation and Remobilization of Trace Contaminants in Simulated Subsurface Aquifers," Health Physics, 30, 215-219 (1976).¹
- Czyscinski, K. S., "The Development of Acid Sulfate Soils ("Cat Clays") on the Annandale Plantation, Georgetown County, South Carolina," Ph.D. thesis, Univ. of South Carolina (1975). Available from University Microfilms, Ann Arbor, MI.
- Czyscinski, K. S., and A. J. Weiss, Brookhaven National Laboratory, "Evaluation of Isotope Migration-Land Burial, Water Chemistry at Commercially Operated Low-Level Radioactive Waste Disposal Sites, Status Report, October 1979-September 1980," NUREG/CR-1862, BNL-NUREG-51315 (1981).²
- Czyscinski, K. S., R. F. Pietrzak, and A. J. Weiss, Brookhaven National Laboratory, "Evaluation of Isotope Migration-Land Burial, Water Chemistry at Commercially Operated Low-Level Radioactive Waste Disposal Sites, Status Report, October-December 1980," NUREG/CR-2124, BNL-NUREG-51383 (1981a).²

¹Available from public technical libraries.

²Available from the National Technical Information Service, Springfield, VA 22161.

- Czyscinski, K. S., R. F. Pietrzak, and A. J. Weiss, Brookhaven National Laboratory, "Evaluation of Isotope Migration-Land Burial, Water Chemistry at Commercially Operated Low-Level Radioactive Waste Disposal Sites, Quarterly Progress Report, January-March, 1981," NUREG/CR/2192, BNL-NUREG-51409, Vol. 1, No. 1 (1981b).²
- Czyscinski, K. S., R. F. Pietrzak, and A. J. Weiss, Brookhaven National Laboratory, "Evaluation of Isotope Migration-Land Burial, Water Chemistry at Commercially Operated Low-Level Radioactive Waste Disposal Sites, Quarterly Progress Report, April-June, 1981," NUREG/CR-2192, BNL-NUREG-51409, Vol. 1, No. 2 (1981c).²
- Dames and Moore, "Assessment of the Levels, Potential Origins and Transport Routes of the Radioactivity Measured in the Vicinity of the Maxey Flats Low-Level Radioactive Waste Disposal Site," prepared for the Executive Department for Finance and Administration, Commonwealth of Kentucky (1977). Available from Dames and Moore, Atlanta, GA.
- Davisson, C. M., "Gamma-Ray Attenuation Coefficients," in Alpha-, Beta-, and Gamma-Ray Spectroscopy, Vol. 1, Appendix 1, pp. 827-843, K. Siegbahn, Ed., North-Holland Publishing Co., Amsterdam (1968).¹
- Eisenbud, M., Environmental Radioactivity, 2nd ed., pp. 354-391, Academic Press, New York (1973).¹
- Forstner, U., and G. T. W. Wittmann, Metal Pollution in the Aquatic Environment, 216-219, Springer-Verlag, New York (1979).¹
- Francis, A. J., S. Dobb., and R. F. Doering, "Biogenesis of Tritiated and Carbon-14 Methane From Low-Level Radioactive Waste," Nuclear and Chemical Waste Management, 1, 153-159 (1980).¹
- Freeze, R. A., and J. A. Cherry, Groundwater, p. 416-420, Prentice-Hall, Inc., Englewood Cliffs, New Jersey (1979).¹
- Friedman, A. M., and S. Fried, "Kinetic Effects in Migration," in Radioactive Waste in Geologic Storage, S. Fried, Ed., pp. 192-199, Am. Chem. Soc., Washington, D.C. (1979).¹
- Gardner, L. R., "Chemical Models for Sulfate Reduction in Closed Anaerobic Marine Environments," Geochim. et Cosmochim. Acta 37, 53-68 (1971).¹
- Garrels, R. M., and C. L. Christ, Solutions, Minerals, and Equilibria, Chap. 5, Harper and Row, New York (1965).¹

¹Available from public technical libraries.

²Available from the National Technical Information Service, Springfield, VA 22161.

- Kirby, L. J., Battelle Pacific Northwest Laboratories, Richland, WA, "Chemical Species of Migrating Radionuclides at Maxey Flats and Other Shallow Land Burial Sites," in Research Program at Maxey Flats and Consideration of Other Shallow Land Burial Sites, USNRC Interim Report NUREG/CR-1832, PNL-3510 (1981).²
- Law Engineering and Testing Co., "Geologic and Hydrologic Studies Near Snelling, South Carolina," Job #6605 (1970). Available from Law Engineering, 412 Plasters Avenue, N.E., Atlanta, GA.
- Lindsay, W. L., Chemical Equilibria in Soils, J. Wiley and Sons, New York (1979).¹
- Means, J. L., D. A. Crerar, and J. O. Duguid, "Migration of Radioactive Wastes: Radionuclide Mobilization by Complexing Agents," Science, 200, 1477-1480 (1978).¹
- Means, J. L., T. Kucak, and D. A. Crerar, "Relative Degradation of NTA, EDTA, and DiPA, and Environmental Implications," Environmental Pollution, 80(1), 45-60 (1980).¹
- Meyer, R. E., Oak Ridge National Laboratory, "Systematic Study of Nuclide Adsorption on Selected Geologic Media," pp. 1-80, in Waste Isolation Safety Assessment Program-Task 4 - Third Contractor Information Meeting, Vol. II, CONF-7910160, PNL-SA-8571 (1980).¹
- NCRP, Natural Background Radiation in the United States, pp. 115-128, NCRP Report No. 45, National Council on Radiation Protection and Measurements, Washington, D.C. (1975).
- Nowell, W. A., and W. L. Lindsay, "Reactions of EDTA Complexes of Fe, Zn, Mn, and Co With Soils," J. Soil Sci. Soc. Am., 33, 86-91 (1969).¹
- Nowell, W. A., and W. L. Lindsay, "Reactions of DTPA Chelates of Iron, Zinc, Copper, and Manganese With Soils," J. Soil Sci. Soc. Am., 36, 778-783 (1972).¹
- Patrick, W. H., B. G. Williams, and J. T. Moraghan, "A Simple System for Controlling Redox Potential and pH in Soil Suspensions," J. Soil Sci. Soc. Am., 37, 331-332 (1973).¹
- Prudic, D. E., and A. D. Randall, "Groundwater Hydrology and Subsurface Migration of Radioisotopes at a Low-Level Solid Radioactive Waste Disposal Site, West Valley, New York, in Management of Low-Level Radioactive Waste, Vol. 2, 853-882, M. W. Carter, H. A. Moghissi, and B. Kahn, Eds., Pergamon Press, London (1974).¹

¹Available from public technical libraries.

²Available from the National Technical Information Service, Springfield, VA 22161.

- Reddy, C. N., and W. H. Patrick, "Effect of Redox Potential on the Stability of Zinc and Copper Chelates in Flooded Soils," Jour. Soil Sci. Soc. Am., 41, 729-732 (1977).¹
- Relyea, J. F., R. J. Serne, and P. Rai, Battelle Pacific Northwest Laboratories, "Methods for Determining Radionuclide Retardation Factors," Status Report, April 1980, PNL-3349.²
- Rickert, P. G., R. G. Strickert, and M. G. Deitz, "Nuclide Migration in Fractured or Porous Rock," in Radioactive Waste in Geologic Storage, S. Fried, Ed., pp. 167-189, Am. Chem. Soc., Washington, D.C. (1979).¹
- Sillen, L. G., and A. E. Martell, Stability Constants of Metal-Ion Complexes, Special Publication No. 17, The Chemical Society, Burlington House, London (1964).¹
- Sillen, L. G., and A. E. Martell, Stability Constants of Metal-Ion Complexes - Supplement No. 1, Special Publication No. 25, The Chemical Society, Burlington House, London (1971).¹
- Singer, P. C., and J. C. Morris, "Oxygenation of Ferrous Ion," Water Pollution Control Series, 14010-06169, U.S. Govt. Printing Office, Washington, D.C. (1969).²
- Sommers, L. T., and W. L. Lindsay, "Effect of pH and Redox on Predicted Heavy Metal-Chelate Equilibria in Soils," J. Soil Sci. Soc. Am., 43, 39-47 (1979).¹
- Stumm, W., and F. J. Morgan, Aquatic Chemistry, p. 540, John Wiley and Sons, New York (1970).¹
- Theng, B. K. G., The Chemistry of Clay-Organic Reactions, John Wiley & Sons, New York (1974).¹
- Tiedje, J. M., "Microbial Degradation of Ethylenediaminetetraacetate in Soils and Sediments," Applied Microbiology, 30, 327-329 (1975).¹
- Tiedje, J. M., "Influence of Environmental Parameters on EDTA Biodegradation in Soils and Sediments," J. Environ. Qual., 6, 21-26 (1977).¹
- Travis, C. C., and E. L. Etier, "A Survey of Sorption Relationships for Reactive Solutes in Soil," J. Environ. Qual., 10(1), 8-17 (1981).¹

¹Available from public technical libraries.

²Available from the National Technical Information Service, Springfield, VA 22161.

- Ugolini, F. C., H. Dawson, and J. Zachara, "Direct Evidence of Particles Migration in the Soil Solution of a Podzol," Science 198, 603-605 (1977).¹
- Vine, E. N., B. P. Bayhurst, W. R. Daniels, S. J. DeVilliers, and B. R. Erdal, Los Alamos Scientific Laboratory, "Radionuclide Transport and Retardation in Tuff," LA-UR-80-2949 (1980).¹
- Wahlig, B., "Mobility and Sorption Processes of Radioactive Waste Materials in Subsurface Migration," in Proceedings of the Task 4 Waste Isolation Safety Assessment Program - Second Contractor Information Meeting, PNL-SA-7352, Vol. 2 (1978).²
- Warren, C. B., "Biodegradation of Nitrilotriacetic Acid and NTA-Metal Ion Complexes," in Survival in Toxic Environments, M. A. Q. Kahn and J. P. Bederka, Eds., 3-496, Academic Press, New York (1974).¹
- Weiss, A. J., and P. Colombo, Brookhaven National Laboratory, "Evaluation of Isotope Migration-Land Burial, Water Chemistry at Commercially Operated Low-Level Radioactive Waste Disposal Sites, Status Report Through September 30, 1979," NUREG/CR/1289, BNL-NUREG-51143 (1980).²

¹Available from public technical libraries.

²Available from the National Technical Information Service, Springfield, VA 22161.

DISTRIBUTION

T. Beck
G. DeBuchananne (10)
L. Duffy
B. Fish
C. Fore
R. Freeman
R. Fry
P. Garrett
P. Hyland
D. Jackson
L. Johnson
M. Kaplan
D. Large
G. Levin
T. Lomenick
A. Lotts
J. Martin
A. Miller

M. Molecke
J. Neiheisel
H. Oakley
O. Oztunali
J. Peel
L. Person
J. Pomeroy
J. Razor
H. Reno
G. Roles
J. Ryan
R. Serne
J. Starmers
T. Tamura
M. Wacks
W. Wood
J. Whitsett

FOREIGN DISTRIBUTION

A. Bell
R. Bonniaud
L. Buckley
K. Johnson

J. Kenchington
J. Morozov
R. Pollock

BNL

C. Anderson
R. E. Barletta
W. Becker
J. Clinton
P. Colombo
R. E. Davis
M. S. Davis
R. Dayal
A. J. Francis
W. Y. Kato

M. Kinsley
H. J. C. Kouts
S. Lane (2)
N. Morcos
R. Neilson
R. Pietrzak
A. J. Romano
V. Sailor
D. G. Schweitzer
H. Todosow (2)

120555078877 1 ANRW
US NRC
ADM DIV OF TIDC
POLICY & PUBLICATIONS MGT BR
PDF NUREG COPY
LA 212
WASHINGTON DC 20555